

Enhanced oil recovery from Sandstones and Carbonates with “Smart Water”

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Dedicated to my beloved wife Laura and my joyful daughter Ela

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- VI. Evaluation of the Smart Water EOR potential in a carbonate oil reservoir**, Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand and Tor Austad. *Technical report.*

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Nomenclature

A_1	<i>Area below the secondary forced drainage curve and the saturation axis</i>
A_2	<i>Area between the forced imbibition curve and the saturation axis</i>
A_{Heptane}	<i>Water-wet area of core with heptane</i>
AN	<i>Acid number, mg KOH/g</i>
ASP	<i>Alkali-surfactant-polymer flooding</i>
At %	<i>Atomic percent, mole %</i>
A_{Wett}	<i>Water-wet area of a sample</i>
B_1	<i>Area between the spontaneous imbibition curve and the saturation axis</i>
B_2	<i>Area between the spontaneous drainage curve and the axis</i>
BET	<i>Brunauer–Emmett–Teller (BET), m²/g</i>
BN	<i>Base number, mg KOH/g</i>
$C_{12}\text{TAB}$	<i>Cationic surfactant Dodecyl Trimethyl Ammonium Bromide</i>
$C_{16}\text{TAB}$	<i>Cationic surfactant Hexadecyl Trimethyl Ammonium Bromide</i>
CAPRI	<i>Catalytic upgrading process in situ</i>
CDC	<i>Capillary desaturation curves</i>
CEC	<i>Cation exchange capacity, meq/100g</i>
CT	<i>Computerized tomography</i>
$d_{10}\text{SW}$	<i>Seawater diluted 10 times</i>
$d_{20}\text{FWI}$	<i>Formation water based on seawater composition diluted 20 times</i>
$d_{20}\text{SW}$	<i>Seawater diluted 20 times</i>
Da	<i>Unified atomic mass unit</i>
DDDC	<i>Dual drop-dual crystal</i>
DI	<i>Deionized water</i>
DLVO	<i>Derjaguin, Landau, Vervy and Overbeek theory of colloidal stability</i>
dP/dx	<i>Pressure gradient, Pa/m</i>
E	<i>Global displacement efficiency</i>
E_D	<i>Microscopic displacement efficiency</i>
EDAX	<i>X-ray Energy Dispersive Spectroscopy</i>
EDS	<i>Energy Dispersive System</i>
EOR	<i>Enhanced oil recovery</i>
E_v	<i>Macroscopic (volumetric) displacement efficiency</i>
FW	<i>Formation water, and 100 000 ppm brine</i>
FWI	<i>Formation water based on seawater composition</i>
FWR	<i>Reservoir formation water</i>

g	Gravitational acceleration constant, 9.8 m/s^2
g_c	Conversion factor
H	Height of the column, m
HPAI	High-pressure air injection
HPAM	Hydrolyzed polyacrylamide
HS	High salinity brine
I_{AH}	Amott-Harvey wettability index
I_{AL}	Hammervold-Longeron wettability index
IDF	International Drilling Fluids
IEA	International Energy Agency
IFP	Institut Français du Pétrole
IFT	Interfacial tension, mN/m
I_o	Amott oil index
I_{O-HL}	Hammervold-Longeron oil index
I_{USBM}	USBM wettability index
I_w	Amott water index
I_{W-HL}	Hammervold-Longeron water index
J	Mean surface curvature
J^*	Leverett dimensionless entry pressure ($J^* \approx 0.25$ for a complete water-wet system)
k	Permeability, m^2
k_{rw}	Relative permeability of water, m^2
k_{ro}	Relative permeability of oil, m^2
L	Length of the capillary tube, m
LS	Low salinity, and 1000 ppm NaCl brine
LSE	Low salinity effect
LSP	Low salinity polymer solution
M	Mobility ratio
meq	Molar equivalent
MIE	Multicomponent ion exchange mechanism
mM	Millimolar, 10^{-3} mol/l
NaCl ₂₅	Brine with 25 000 ppm NaCl
N_B	Bond number
N_c	Capillary number
NPD	Norwegian Petroleum Directorate
nSW	Nano-filtrated seawater
OOIP	Original oil in place
P_c	Capillary pressure, Pa
pH	The negative of the logarithm to base 10 of the activity of the hydrogen ion of an aqueous solution

P_{NW}	Pressure of the non-wetting phase at interface, Pa
ppb	Part per billion, $\mu\text{g/l}$
PV	Pore volume, ml
PV/D	Pore volume per day
P_W	Pressure of the wetting phase at interface, Pa
r	Pore radius, m
SAGD	Steam assisted gravity drainage
SEM	Scanning Electron Microscope
S_{oi}	Initial oil saturation
S_{or}	Residual oil saturation
$(S_{orw})_{HS}$	Residual oil saturation after flooding with a high salinity brine
$(S_{orw})_{LS1}$	Residual oil saturation after the low salinity slug
$(S_{orw})_{LS2}$	Residual oil saturation obtained during the LS injection
S_{wi}	Irreducible water saturation
S_{wi}	Initial water saturation, % PV
T	Temperature ($^{\circ}\text{C}$)
T.O.C	Total organic carbon
TDS	Total dissolve solids, mg/l
THAI	Toe to Heel Air Injection
T_{res}	Reservoir temperature
Triton X-100	Non-ionic surfactant Octyl Phenol Ethoxylate
u	Flow rate, m^3/s
USBM	United States Bureau of Mines
USD	United States Dollars
v_{avg}	Average flow velocity in the capillary tube, m/s
v_o	Velocity, m/s
WAG	Water-alternating gas
WI_{CT}	Wettability index from chromatographic wettability tests
wt %	Weight percent
XRD	X-ray diffraction
ΔP	Pressure difference across capillary tube, Pa
ΔP_g	Pressure difference over the oil-water interface due to gravity, Pa
ΔpH	pH gradient
ΔR_t	Amount of oil recovered in the tertiary LS EOR process
ΔS_{of}	Change water saturation during the forced imbibition of oil
ΔS_{os}	Change in water saturation during the spontaneous imbibition of oil
ΔS_{wf}	Change of water saturation during the forced imbibition of water
ΔS_{ws}	Change in water saturation during the spontaneous imbibition

$\Delta\rho$	<i>Difference in density of the two phases, Kg/m³</i>
μ	<i>Viscosity, Pa.s</i>
μ_o	<i>Oil viscosity, Pa.s</i>
μ_w	<i>Water viscosity, Pa.s</i>
r	<i>Pore radius, m</i>
u	<i>Flow rate, m³/s</i>
θ	<i>Contact angle measured through the denser phase</i>
θ	<i>Contact angle (°)</i>
θ_A	<i>Advancing contact angle (°)</i>
θ_R	<i>Receding contact angle (°)</i>
λ_D	<i>Mobility of the displacing fluid, m²/ Pa.s</i>
λ_d	<i>Mobility of the displaced fluid, m²/ Pa.s</i>
λ_o	<i>Mobility of oil, m²/ Pa.s</i>
λ_w	<i>Mobility of water, m²/ Pa.s</i>
Π	<i>Disjoining pressure</i>
ρ	<i>Density, g/cm³</i>
σ	<i>Interfacial tension (IFT), N/m</i>
σ_{os}	<i>Interfacial tension between oil and solid, N/m</i>
σ_{ow}	<i>Interfacial tension between oil and water, N/m</i>
σ_{ws}	<i>Interfacial tension between water and solid, N/m</i>
φ	<i>Porosity</i>

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Executive summary

According to the International Energy Agency crude oil is expected to contribute approximately with 26% of the world's energy supply by 2040. In a per year basis, new oil discoveries have dropped to a 60-year low in 2015, and capital expenditure is in the longest period of retrenchment in 40 years. Therefore, oil in place from already discovered reservoirs has become an important target for oil companies.

“Smart Water” injection is a relatively new EOR method that improves oil recovery by wettability alteration in both sandstones and carbonates. It disturbs the established chemical equilibrium in the reservoir causing wettability alteration, and during this process, capillary forces increase and water imbibition occurs, resulting in improved microscopic sweep efficiency. The EOR potential is affected by the initial reservoir wetting condition, which is dependent on parameters like mineralogy, formation water composition and crude oil. The same parameters also influence the wettability alteration process. The optimum conditions for observing “Smart Water” EOR effects appear to be mixed-wet conditions.

The objective of this work was to improve the understanding of the initial wetting and wettability alteration in sandstones and carbonates by studying the interactions among the different phases involved in these processes. Furthermore, maturing and gaining confidence with the screening techniques for evaluation of the “Smart Water” EOR potential was also an important part of the project.

Focus was made on explaining the role of the mineralogy in the wetting mechanisms and the “Smart Water” EOR potential in a range of lithologies. A correct mineralogical characterization plays an essential role in the selection of the “Smart Water” brine.

In the case of sandstones, the effect of formation water and “Smart Water” brine compositions were studied, the observations indicated that both formation brine and injection brine compositions are factors that can influence the “Smart Water” EOR potential. By studying the temperature effect in cores containing reactive plagioclase minerals, it was found that the overall low salinity “Smart

Water” EOR effect was not affected by temperature. Additional studies on injection strategies were carried out, and the results confirmed that low salinity “Smart Water” EOR effects are dramatically improved if injected in secondary mode, as opposed to tertiary mode.

The experiments carried out on a carbonate reservoir system showed that for limestone and dolomitic limestone, “Smart Water” EOR effects could also be observed at the challenging low reservoir temperature of 65 °C. The selection of the “Smart Water” composition was crucial to observe the EOR effects, and accurate mineralogical analyses were fundamental for the suitable selection.

Confidence was gained in the implementation of screening techniques for identifying positive and negative scenarios linked to “Smart Water” EOR potential in sandstones and carbonates. The combination of different experimental techniques can rapidly indicate a high or low “Smart Water” EOR potential for a reservoir. A valuable relationship was observed between the screening methods and the amount of oil produced by “Smart Water” injection. However, quantitative information about improved oil recovery with “Smart Water” can only be determined by running oil recovery tests.

In light of the current reservoir chemistry knowledge, this experimental work constitutes a summary of the present understanding of “Smart Water” EOR processes. Hopefully, this work may also serve as a simple guide for evaluating “Smart Water” EOR processes.

1 Motivation and objectives

Important advances in the understanding of “*Smart Water*” enhanced oil recovery (EOR) processes had been previously achieved. Particularly, the surface chemistry approach used to address the theme, has facilitated the understanding of complex chemical systems, regardless of the type of mineralogy, brine complexity or oil composition. However, it is important to expand this knowledge with the purpose of having less uncertainty about the contribution of each factor involved in these processes. This thesis was ambitiously planned with the objective of gaining a better control of positive and negative Smart Water outcomes in specific sandstone and carbonate systems, where the wettability alteration mechanisms are different. Thereby, different research topics were planned with the purpose of extending the understanding of the Smart Water EOR effect.

The fundamental idea was to begin tackling both systems, sandstones and carbonates, by exploring possibilities and limitations when using Smart Water as an EOR fluid, and by doing so; a clearer picture of the factors triggering the enhanced oil recovery should be drawn. Furthermore, if overlapping or converging factors were found, they should be well interpreted and explained, by being consistent with experimental evidence. This may sound obvious, but in several cases found in the literature, important factors have been overlooked and therefore the overall EOR effect has been misinterpreted. This thesis attempts to dig deeper into important factors behind the two well-established chemical EOR mechanisms, and if appropriate, to find points of convergence.

The study of different systems will mainly rely on their mineralogical characteristics, because they appear to be the crucial factor that dictate which type of mechanism that may trigger the Smart Water EOR effect. In sandstones, the interactions of clays, feldspars or micas with the fluid phases, will be studied to know how they influence initial wetting and therefore the potential to observe EOR effects. Likewise, different types of carbonate surfaces, i.e., limestone or dolomite, will be studied in relation to the different wetting stages in a Smart Water flooding process. Furthermore, side effects caused by trace minerals such as calcium sulfate minerals in both sandstones and carbonates will be discussed.

Objectives

This work makes a major focus in sandstones, the experimental basis to improve our knowledge of the fundamental theory consists of a combination of characterization and screening techniques used to evaluate the EOR potential with Smart Water, as well as oil recovery tests to validate the observations. Previously, the pH has been identified as the master variable of the Smart Water wettability alteration mechanism in sandstones. The pH development in a system will be used to link wettability and the potential of observing EOR effects during Smart Water injection. In addition, the impact of formation water and Smart Water compositions on the wettability will be assessed. Other important characteristics related to wettability alteration, as the reactivity of surface minerals, temperature effects, and injection strategies will also be studied. Experiments with greater theoretical focus have been carried out in cores that have shown highly reproducible results in the past.

In connection to carbonates, a proper identification of limestone or dolomitic core material will be performed, and in function of their mineralogy different Smart Water brines will be suggested and tested. A general screening for reservoir Smart Water EOR potential will be carried out. In order to validate their potential, spontaneous imbibition tests are used to confirm effective changes in wetting. Furthermore, the effect of low temperature conditions will be explored for the Smart Water EOR effect in limestone and dolomite cores. It will be interesting to study if the reported lower reactivity of the potential determining ions towards the calcium carbonate surface can be compensated by other factors, i.e., presence of dissolvable calcium sulfate for positive EOR effects. Although, the chemical Smart Water EOR effect in dolomites is not fully understood, experimental evidence has been collected to gain more knowledge in relation to the topic.

2 Introduction to enhanced oil recovery

The life cycle of a reservoir consists of different phases, which include exploration, discovery, delineation, development, production and abandonment (Dake 1983). Reservoir engineering is a science that deals with technical and economic challenges that arise during the development and production of oil and gas in a well.

2.1 Oil recovery mechanisms

Oil recovery operations have been historically divided into three main stages, primary, secondary and tertiary recovery in conventional reservoirs; this definition is structured from a chronological point of view. However, depending on the reservoir characteristics, this order can be altered and some stages can be bypassed if the crude is not recovered at economic flow rates, e.g., heavy oil reservoirs (Green and Willhite 1998).

2.1.1 Primary recovery

Being aware of such operational situations which appear to be frequent (Curtis et al. 2002), in the conventional definition, primary recovery describes the stage where oil production is driven by the energy that is initially stored in the reservoir. The main driving mechanisms are rock and liquid expansion drive, depletion drive, gas cap drive, water drive, gravity drainage and combination drive (Green and Willhite 1998, Ahmed 2010).

2.1.2 Secondary recovery

As the primary depletion reduces its driving force, an increment of the reservoir energy can be supplied in form of water or gas injection (Ahmed 2010), it is called secondary recovery, this technique aims to displace oil towards producing wells (Green and Willhite 1998) and maintain the reservoir pressure.

Under secondary recovery outstanding high quality reservoirs can yield up to 70% of original oil in place, OOIP, (Lake 1989). Nevertheless, if unfavorable reservoir conditions happen to exist the reservoir performance can drop

drastically as low as 20% of OOIP, average worldwide recoveries in secondary mode are in the range of 20% to 40% of OOIP (Castor et al. 1981, Muggeridge et al. 2014). The reasons behind these disadvantageous executions can be explained by reservoir heterogeneity, this includes fractures, large differences in permeabilities in different layers or sections, non-favorable wettability, high capillary entrapment or bypassed areas targeted by the water or gas injection. Gas injection in secondary mode is usually less effective than a waterflood process, and therefore is less frequent nowadays; waterflooding was for a long time a synonym of secondary recovery (Green and Willhite 1998).

2.1.3 Tertiary recovery-enhanced oil recovery

Tertiary recovery concerns to the additional oil that can be recovered after a re-pressurization method or secondary recovery, the latter definition can be controversial because depending on the logistical, economic and technical constrains a conventionally tertiary recovery method can be deployed right after primary depletion. Thus, the term EOR has become more accepted by the scientific community (Green and Willhite 1998).

2.1.4 EOR and IOR definitions

Enhanced oil recovery refers to advanced processes that can reduce the oil saturation by improving microscopic sweep efficiency beyond what is or could be produced by reservoir re-pressurization (Stosur et al. 2003, NPD 2016). EOR involves the injection of a fluid into a reservoir that interacts with the rock-oil system to increase the oil production, this could result in a lower interfacial tension, IFT, oil swelling, oil viscosity reduction, wettability modification or favorable oil mobility (Lake 1989, Green and Willhite 1998). Chemical, physical and biological mechanisms can be the main interaction to trigger an increment in oil recovery (Muggeridge et al. 2014).

According to Stosur “*Improved oil recovery, IOR, comprises all but primary recovery technologies*” (Stosur et al. 2003). Thus, IOR comprehends all practices used to boost oil production, which includes among others techniques like EOR processes, secondary recovery, infill drilling, horizontal wells or conformance control.

In order to get a more efficient EOR project, it is strongly recommendable to include an EOR strategy in the development plan of the reservoir. Depending on the price environment and time execution, the outcome of such strategies can be translated into an efficient usage of the hydrocarbon resources (Strand 2005).

The meaning of waterflooding has shifted from being almost a synonym of secondary recovery to be one of the most cost efficient and versatile EOR methods. Depending on the mineralogy and properties of the reservoir injected water (Morrow et al. 1998) chemical composition can be optimized to recover significant amounts of oil from both sandstones (Austad et al. 2010) and carbonates (Austad et al. 2008, Fathi et al. 2011).

2.2 The need for EOR

The demand for oil is still strong and according to the International Energy Agency, IEA, it constituted a 31.1% of the total energy supply in 2015 (IEA 2015). However, the current world's oil production is mainly dominated by mature fields (Alvarado and Manrique 2010) and the pressure to keep a positive reserve balance is a major concern for private and public oil companies.

The different ways of adding up reserves are (Lake 1989):

- Discovering new fields.
- Discovering new reservoirs.
- Extending reservoirs in known fields.
- Redefining reserves because of changes in economics of extraction technology.

The prospects of finding giant oil and gas fields are in decline (Birks 1980, Cook 2013), and EOR is a powerful tool that can unlock significant amounts of oil. From a general point of view, EOR aims to produce approximately a 30% of OOIP in already discovered fields that is difficult to recover with standard secondary methods (Lake 1989, Green and Willhite 1998, Bondor 2010).

2.3 General description of EOR

From a very broad point of view, EOR processes have the potential to improve recovery by mobility ratio reduction, interfacial tension reduction or wettability alteration. All these factors can influence the oil droplets mobilization inside the porous media. A favorable mobility ratio can be obtained by reducing oil viscosity or increasing water viscosity (Lake 1989), and methods like polymer flooding or gas injection are good examples of it. Surfactant flooding was introduced to alter the interfacial tension and/or to produce a wettability changes. The potential of wettability alteration by surfactants is of high importance (Spinler and Baldwin 2000), but it was not a main focus of research in the past. In situ combustion or upgrading of crude oil such as “Toe to Heel Air Injection” (THAI) or in situ catalysis (CAPRI) are also interesting techniques that might have a future impact in the heavy crude oil market, which is mainly dominated by standard in-situ combustion methods. Another gas injection method is the high-pressure air injection (HPAI), which has been implemented in light oil carbonate reservoirs.

Combined methods have also proved to be feasible, typical examples are surfactant flooding (SP), alkali-surfactant-polymer flooding (ASP), steam assisted gravity drainage (SAGD), and water-alternating gas (WAG). WAG projects have been notoriously successful. Since its implementation, it has contributed in average to increase production from 5 to 10% of OOIP, with very few exceptions underperforming in relation to these values. WAG has been used in both carbonates and sandstones formations, but with especial focus in onshore applications (Christensen et al. 2001). However, offshore applications in the North Sea have led to positive findings and results, as in the case of the Snorre Field (Skauge et al. 2002). CO₂ flooding has been used as an EOR method for medium and light oil, but its deployment is dependent on CO₂ availability. Thereby, CO₂ flooding has grown in locations where CO₂ is highly available from natural or industrial sources, as is the case of the U.S.A., CO₂ EOR still has a huge potential to widespread in different world regions because it has been effectively used in carbonates and sandstones formation (Manrique et al. 2010). Moreover, due to continuous restrictions of greenhouse emissions, CO₂ flooding has become more attractive as a storage method (Denney 2013).

Another approach is to alter the wettability of the reservoir (Morrow 1990). This is a process that aims to desorb crude oil from the porous media surface. Austad et al. (Standnes and Austad 2003), performed studies on a cationic surfactant that aimed to improve the wetting properties of carbonate rocks (Strand et al. 2003). Based on the latter studies, an interesting approach that aimed to change the rock wetting by only modifying the water composition was found. This was called Smart Water, which is a method that involves wettability alteration without lowering significantly the present capillary forces (Austad 2013). This implies that these forces will act in favor of increasing oil production. Economically Smart Water injection is very advantageous, because no expensive chemicals are added and composition can be made up from relatively simple filtration systems by processing formation water.

In summary, most of all chemical flooding processes are highly linked to variations of different factors that aim to lower the residual oil saturation; a significant drawback is that most of them usually involve high implementation costs.

2.4 General classification of EOR processes.

EOR processes are often classified in four different categories, these are: thermal methods, gas injection, chemical flooding and emerging processes (Taber et al. 1997). The main driving mechanism is the major reason to fall into one of the sub divisions presented in the general classification of EOR processes that is described in Table 1.

Table 1. General EOR Classification

Chemical EOR processes	Surfactant flooding Polymer flooding Alkaline flooding Alkaline/surfactant/Polymer (ASP) Gels for water diversion/shut off Solvent flooding
Gas EOR processes	Hydrocarbon injection (miscible/immiscible) CO ₂ flooding (miscible/immiscible) Nitrogen injection Flue gas injection (Miscible and immiscible) Water-Alternating-Gas (WAG)
Thermal EOR processes	Steamflooding Cyclic steam stimulation In-situ combustion Hot waterflooding Steam-assisted gravity drainage
Emerging EOR processes	Smart Water Low Salinity Water Flooding Carbonated waterflood Microbial EOR Enzymatic EOR Electromagnetic heating Surface mining and extraction Nano particles

2.5 EOR performance and application

The oil industry is highly dependent on oil prices, therefore the decision to deploy or not an EOR project is highly dependent of the current price status (Lake 1989, Alvarado and Manrique 2010). Once that the economic constraints allow the decision of implementing a project, a cost-benefits balance is taken into account. A general screening criteria can provide useful information about the right decision to make (Taber et al. 1997). A technical factor used to evaluate the performance is the incremental oil recovery, which is usually expressed as a percentage of original oil in place, (OOIP). From an economic standpoint the utilization factor is a simple but important tool, it describes the amount of EOR agent spent to produce one barrel of incremental oil (Fathi

2012). This serves to compare the cost efficiency of different EOR processes at a specific period of time.

Technical, economical and managerial challenges constitute the main factors slowing down the implementation of EOR projects. Despite of having nowadays more cost-efficient methods of manufacturing commercial EOR products, it has not been enough to observe a high growth rate of commercial projects.

However, it is estimated that about 3% of the worldwide production is derived from EOR projects (Ela et al. 2014). Figure 1 shows the increment of projects by category within the last decade.

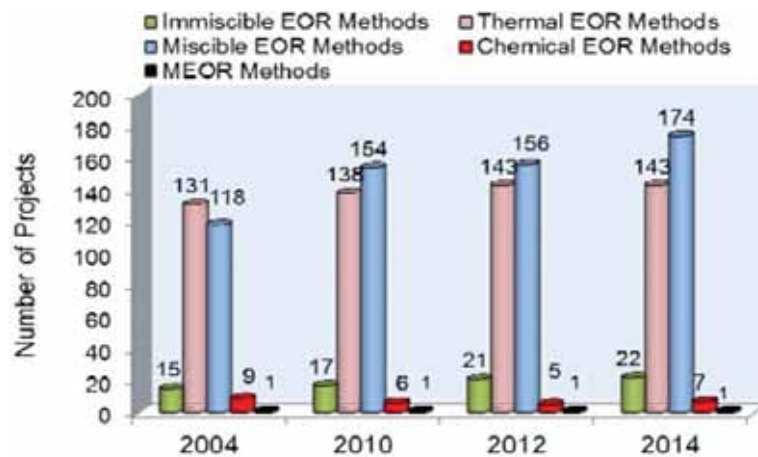


Figure 1. EOR projects in 2004, 2010, 2012 and 2014 (Ela et al. 2014).

2.6 EOR in sandstones

Sandstones have been by far the main target for EOR projects, according to the data based referenced by Manrique (Manrique et al. 2010). In 2010 they constituted approximately 78% of international EOR projects. Sandstones present the highest potential for deployment due to confidence in the current “*State of art*”. Most of the EOR processes have been tested at both pilot and commercial scale. Among the standard methods to boost oil production, thermal and surfactant methods are commonly used in sandstones, as shown in Figure 2.

The most used EOR process in sandstones has been cyclic steam injection followed by Steam-Assisted Gravity Drainage (SAGD) and in situ combustion, these type of methods mainly aim to recover heavy and extra heavy oil.

Medium and light oil have been the objective of most chemical EOR processes. Chemical EOR projects were numerous in the 1980s, but they also peaked in the same period (Lake 1989, Manrique et al. 2010, Ela et al. 2014). Historically, polymer flooding has been the most important of all these methods followed by micellar polymer flooding. Polymer flooding has represented a suitable solution for reservoirs with high heterogeneity and non-favorable mobility ratio. Not very much attention has been given to processes like alkali, surfactant, alkali polymer (AP), surfactant-polymer (SP), and Alkali-Surfactant-Polymer (ASP), which have been tested in a limited number of fields.

WAG has especially targeted sandstone reservoirs contributing approximately with a 57% of the total amount of projects by 2001, WAG has continued adding up projects since then, and has become a well-known technique and is positioned as an EOR method with high likelihood of success (Brodie et al. 2012). Furthermore, continuous improvements in relation to conformance control have substantially increased the sweep efficiency when using this type of EOR processes (Lane et al. 2013).

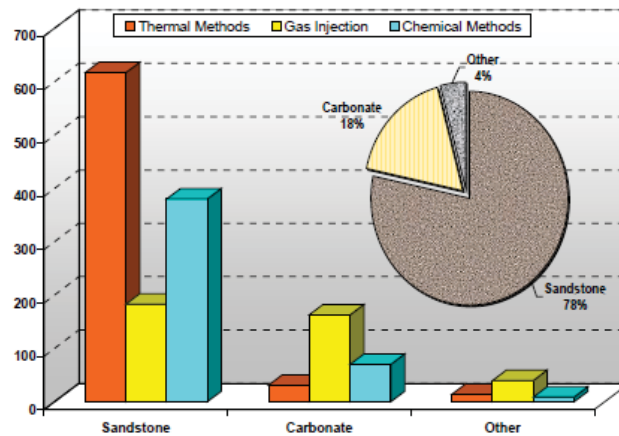


Figure 2. EOR projects by lithology (Manrique et al. 2010).

Increased awareness about the effects of chemical usage in the environment has become a major concern for the oil companies and governments. Thus, techniques that can minimize such impact and being cost effective will thrive in the benefit of society. Among all the techniques, Smart Water is a technique that is both environmentally friendly and cost effective in comparison to other chemical methods. Furthermore, it can also be a platform to develop other type of EOR process in sandstones formations like polymer flooding, surfactant flooding or any combination of alkali, surfactant, polymer processes.

2.7 EOR in carbonates

Carbonates formations are the repositories of the largest oil reserves worldwide (Treiber and Owens 1972). Common features are low porosity, presence of fractures and a wettability generally described as mixed-wet to oil-wet (Cuiec 1984). Such characteristics establish harsh conditions for oil recovery, and as a consequence of this, lower recoveries are usually observed in comparison to the recoveries in sandstones. The dominating EOR process in carbonates is gas injection as shown in Figure 2 (Manrique et al. 2010). In relation to chemical EOR processes, polymer flooding has proven to be successful in carbonate formations, but its total contribution is not large (Manrique et al. 2006). On the opposite side, thermal processes have been the least attractive methods, and its implementation in large scale is minimal (Alvarado and Manrique 2010). Among the chemical methods, surfactant flooding has gained more importance. Surfactant flooding in combination with active displacement forces, like gravity forces or capillary forces can change wettability or reduce IFT to promote oil recovery, especially in fractured reservoirs where spontaneous imbibition is an important mechanism of oil recovery (Mohanty 2006).

Another promising method in carbonates is Smart Water which through a change in wetting towards a more water-wet state induces increased capillary forces and promotes spontaneous imbibition (Fathi et al. 2010, Fathi et al. 2011, Yousef et al. 2011, Fathi et al. 2012, Austad 2013, Shariatpanahi et al. 2016).

2.8 Waterflooding

Historically, waterflooding has been practiced to keep adequate levels of pressure inside the reservoir after primary recovery and to physically displace oil towards the production wells, increasing the pace of oil production as well as slowing the production decline (Craig 1971, Morrow and Buckley 2011). This technique has been successfully applied over a wide range of reservoirs and conditions (Wade 1971). It also brought new operational challenges such as water treatment, corrosion control, water handling, sand production, water-oil ratio control, waste disposal and hydrogen sulfide control among others. Additionally, a good execution must include a good knowledge about the complexity of the reservoirs. Key parameters that influence the performance of a waterflooding operation are linked to reservoir geology, petro-physical properties, mineralogical composition and fluid properties (Ahmed 2010).

The effectiveness of waterflooding has been especially high in light and medium oil reservoirs, but it has also been applied to heavy oil reservoirs with mixed results (Alvarez and Sawatzky 2013). According to Wade (Wade 1971), from a statistical analysis of a group sample of 53 waterflood projects, the primary recovery averaged a 9.4% of the total pore volume, PV, whereas the recovery after implementing a waterflood reached a 23.3% of the PV. This means that the reserves can be significantly increased by implementing this method.

In a standard waterflooding process, i.e., formation water injection, the reservoir wettability will not significantly be affected (Anderson 1986, Morrow 1990). In this case waterflooding is regarded as secondary recovery and not as an EOR method. However, several waterflooding studies have proved that, by modifying the composition of the water injected, wettability alteration can be induced, boosting oil production. Therefore, if spoken in terms of manipulation of the water composition, waterflooding definitely falls into the EOR fluid category.

That is why, another chapter of water injection is being written these days, and it is closely related to the understanding of water chemistry and its chemical interactions with the crude oil and the rock to improve oil recovery processes (Morrow and Buckley 2011, Austad 2013). The main purpose of this work is

to use the established knowledge about Smart Water processes, highlighting the importance and the effect of the mineralogy in the different wetting stages found in a Smart Water flood.

3 Fundamentals in EOR with Smart Water

The performance of the Smart Water EOR effect depends on multiple factors. Among the most important parameters is possible to find the mineralogy of the system, surfaces forces, displacement forces and the wetting development of the system during Smart Water injection. A summary of the main factors influencing the Smart Water EOR effect and a short review of how the wetting development can be estimated is presented below.

3.1 Displacement forces

The overall displacement during an EOR process can be divided into different scales. At the microscopic scale, parameters like wettability, viscosity of the fluids, IFT and others will dictate the residual oil saturation after applying a specific EOR method. At a larger scale, other factors can set restrictions to reach higher recovery yields, among them reservoir heterogeneity, gravity forces or conformance control of the EOR fluids can have a major impact in the overall efficiency. In the next section, a general description of the displacement efficiency at different scales is presented.

3.1.1 Microscopic and macroscopic displacement

The global efficiency of oil displacement in the reservoir is described by the product of both microscopic and macroscopic displacement efficiencies, which is defined by the following equation:

$$E = E_D E_V \dots\dots\dots Eq.1$$

Where, E = Global displacement efficiency (oil recovery by process/oil in place at the beginning of the process), E_D = microscopic displacement efficiency is expressed as a fraction and E_V = macroscopic (volumetric) displacement efficiency is also expressed as a fraction.

Hence, it is convenient to have values of E_D and E_V approaching to one in order to obtain a high global displacement efficiency. E_D details the mobilization of

oil at pore scale, and it is usually displayed in the magnitude of the residual oil saturation reached (S_{or}). On the other hand, macroscopic displacement efficiency is linked to the effectiveness of the displacing fluid when it enters in contact with the reservoir, volumetrically wise. Alternatively, it is a measure of how efficient is the volumetric sweep (Green and Willhite 1998).

The main purpose of EOR processes lies in the reduction of S_{or} , by an increased displacement efficiency at the microscopic level and it is affected by the different chemical and physical interactions that occur when an EOR fluid is injected to displace oil. Valuable examples of it are IFT, oil volume expansion and wettability alteration. If all these factors are well managed, they will help to promote lower S_{or} values, which will affect microscopic sweep. E_D is described by the following equation:

$$E_D = \frac{S_{oi} - S_{or}}{S_{oi}} \dots\dots\dots Eq.2$$

Where:

- S_{oi} Initial oil saturation
- S_{or} Residual oil saturation

Equally important is macroscopic displacement efficiency, which is influenced by characteristics such as reservoir structure, viscosity ratios, and density differences. However, several factors can play against favorable displacement efficiencies. Among others, a non-favorable reservoir geology, large differences in densities and poor mobility ratios could bring consequently low displacement efficiencies. All these characteristics can lead to fingering effects, underriding or overriding of the displaced fluid. The major negative consequence of it, is lower macroscopic displacement efficiency, E_V . Complementary to this, the continuity of the main properties during a flooding operation is of high importance in relation to macroscopic displacement efficiency; in an ideal situation, the properties of the injected fluid and by consequence the type of interaction created with the surrounds should be uniform from the injection until the breakthrough.

In some cases, sequential injection of different fluids can take place, favorable and unfavorable aspects of each type of flooding must be weighted to take

advantage of the positive physical and chemical interactions at each flooding stage (Shiran and Skauge 2013).

3.1.2 Fluid flow in porous media

A key aspect to recover oil from reservoirs is fluid flow in porous media. Darcy's law constitutes a relationship of flow rate through, a porous media, viscosity of the fluid and pressure drop over a given distance; it is applicable to the fluid flow of unfractured reservoirs and described by the next equation:

$$u = -\frac{k}{\mu} \frac{dP}{dx} \dots\dots\dots Eq.3$$

The parameters of the equation are defined as follows:

- u Flow rate (m³/s)
- k Permeability (m²)
- μ Fluid viscosity (Pa.s)
- $\frac{dP}{dx}$ Pressure gradient (Pa/m)

In systems where two fluid phases co-exist, as it is the case of waterflooding in oil reservoirs, the viscosity and the wettability of the system drive the overall displacement efficiency. The mobility ratio, M , is estimated as follows:

$$M = \frac{\lambda_D}{\lambda_d} = \frac{\lambda_w}{\lambda_o} = \frac{\left(\frac{k_{rw}}{\mu_w}\right)_{s_{or}}}{\left(\frac{k_{ro}}{\mu_o}\right)_{s_{wi}}} \dots\dots\dots Eq.4$$

Where:

- M Mobility ratio
- λ_D Mobility of the displacing fluid (m²/ Pa.s)
- λ_d Mobility of the displaced fluid (m²/ Pa.s)
- λ_w Mobility of water (m²/ Pa.s)
- λ_o Mobility of oil (m²/ Pa.s)
- k_{rw} Relative permeability of water (m²)
- μ_w Water viscosity (Pa.s)

- k_{ro} Relative permeability of oil (m²)
- μ_o Oil viscosity (Pa.s)
- S_{or} Residual oil saturation
- S_{wi} Irreducible water saturation

In fractured reservoirs, spontaneous imbibition can be an important recovery mechanism and its efficiency is associated to the wettability of the system. If the process occurs in an oil-wet scenario, the imbibing fluid must overcome the entry pressure of the matrix. The Leverett J-function can calculate the capillary entry pressure.

$$P_c = \sigma \sqrt{\frac{\phi}{k}} J^* \dots\dots\dots Eq.5$$

Where:

- P_c Capillary pressure (Pa)
- σ Interfacial tension (IFT) (N/m)
- ϕ Porosity
- k Permeability (m²)
- J^* Leverett dimensionless entry pressure ($J^* \approx 0.25$ for a complete water-wet system)

3.1.3 Capillary forces

Capillary forces are the major driving forces in fluid flow in porous media. They are a consequence of the interplay of the geometry and dimension of pore throats, wettability and the surface/interfacial tension generated by the fluids and rocks of a given system. Depending on the system, they can act against or in favor of oil production. As mentioned before, in fractured reservoirs they can be an important mechanism of oil recovery, whereas in a waterflooding operation performed in a non-fractured reservoir, the same type of forces can induce oil trapping and because of that, high residual oil saturation can be observed. Capillary pressure (P_c) is the difference in pressure across the interface of two immiscible fluids (Green and Willhite 1998). It is expressed by the equation:

$$P_c = P_{NW} - P_W = \frac{2\sigma \cos \theta}{r} \dots\dots\dots Eq.6$$

Where:

- P_{NW} Pressure of the non-wetting phase at interface (Pa)
- P_W Pressure of the wetting phase at interface (Pa)
- σ Interfacial tension (N/m)
- θ Contact angle (°)
- r Pore radius (m)

3.1.4 Gravity forces

In the same way that capillary forces can be positive or negative in oil recovery processes, gravity forces can lead to problems like overriding or underriding, or to successful operations based on fluids segregation (Green and Willhite 1998). They are a major concern when density differences between oil and water are large, but are also important at low oil-water IFT conditions (Chen et al. 2000). Due to the immiscibility of the fluids, the lighter phase will be always subjected to a buoyancy force, which is described as follows:

$$\Delta P_g = \Delta \rho g H \dots\dots\dots Eq.7$$

Where:

- ΔP_g Pressure difference over the oil-water interface due to gravity (Pa)
- $\Delta \rho$ Difference in density of the two phases (Kg/m³)
- g Gravitational acceleration constant, 9.8 (m/s²)
- H Height of the column (m)

3.1.5 Viscous forces

In the case of flow in porous media, viscous forces are reflected in the magnitude of pressure drop that happens as a result of flow through the medium (Green and Willhite 1998). If by simplification, the porous media is considered as a bundle of parallel capillary tubes, and laminar flow is assumed within the system, the pressure drop can be calculated with the following equation:

$$\Delta P = - \frac{8\mu L v_{avg}}{r^2 g_c} \dots\dots\dots Eq.8$$

Where:

- ΔP Pressure difference across capillary tube (Pa)
- μ Viscosity (Pa.s)
- L Length of the capillary tube (m)
- v_{avg} Average flow velocity in the capillary tube (m/s)
- r Radius of the capillary tube (m)
- g_c Conversion factor

3.1.6 Interrelation of forces, capillary number and bond number

Due to the complexity of porous media, different relations have been established by several scientists with the aim of weight the importance of each force in a determined situation, the most relevant relations are presented below.

3.1.7 Capillary number

The capillary number (N_c) is the dimensionless ratio of viscous and capillary forces. It is important, because it establishes the relative degree of influence of gravity forces over capillary forces, as the viscous forces become more dominant the capillary number increases, allowing oil mobilization and therefore lower residual oil saturations (Morrow 1979). The capillary number relation is given by:

$$N_c = \frac{\mu_w v_o}{\sigma_{ow}} \dots\dots\dots Eq.9$$

Where:

- μ_w Water viscosity (Pa.s)
- v_o Velocity (m/s)
- σ_{ow} Surface tension between oil and water (N/m)

Capillary number has received a lot of criticism from several authors, because the mobilization of crude oil of systems that are not water-wet do not match the common definition of the non-wetting fluid mobilization at the critical $N_c \sim 10^{-5}$. In some cases, oil saturation does not drop by a capillary number increase (Armstrong et al. 2014, Guo et al. 2015). Besides that, comprehensive studies have been done on different variables, and yet, more experimental work is needed using two-phase flow at residual oil saturation with different wetting states to validate the theory. Additionally, the behavior at pore scale is not easily predicted by this method, since the wettability of the system plays an important role as well as the pores heterogeneity; this complicates the issue on the macro scale. However, with the current need to simulate EOR processes, the need for understanding desaturation processes has led to new contributions and interpretations to the capillary number definition at different wetting states. When the method is contrasted at a broader range of wetting states and conditions many deviations from the expected behavior emerged, and they are explained by capillary end effects, dependence of S_{or} and S_{wr} to the PVs injected or to misuse of the capillary desaturation curves (CDC), (Fulcher et al. 1985, Abeyinghe et al. 2012, Guo et al. 2015).

3.1.8 Bond number

The Bond number (N_B) is also a dimensionless group that represents the effect of gravitational forces over the capillary forces in an oil ganglion located in a saturated porous media; the bond number is defined as (Gioia and Urciolo 2005) as follows.

$$N_B = \frac{k k_{rw} \Delta \rho g}{\sigma_{ow}} \mathbf{k} \quad \dots \dots \dots \quad Eq.10$$

Where:

- k Intrinsic permeability (m^2)
- k_{rw} Relative permeability to water (m^2)
- $\Delta \rho$ Density difference between oil and water (Kg/m^3)
- g Gravitational acceleration constant, 9.8 m/s^2
- σ_{ow} Surface tension between oil and water (N/m)
- k Unit vector

For Bond number values less than 1, capillary forces will have a dominant effect, whereas for values greater than 1, gravitational forces can mobilize the oil ganglion due to the effect of buoyancy forces (Morrow 1979). A major drawback from the relation is that wettability is not included

3.2 Surface forces

Different models have been used to understand wettability, and often, intermolecular forces have been interpreted with mathematical and physical models; in the road to achieve a proper understanding to foresee the behavior of different systems, many simplifications were needed. Thereby, the study of these forces have been extremely useful to conciliate the wetting phenomena, but on this road, some important factors have been ignored. The main attributes and restriction of the models are included in the next subsections.

3.2.1 Electrical double layer

The electrical double layer is a model that aims to explain the distribution of ions that are close to a charged surface. The model describes that the charges in the fluid phase will not be uniformly distributed. A sort of segregation will occur due to the effect of the charged solid surface. This will generate an increased concentration of counter-ions close to surface that have a tendency to balance the surface charge. According to this theory, the double layer consists of the surface charges distributed on the solid phase and the counter-ions of the solution.

Gouy and Chapman (Gouy 1910, Chapman 1913) contributed independently to the model by explaining that the counter ions have a tendency to diffuse into the bulk fluid until that the interactions were not significant. This was called “the *diffuse double layer*”, in which the concentration change was associated to the Boltzmann distribution. However, it assumed that activity was equal to molar concentration and this was not true near to the charged surface.

The Stern modification of the diffuse layer (Stern 1924), took into account the finite size of the ions and assumed that some ions can be adsorbed onto the surface. This theoretical alignment is known as the “*Stern layer*”. Such ion distribution will cause a drop in the surface potential, which at the surface

boundary is called zeta potential. The new ionic distribution in the fluid phase will consist of two zones, the Stern layer where the ions remain adsorbed and the diffuse region where the ions have more freedom but are segregated due to the effect of the charges on the surface (Israelachvili 2011).

3.2.2 DLVO theory

Derjaguin, Landau, Verwey and Overbeek developed the DLVO theory of colloidal stability (Derjaguin and Landau 1941, Verwey and Overbeek 1955). The theory combines the attractive Van der Waals forces and repulsive forces caused by the presence of a double layer (Derjaguin et al. 1987). It is used to relate forces between planar substrates and fluid films. It can fairly describe interaction forces as well as aggregation rate constants.

In the context of reservoir engineering, DLVO can be used to interpret the forces derived from the present charges at the different solid-fluid or fluid-fluid interfaces. However, issues such as the assumption of smooth and homogenous surfaces, deviation at high salinity concentration, or that contact angles are ignored, makes difficult to get an adequate interpretation of the interactions taking place in oil/brine/solid systems (Ninham 1999). Yet, it has been a useful framework to model interactions. In addition, many scientists have incorporated missing forces to the model to compensate its limitations (Ninham 1999, Busireddy and Rao 2004, Israelachvili 2011). DLVO theory is not efficient at explaining experimental evidence of LSE in sandstones, especially at high salinities, where it does not show a high pH dependence. As argued by Shi et al. (2016), it fails because the theory is limited to interactions between single particles with certain surface charges and it is not developed for a complex electrolyte solution (Shi et al. 2016).

3.2.3 Disjoining pressure

Disjoining pressure is a force that tends to separate two identical interfaces (Hirasaki 1991), if the value is negative it will tend to attract both interfaces. The augmented Young-Laplace is used to describe the equilibrium conditions of two interfaces with equal temperature and chemical potentials. Its importance resides in that it can be used to interpret the wetting phenomena through fundamental

forces. This includes, films stability, contact angles description and reservoir wettability.

$$P_c = \Pi + 2\sigma_{ow}J \quad \dots\dots\dots \text{Eq.11}$$

Where:

- P_c Capillary pressure between wetting and non-wetting phases
- Π Disjoining pressure
- σ_{ow} Interfacial tension between oil and water
- J Mean surface curvature

3.3 Wettability

To understand properly wettability and its relation with EOR is a demanding task, and many efforts and resources have been allocated worldwide only for this purpose. For a crude oil/rock/brine system, the complexity lies in the multiple interactions of the three phases. Each phase has many components that can affect wetting, in addition to this, it is important to obtain an adequate physical description of the rock. This includes porosity, permeability and pore size distribution. The chemical composition of brines and oil are of high importance because when interacting with the rock they establish the wetting conditions of the system (Anderson 1986, Buckley 1996, Drummond and Israelachvili 2002).

3.3.1 Definition and classification

Wettability is defined as “*the tendency of one fluid to spread on or to adhere to a solid surface in the presence of other immiscible fluids*” (Craig 1971). Initial reservoir wettability has a crucial role since it determines the waterflood performance of a reservoir and other fundamental petrophysical properties, such as capillary pressure P_c , relative permeabilities of oil and water, k_{ro} , k_{rw} , as well as it regulates the fluid distribution along the porous media configuration.

A general classification of the wetting state of a reservoir can be divided in homogeneous and heterogeneous wetting (Anderson 1986). In the homogenous wetting, the reservoir rock has a uniform wetting behavior throughout the reservoir, and this is translated in constant affinities to the wetting and non-

wetting phases. For this type of system, the wetting categories are water-wet, intermediate-wet and oil-wet. Most of the reservoirs present mixed wettability (Anderson 1986, Anderson 1986). This variability can be observed in different sections as well as with depth (Hamon 2004). The definition of heterogeneous wettability covers mixed wettability, in which the smaller pores and grain contacts behave water-wet, and the surfaces of the bigger pores are more oil-wet. Fractional wetting consists of some surfaces that are water-wet and oil-wet that co-exist, and the coverage can mix different proportions of the porous media surface (Salathiel 1973). The presence of uninterrupted oil-wet areas in the larger pores of a system enables a very small oil permeability to exist at quite significantly low saturations. This fact, allows the process of oil recovery by waterflooding until reaching low oil saturations (Donaldson et al. 1969, Anderson 1986).

For strongly oil-wet conditions, the oil will be distributed over the rock surface including in the smaller pores, and the water will be distributed in the middle of the larger pores. When a waterflooding process begins, the water will flow through the larger pore channels avoiding smaller pores, while the oil will remain covering the rock surface, Figure 3.

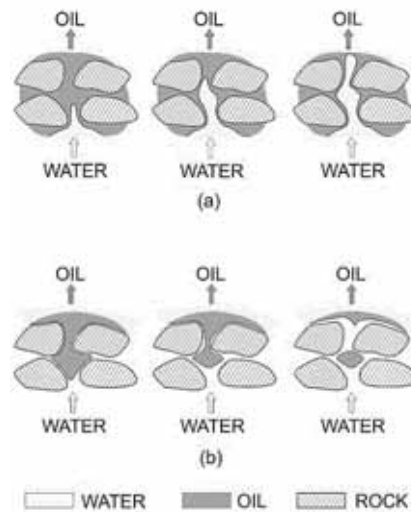


Figure 3. Displacement of oil by water for (a) oil-wet sand, and (B) water-wet sand. Redrawn after Forrest (1980).

In a strongly water-wet state, the oil is distributed in the center of the larger pores and the water is mostly in contact with the rock surface, it also fills the smallest pores. In a waterflooding process, a fraction of the oil is pushed out of the porous media but oil snap-off may occur, leaving behind oil trapped in form of globules in the middle of the larger pores.

3.4 Wettability measurements

Wettability quantification is not an easy task, in order to get more reliable results, different experimental approaches have been used. They cover from fundamental studies to complex studies in porous media. Shown below is a brief description of the most commonly used methods to estimate the wettability of a system.

3.4.1 Wettability measurements in smooth surfaces

In order to study the fundamental principles of wettability, the simplest systems are the ones that involves smooth surfaces. They provide several advantages as fast wettability estimations, high reproducibility, and straightforward comparisons of significantly different systems.

3.4.1.1 Contact angle

Contact angle measurements are used as a primary approach to evaluate the wetting state of a rock surface (Yuan and Lee 2013). It is one of the several quantitative methods used to evaluate the wettability of pure fluids on surfaces (Anderson 1986, Morrow 1990), where pure calcite and different types quartz have been used as model surfaces. Besides, it has been often used as a reservoir wettability measurement (Treiber and Owens 1972).

The measurement method can be static or dynamic, in a static equilibrated oil-water-solid system; the degree of wettability is expressed in function of the angle measured through the denser phase. The static equilibrium can be defined by Young's equation *Eq. 12*, which was developed on a thermodynamic basis stated by Gibbs (Berg 1993). The main parameters of the equation are the interfacial tensions, σ_{os} , σ_{ow} and σ_{ws} , which are in mechanic equilibrium, Figure 4 (a).

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos \theta \quad \dots\dots\dots \text{Eq.12}$$

Where:

- θ Contact angle measured through the denser phase
- σ_{os} Oil-solid interfacial tension
- σ_{ow} Oil-Water interfacial tension
- σ_{ws} Water-solid interfacial tension

In the case of a dynamic system, the contact angle will appear to be bent by an applied force. The angles to be characterized under such circumstances are the advancing contact angle (θ_A) and receding contact angle (θ_R); their difference is described as the contact angle hysteresis of the system, Figure 4 (b). The methods used to measure these angles are the modified sessile droplet method (Shedid and Ghannam 2004) or the dual-drop-dual-crystal (DDDC) (Rao 1999).

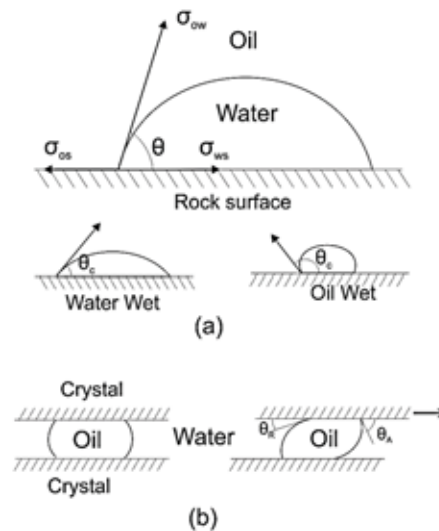


Figure 4. Contact angle measurements, θ , (a) Static system and (b) dynamic system

A general classification of the wettability in function of the contact angle measurement is described in Table 2.

Table 2. Wettability classification in function of contact angles

Contact angle (°)	Wettability
0-30	Strongly-wet
30-90	Water-wet
90	Neutral wet
90-150	Preferentially oil-wet
150-180	Strongly oil-wet

3.4.2 Wettability in porous media

A proper estimation of reservoir wettability is fundamental for the success of a waterflooding operation. However, contact angle measurements are not representative of porous media due to the complex geometry of pores structure. Nevertheless, different experimental techniques are at our reach, the most widespread in the scientific community are summarized below.

3.4.2.1 Amott Harvey and Amott-IFP

The Amott test (Amott 1959), broadly consists of fluid saturation changes within the porous media, and the logic behind it is that the wetting fluid will spontaneously imbibe into the porous media, displacing the non-wetting fluid. The test consists of 4 different stages that involve spontaneous and forced imbibition, as well as drainage of oil and water. The forced displacement process can take place by either centrifuging as initially proposed by Amott or by flooding as in the Amott-IFP test (Morrow 1990). These main 4 steps are described in Figure 5 with the arrows from 2 to 5, since arrow 1 symbolizes the first drainage cycle where oil displaces water to residual water saturation, S_{wr} , as summarized by McPhee et al. (2015):

Spontaneous brine imbibition: A brine is allowed to spontaneously imbibe into the core that is initially at irreducible water saturation (arrow 2 in Figure 5), the core is placed in a graduated Amott cell in order to have control of the oil displaced by the imbibing brine, oil production is monitored as a function of time.

1. *Forced brine imbibition:* The brine is then forced to imbibe into the core by means of pressure (arrow 3 in Figure 5), lowering the oil saturation

towards residual oil saturation, (S_{or}). This can be carried out by either centrifuging or by core flooding. Viscous instability and capillary end effects in dynamic flooding may have higher impact, if a flood is implemented.

2. *Spontaneous oil imbibition*: At this stage, oil is allowed to spontaneously imbibe into the core at (S_{or}), (arrow 4 in Figure 5). In this step, the core is placed into an Amott cell that is placed up side down, the volume of brine produced is measured against time.
3. *Forced oil imbibition*: The oil phase is then forced to imbibe the core material by exerting the same pressure of that used during the force brine imbibition process; this step is described in Figure 5 with the arrow number 5. This process moves the saturation again towards irreducible water saturation (S_{wr}). Similarly, as in the force imbibition stage, this step can be performed by using a centrifuge or by core flooding.

The Amott tests wetting indices of oil, I_o , and water, I_w , are evaluated separately, in the case of the Amott-Harvey the indices are merged by using the difference between I_o and I_w (Amott 1959, Anderson 1986).

The original indexes are defined as follows:

$$I_w = \frac{\Delta S_{ws}}{\Delta S_{ws} + \Delta S_{wf}} \dots\dots\dots Eq.13$$

$$I_o = \frac{\Delta S_{os}}{\Delta S_{os} + \Delta S_{of}} \dots\dots\dots Eq.14$$

The Amott-Harvey wettability index is defined by the original Amott indices as shown below:

$$I_{AH} = I_o - I_w \dots\dots\dots Eq.15$$

Where ΔS_{ws} , is the change in water saturation during the spontaneous imbibition of water and ΔS_{wf} is the change of water saturation during the forced imbibition of water. Additionally, ΔS_{os} is the change in water saturation during the spontaneous imbibition of oil and ΔS_{of} is change water saturation during the forced imbibition of oil.

Therefore, the Amott-Harvey index ranges from -1 to 1, where -1 is designated to a strong oil-wet state and +1 represents a strong water-wet state (Cuiec 1991). A neutral wettability has an I_{AH} equal to 0. A drawback of the Amott methods is that they are not sensitive to neutral wettability (Anderson 1986) and they do not state clear differences at strong water-wet conditions (Morrow 1990, Ma et al. 1999).

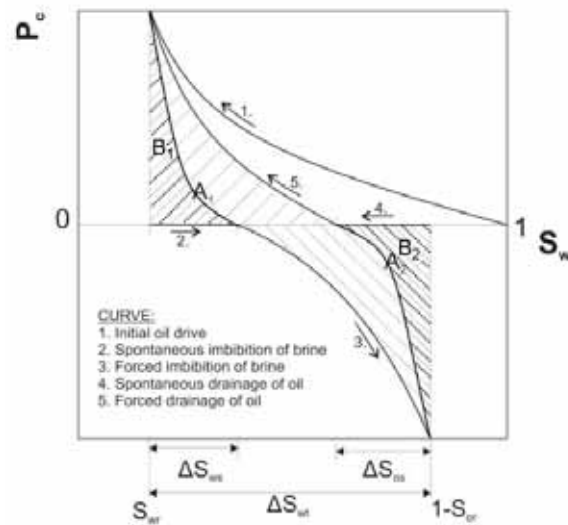


Figure 5. Capillary pressure curves for different Amott tests, USBM and membrane methods. Redrawn after Strand (2005).

3.4.2.2 USBM and membrane methods

The USBM method (Donaldson et al. 1969) consists in measuring the average wettability of the core, it compares the work needed to displace one fluid with the other. Thermodynamically wise, the work done with the wetting fluid as it displaces the non-wetting fluid is less than the work required with the non-wetting fluid when it displaces the wetting fluid; this is due to the favorable free-energy change of the system. This energy is proportional to the area located under the imbibition and drainage capillary pressure curves, these areas are symbolized in Figure 5 as A_1 and A_2 . In comparison with the Amott tests, in the USBM method, the process of spontaneous imbibition is not clearly measured,

but it does happen during the initial centrifugation at low pressures (McPhee et al. 2015).

The USBM wettability index (I_{USBM}) is defined by the equation:

$$I_{USBM} = \log \frac{A_1}{A_2} \dots\dots\dots Eq.16$$

Where A_1 is the area below the secondary forced drainage curve and the saturation axis, and A_2 is the area between the forced imbibition curve and the saturation axis. If the index I_{USBM} value is positive it indicates a water-wet state, and the water wetness increases the larger the index is. Conversely, a negative value represents oil wetness, and as the index value is more negative the degree of oil wetness increases. Strongly oil-wet systems have values close to -1, and similarly, strong water-wet systems have values around +1. A drawback is that the Amott method is more sensitive at neutral wettabilities, but the combined method Amott-USBM, allows to run spontaneous imbibition in an Amott cell increasing the sensitivity at neutral wettabilities. However, the use of the centrifuge may cause damage in form of fractures at very high spin velocities; this can also be solved with other methods which calculate the capillary curves using membranes instead of a centrifuge, making a suitable test for samples that cannot stand high stresses during centrifugation (McPhee et al. 2015).

As the spontaneous processes of imbibition and drainage are not part of the USBM index. Was proposed a wettability index named the Hammervold-Longeron index, I_{HL} (Longeron et al. 1995). The index which includes both spontaneous and forced capillary pressure curves, this new index uses the areas between the spontaneous imbibition curve and the saturation axis, B_1 , as well as the area between the spontaneous drainage curve and the axis, B_2 , Figure 5. The advantage of this method is that by using it, it is possible to differentiate among intermediate-wet, spotted wet and mixed-wet samples (Hammervold 1994). The Hammervold-Longeron Index is defined as:

$$I_{HL} = I_{W-HL} - I_{O-HL} \dots\dots\dots Eq.17$$

Where:

$$I_{W-HL} = \frac{B_1}{B_1 + A_2} \dots\dots\dots Eq.18$$

$$I_{O-HL} = \frac{B_2}{B_2 + A_1} \dots\dots\dots Eq.19$$

Where, I_{HL} is the Hammervold-Longeron wettability index that is obtained by subtracting the Hammervold-Longeron oil index, I_{O-HL} , from the Hammervold-Longeron water index, I_{W-HL} .

3.4.2.3 Chromatographic wettability test

The chromatographic wettability test was developed for chalk surfaces (Strand et al. 2006) but is also valid for limestone surfaces (Fathi et al. 2010), and it is performed at S_{or} using a core flooding set up. The main principle behind it is the chromatographic separation of ions with different affinities towards the water-wet regions of the chalk surface. The component with no affinity is the tracer, thiocyanate, SCN^- , and the adsorbing ion is SO_4^{2-} (Strand et al. 2006), which has a greater affinity towards the chalk surface.

As SO_4^{2-} has a higher tendency to adsorb onto the chalk surface, during chromatographic analysis of the anions at the effluent, the sulfate concentration will appear to be delayed in relation to the thiocyanate concentration, as shown in Figure 6.

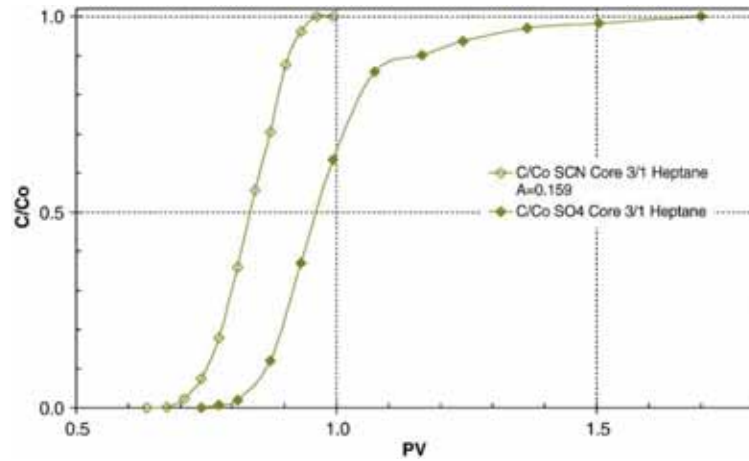


Figure 6. Effluent profiles of SCN^- and SO_4^{2-} for a water-wet system containing heptane at $S_{or}=0.22$. After Strand et al (2006).

Complete water wetness can be assumed by using a core 100% water saturated or a core containing n-heptane as reference oil. The separation of the curves of SCN^- and SO_4^{2-} is proportional to the water-wet spots contacted by water during the core flooding process. The area of a water-wet core with heptane $A_{Heptane}$, can be compared with the water-wet area of a sample, A_{Wett} , to estimate the wettability of the system, because SO_4^{2-} can only adsorb onto the water-wet areas of the sample. The ratio that express the fraction of water-wet areas is defined as:

$$WI_{CT} = \frac{A_{Wett}}{A_{Heptane}} \dots\dots\dots Eq.20$$

In relation to wettability, the values obtained with the wetting index, WI_{CT} , they are classified as follows:

- $WI = 1.0$ represents a completely water-wet system
- $WI = 0.5$ represents neutral wettability
- $WI = 0.0$ represents a completely oil-wet system

The advantage of this tests is that is time effective since the test can be carried out in approximately 1 day, it has a high reproducibility, $\pm 2\%$ and it has a good sensitivity close to neutral wetting conditions. Furthermore, this wettability

index correlates well with Amott indices (Zhang and Austad 2005). The drawback is that its applicability is restricted to carbonates.

3.4.2.4 Spontaneous imbibition

This method is a practical way to approach and quantify the wettability of oil/brine/rock systems (Anderson 1986). It is performed by measuring the spontaneous imbibition rate of a system, this is a useful measure because the driving force of the rate is proportional to the imbibition capillary pressure (Morrow 1990). To perform an adequate interpretation, it is important to count with reference results that are near to the initial wettability of the cores (Denekas et al. 1959, Ma et al. 1999). Furthermore, this test can provide information about dynamic IFT and other wetting processes that could be of interest for reservoir engineers, but are not explicitly exposed in the Amott or USBM method. For instance, in some cases imbibition capillary pressure can be near to zero but the imbibition process can continue at a very slow pace (Morrow 1990).

However, in order to discriminate well the wettability of systems in which the spontaneous imbibition is not occurring in significant quantities, it is more convenient to employ other methods like USBM or the aforementioned chromatographic wettability test (Donaldson et al. 1969, Cuiec 1984, Strand et al. 2006).

3.4.2.5 Cryo-ESEM analysis

In the study made by Kowalewski et al. (2006), a combination of techniques (Cryogenic Environmental Scanning Electron Microscope) and X-ray energy dispersive system, (EDS), showed that it was possible to determine different fluid distributions on the rock surface; this method can complement the information of other core analyses. A positive point of this technique is that the samples are not using any conducting material on the surface and no dopants are added to the fluids (Kowalewski et al. 2006, Schmatz et al. 2015).

The major benefits of using this method, is that the fluid distribution can be related to specific pore sizes or to the mineralogy. The fluid saturation can be quantified by image analyses and processed X-ray images. In addition, preserved cores can be studied in a fresh state before cleaning or restoration, and this

attribute can be useful to validate hypotheses that emerged from other methods (Kowalewski et al. 2006).

Detection of aggregates on fluids can also be done, as it is the case of the BaSO₄ particles presented in Figure 7. These particles created shells covering oil droplets; to facilitate the visualization of such events, a sublimation of the water phase is carried out during analysis, this is done to locate small oil droplets from emulsions. The spots where the water was sublimated can be detected by the presence of ions like Na⁺ or Cl⁻.

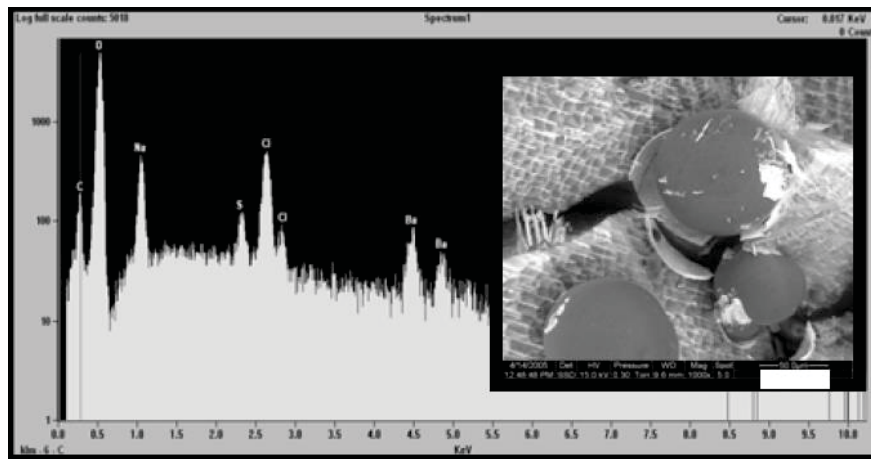


Figure 7. BaSO₄ particles on the surface of oil droplets in water (scale bar 50µm). After Kowalewski et al (2006).

3.4.2.6 Methylene blue adsorption

Adsorption of a chemical component through a fluid phase can also be a way to determine wettability. Back in 1958 Holbrook and Bernard used different mixtures of water-wet and oil-wet sand determining quantitatively the fraction of water-wet and oil-wet surfaces in different sand packs (Holbrook and Bernard 1958).

Torske and Skauge (1992), presented a study based on Holbrook and Bernard's work that attempted to determine the wettability of a core material by dynamic adsorption using n-heptanol and methylene blue (Torske and Skauge 1992). They found that methylene blue adsorbs on both water-wet and oil-wet sites. On

the other hand, n-heptanol presented adsorption on the hydrophobic sites. However, the sum of the areas of adsorption by both chemicals did not match the values obtained from BET-analysis and the wettability index did not correlate with the classic tests as Amott or USBM methods (Torske and Skauge 1992).

3.5 Factors influencing the wettability

Wettability is affected by several factors; all of them are strongly linked to different interactions among the mineralogy of the system, brine composition and crude oil. If these parameters are changed, the outcome can give an utterly different picture of the wetting state. Therefore, it is important to be aware of how each of these factors can influence the wetting of a system.

3.5.1 Mineralogy

The mineralogical nature of the reservoir is a fundamental property that sets the type of interaction that controls the adsorption of polar components. The major difference between sandstones and carbonates, is that at standard pH reservoir conditions the surface charge of carbonates is positive (Stumm et al. 1992), whilst sandstones surfaces are negatively charge due to the presence of clays and different silicates with points of zero charge generally ranging from 2.2 to 2.8 (Jaafar et al. 2014).

The major consequence of the difference in surface charge, is that the rock-crude oil interactions will differ in its behavior depending on the mineralogy, especially in the way that crude oil wets the surface of the porous media (Denekas et al. 1959, Buckley and Liu 1998).

Tangible differences between sandstones and carbonates are found in the literature; carbonate surfaces have a higher sensitivity to acidic components (Madsen and Lind 1998, Standnes and Austad 2000, Standnes and Austad 2003), because carbonate surfaces are in most cases positively charged, at pH values below 8 to 9.7 (Stumm et al. 1992, Stumm and Morgan 1996, Jaafar et al. 2014). Hence, adsorption of the negatively charged carboxylates, RCOO^- , present in the crude oil is likely to occur (Fathi et al. 2011). On the other hand, the literature shows evidence of a divergent trend in sandstones, where their wettability drifts to a less water-wet state after entering in contact with basic crude oil components (Torsaeter et al. 1997, Skauge et al. 1999, Kowalewski et al. 2002, Austad et al. 2010, Aksulu et al. 2012). These trends in wetting are in line with the surface charge of sandstones, which is negative at standard reservoir pH conditions. This latter fact, allows the interaction of the sandstone surface with positively charged components.

3.5.2 Crude oil

As mentioned earlier, the mineralogy predisposes the type of rock and oil interactions that can take place influencing the wetting of the rock (Buckley et al. 1989). However, understanding this is not an easy task, crude oil is one of the most complex mixtures of organic compounds. Hence, it has taken countless efforts to understand the effect of crude oil wetting processes.

It is defended by several researchers, that the crude oil fractions that have the largest impact on wetting rock surfaces are the asphaltenes and resins (Buckley 1995, Buckley et al. 1998, Buckley 2001). Asphaltenes are the constituents of crude oil with the highest molecular weight, that ranges from a few hundred to millions of grams per mole (Speight 2004). Resins are often more polar than asphaltenes due to a relatively higher presence of organic compounds that contain nitrogen, sulfur and oxygen, NSO compounds. These NSO-compound rich fractions, have a higher surface activity and for this reason, they can influence wetting (Madsen and Lind 1998, Standnes and Austad 2000, Hirasaki and Zhang 2004, Puntervold et al. 2007, Aksulu et al. 2012). The chemical nature of these polar compounds are of acidic and basic characteristics, that can be easily quantified by titration methods (Fan and Buckley 2000, Fan and Buckley 2007).

When oil enters in contact with water, the oil-water interface becomes charged, exposing the electrical attributes of the polar compounds that vary in function of the type of components present, and their concentration. It is possible to have presence of both positive and negatively charged zones in the interface, in other words, the interface can take part in different electrostatic interactions with the mineral surface. Crude oil adsorption onto the rock surface may occur when opposite charges of the oil-water interface and the rock surfaces interact, via intermolecular or inter-ionic forces (Hirasaki 1991, Buckley et al. 1998). Processes of adsorption may also occur when having the same charges in the interface and the mineral surfaces, this is due to presence of discrete and oppositely charged areas, which are scattered in the oil and water interface.

Transport of polar components through the aqueous phase can also determine the stability of water films, causing wettability alteration or intensifying the oil wetness of a system (Kaminsky and Radke 1997, Fathi et al. 2011).

According to Buckley et al. (1998), the main mechanisms of interaction are attributed to:

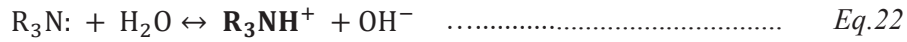
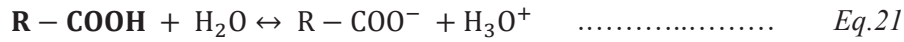
- Polar interactions that predominate in the absence of a water film between oil and solid.
- Surface precipitation, dependent mainly on crude oil solvent properties with respect to the asphaltenes.
- Acid/base interactions that control surface charge at oil/ water and solid water interfaces.
- Ion binding or specific interactions between charged sites and higher valency ions.

The polar organic components or NSO compounds are found in crude oil as acidic and basic organic material, which can be quantified by the acid number (AN) and base number (BN). The unit of measurement is mg KOH/g for both cases. In AN analyses, the unit of measurement represents the amount of KOH needed to neutralize the acidic components in a gram of oil. Whereas, for BN quantification the measurement unit represents the equivalent concentration of basic organic material present in one gram of crude oil.

The acidic material is usually represented by the most influential functional group, the carboxylic group, -COOH. On the other hand, basic material with high polarity contains nitrogen in the aromatic molecules, which is represented as $R_3N:$.

In order to assess correctly the potential of an oil to change the wettability of a surface, mineralogy and water chemistry must be taken into account, because they can play an important role in the interactions between the rock surface and the oil (Morrow et al. 1998, Austad 2013). Usually, the carboxylic functional group decomposes during geological time and temperature. Basic material is more resistant to decomposition, and that is why it is common to find BN values larger than AN in crude oil samples.

A determining characteristic of acid and basic material is that they are polar components. Acid and basic material present at the oil-water interface is susceptible of undergoing fast proton exchange reaction that are conditioned by the pH of the aqueous media, as described in *Eq.21* and *Eq.22*.



The pKa values of many components containing the functional groups R – COOH and R₃NH⁺ are similar (Hodgman 1951, Brown and McDaniel 1955). This similarity means that the concentrations of the reactive species will vary in a comparable way in relation to the pH of the system. The protonated species, i.e., R – COOH and R₃NH⁺, have the highest affinity towards the negatively charged clay minerals. And their presence is promoted at lower pH values. As an example

Under acidic conditions, adsorption of polar components can take place. It was reported that adsorption of quinoline onto illite (Aksulu et al. 2012), and crude oil onto kaolinite (Fogden 2012) was optimum at around pH 5. The adsorption of basic and acidic polar components is crucial to promote the oil-wetness of the clay in sandstone.

As an example, the major microspecies at low and high pH of two polar organic compounds are presented below. Benzoic acid represents the carboxylic material while quinoline represents a nitrogenated heterocyclic base, Figure 8. Note that at low pH the microspecies have a proton incorporated to their structure whereas at high pH that proton is released. The presence or absence of the proton give a different electrostatic charge to the molecules, which influence their affinity for different types of mineral surfaces.

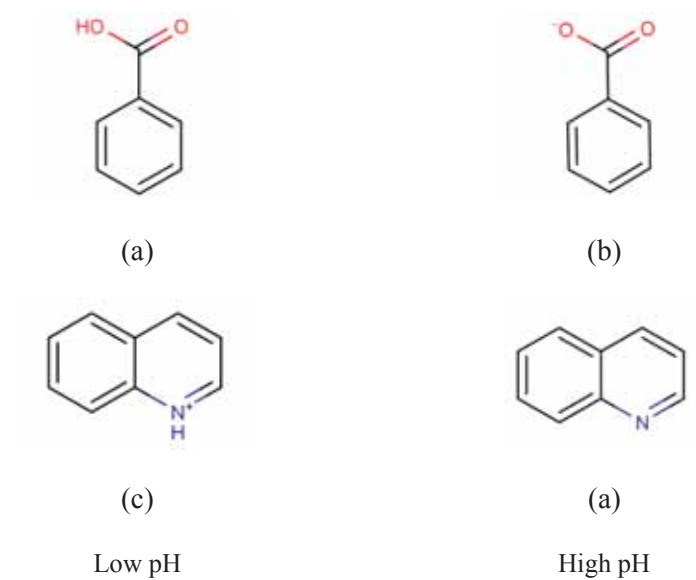


Figure 8. Major micro species of benzoic acid (a) and quinoline (c) at low pH values (left), and major microspecies of benzoic acid (b) and quinoline (d) at high pH values (right).

It is important to note that in sandstones reservoirs local pH increments control the relative concentration of species, favoring adsorption at low pH values where the most active species are the non-dissociated carboxylic acids and the protonated bases, these species are in bold in Eq.21 and Eq.22. Likewise, adsorption will be reduced at higher pH values because the major species will be dissociated carboxylic acids and non protonated bases. On the other hand, in carbonate reservoirs the pH is buffered. Thereby, the dominant species will be the dissociated carboxylic acids and non protonated bases.

3.5.3 Brine composition

Different brine properties are of high importance in the wetting processes, being the chemical composition, salinity, and the pH of brine the most dominating factors (Anderson 1986). The water composition is capable of inducing surface charge changes on a solid surface or at the oil-water interface (Buckley 1994, Buckley and Liu 1998, Buckley et al. 1998, Buckley and Fan 2007, Alroudhan et al. 2015). The effect of each parameter in a brine is constantly depending on the interactions created in crude oil-rock-brine system. Various authors have confirmed these hypotheses using different wettability tests (Zhang et al. 2007, Morrow and Buckley 2011, RezaeiDoust et al. 2011).

The hypothesis that some reservoirs might be mixed wet, instead of complete water-wet was originated when low residual oil saturations were described by Salathiel (Salathiel 1973). He suggested that the wetting state is dependent on the initial water saturation; other scientists validated that idea with the observation of a clear trend in sandstones, which affirms that the water wetness of core material is increased as the initial water saturation increases (Buckley 1995, Jadhunandan and Morrow 1995, Zhou et al. 2000). From there on, the potential of waterflooding processes has been associated to the initial wetting.

It is known that the highest incremental recovery with waterflooding in sandstones is achieved when initial neutral or mixed-wet conditions are met (Jadhunandan and Morrow 1995, Tang and Morrow 1999, Morrow and Buckley 2011). For this purpose, the adequate exposure of core material to crude oil is recommended. Jadhunandan and Morrow (1995) concluded, in a study where 50 Berea sandstone core floods were performed, that oil recovery by waterflooding increased with a wettability change from strongly water-wet to a maximum, close to neutral wettability, Figure 9. In recent years, wettability alteration in sandstones has been a focus of attention for many scientists and oil companies, and today the effect of brine composition on the initial wetting, has been validated by experimental evidence (Madsen and Lind 1998, Burgos et al. 2002, Morrow and Buckley 2011, RezaeiDoust et al. 2011, Fogden 2012).

There have been several interpretations that aimed to uncover the wetting phenomena. Lately, the community has given more attention to the effect of pH on initial wetting and its implications on wettability alteration in sandstones by

studying the low salinity effect, LSE (Austad et al. 2010, Morrow and Buckley 2011, Didier et al. 2015, Shi et al. 2016).

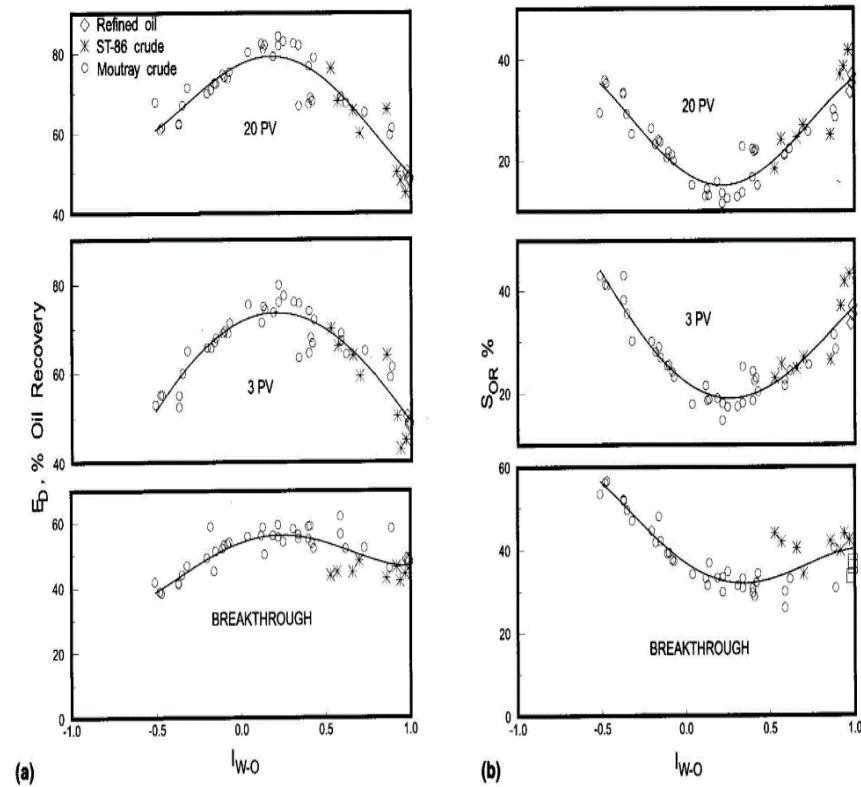


Figure 9. Oil recovery (a) and residual oil (b) vs. I_{w-o} . After Jadhunandan and Morrow (1995).

Different studies demonstrated that the pH has a relevant role in the processes of protonation and deprotonation of polar components in the oil phase, that can also affect their affinity towards the sandstone surface, regulating the initial wetting of a system (Buckley et al. 1989, Austad et al. 2010, Brady et al. 2015). Moreover, the presence of clays and other silicates that can interact with the brine through cation exchange processes are extremely important due to the requirement of a charge balanced surface. The different degrees of affinities originated by the crude oil-brine-rock interactions will dictate the wetting state of the system, where electrolytes in the aqueous solution, polar components and hydrogen ions present in the water will compete for sites of adsorption.

Carbonate reservoirs are regarded as oil-wet (Treiber and Owens 1972), but prior to oil migration into the reservoir it is very likely that the carbonate reservoirs were water-wet. Different statistical studies have presented data showing that most of the carbonate reservoirs behaved oil-wet (Treiber and Owens 1972, Chilingar and Yen 1983). However, carbonates are constituted by several types of minerals that were originated during geological time or that have been subjected to different geochemical processes that could have influenced their wettability. Simple examples could be recrystallization, previous interaction with organic material, chemical breakdown, precipitation of minerals or biological activity (Lucia 1999). In addition, it is very common to find fractures in this type of reservoirs. Fractures make waterflooding a difficult operation because the water will tend to flow through paths of higher permeabilities, avoiding the matrix. However, if the rock is water-wet, spontaneous imbibition can be of benefit. Given the oil-wet tendency of such reservoirs, new methods to change wetting in favor of enhancing the oil recovery are of high importance.

3.5.4 Pressure and temperature

It has been observed that the solubility of polar active components in crude oil is increased as pressure and temperature is increased (Anderson 1986). The author claimed that at atmospheric conditions the cores could behave more oil-wet because of the reduction in solubility of the wettability altering components. Anderson argued that the change in pressure during the extraction of core material could cause fluid expelling from the porous media, changing the spatial distribution of fluid (Anderson 1986). Because of this, a loss of light ends from the crude may occur, making more likely the deposition of asphaltenes, which at the same time shift the wettability towards a less water-wet state. However, other studies have demonstrated that the pressure effect is not very significant, for example, Wang and Gupta carried out a set of experiments where it was found that the pressure effect on wettability measurements was not very sensitive (Wang and Gupta 1995).

Polar components reactivity has also been studied (Sayyoub et al. 1991), and it appears to be affected by the mineralogy of the system. For instance, in high temperature carbonate reservoirs a process of decarboxylation could occur, lowering the AN value. This is due to the presence of calcium carbonate that

can act as a catalyst for such process (Zhang and Austad 2005). As previously mentioned, the wetting of carbonate surfaces is sensitive to carboxylic material, therefore, such effects must be also evaluated in terms of the mineralogy of the system. Furthermore, it has been reported by Hjelmeland and Larrondo (1986) that in a carbonate system, increasing temperatures led to an IFT reduction, while the effect of increased pressure on wettability was low (Hjelmeland and Larrondo 1986). A similar observation in relation to the temperature has also been reported for other carbonate systems that are regarded as more water-wet (Hamouda and Rezaei Gomari 2006).

It was presented by Rao that the quartz surface tends to become more oil-wet as the temperature increases and the opposite result was found in carbonates where the calcite surface tend to get more water-wet (Rao 1999). It has also been shown in Berea sandstone cores that the wettability shifted towards a less water-wet system as the aging temperature was increased (Jadhunandan and Morrow 1995).

3.5.5 Core restoration

The need to preserve the native wettability of reservoir cores has been always a major challenge. Even in the best circumstances, there is always a chance to change the wettability by different processes, such as oxidation, deposition or by changes in temperature and pressure as discussed before. Core restoration consist of three basic steps, which are listed as follows:

1. Core cleaning
2. Core saturation
3. Aging

The cleaning process aims to remove of oil, brines and mud components from core samples. This is followed by the saturation of reservoir fluids, which is a process dedicated to achieve oil and water saturations as found at the reservoir conditions of study. In the last stage the core is aged with the purpose of achieve comparable wetting properties in relation to the reservoir. It is well known that the cleaning process is the most difficult one, since the solvent chosen can significantly change the rock wetting (Shariatpanahi et al. 2012).

The most common methods involve a cleaning process that return the core to a water-wet state, emulating the wettability before the oil invasion in the reservoir. In order to do this, different organic solvents and water should be used to remove the hydrocarbons present in the core, as well as the connate water. The water or brine used to displace the connate water will also remove dissolvable salts that can affect the restoration process, by re-dissolution or precipitation with the formation water. Once the cleaning protocol is finished, initial water saturation is achieved by injecting formation water, FW, and then lowering its saturation by crude oil flooding, simulating the inflow of oil into the reservoir (Anderson 1986). The aging process is needed to assure the adsorption of crude oil onto the surface to create an initial wetting close to the original wettability; aging can take long periods of time, e.g., 1000 hours are needed to reach stable states of wetting. However, other experimentalists have presented evidence of no significant changes after aging for more than 10 days (Rühl et al. 1963, Kowalewski et al. 2002).

For a long period of time, aging was required for creating a mixed wetting. But recent studies in carbonates have confirmed that adsorption of polar components occurs immediately as the core enter in contact with oil (Hopkins et al. 2016). In addition, it has been suggested that using non-aggressive solvents like kerosene and n-heptane in a mild core cleaning process can help to preserve in a better manner initial reservoir wettability. The mild core cleaning can preserve the polar components initially adsorbed onto the chalk core surfaces (Hopkins et al. 2015).

Hence, several progresses have been done to understand initial wettability and improve core restoration methods, but there is a lack of common agreement to evaluate which are the best protocols to follow. However, a combination of new screening techniques could help to reduce uncertainty in the evaluation of initial wetting, which is of high importance in the EOR field.

3.6 Wettability alteration

A substantial amount of oil is left behind in the reservoirs after primary recovery, and a rough estimate is that more than 50 % of OOIP is trapped by different mechanisms, that are significantly driven by the reservoir wetting and its production record (Araujo and Araujo 2005).

Wettability alteration literature counts with several contact angle measurements that are regarded as the universal measure of surface wettability, and more often with spontaneous imbibition experiments. In order to understand the complexity of the wetting phenomena in porous media, spontaneous imbibition appears to be an useful method because it provides information about dynamic IFT, imbibition capillary pressure and the effect of gravity forces (Morrow 1990).

Implementation of spontaneous imbibition experiments is convenient to discriminate which type of forces might be influencing the recovery process (Ravari 2011). The regime can be differentiated depending of the shape of the curve of a spontaneous imbibition process; the different regimes can be identified as follows: (1) Capillary forces, (2) Capillary and gravity forces and (3) mainly gravity forces, as described in Figure 10.

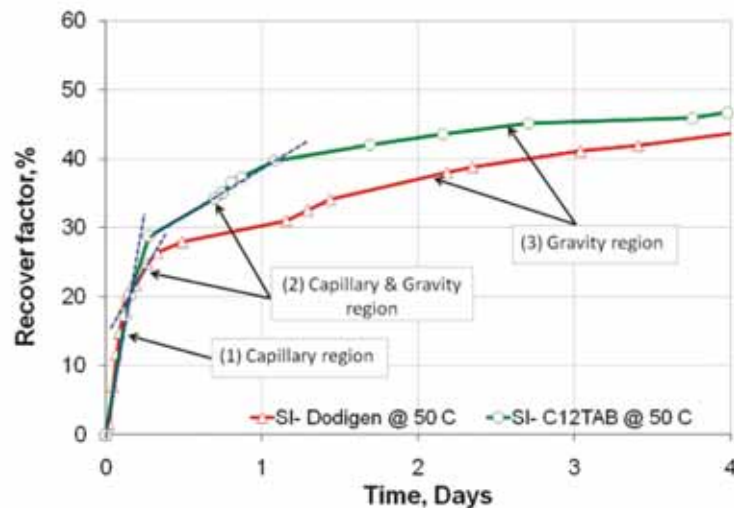


Figure 10. Spontaneous imbibition at 50 °C, comparison of C₁₂TAB and Dodigen (Ravari et al. 2011).

In the capillary region (1), oil production is mainly controlled by capillary forces. These forces are more intense in strongly water-wet situations, in neutral and oil-wet states capillary forces are not expected to have any effect. Steep slopes of oil production also characterize the capillary region. In the capillary and gravity region (2), gravity begins to be more active in the oil production by fluid segregation, and the production slope become less positive. In the last region where gravity is the main driving force (3), the oil production is slowed and the slope of production is usually characterized by a more stable value until that oil production ceases.

3.6.1 Carbonates and wettability alteration

Originally, chemical EOR processes were the object of study to mobilize capillary trapped oil. For this purpose, surfactants were of high interest due to their ability to lower IFT. As a result of this, gravity and viscous forces could act to mobilize a fraction of the previously trapped oil (Adibhatla and Mohanty 2006, Ravari et al. 2011, Kalaei et al. 2012). Though the IFT drop in some cases was not beneficial because it reduced the spontaneous imbibition rates, and spontaneous imbibition can be an important recovery mechanism in fractured carbonate reservoirs.

Thus, numerous authors have dedicated their efforts to enhance the oil recovery from fractured carbonates by wettability alteration to more water-wet states by using surfactants (Austad et al. 1998, Spinler and Baldwin 2000, Standnes 2001, Standnes and Austad 2003, Strand et al. 2003, Mohanty 2006, Somasundaran and Zhang 2006).

The findings of these common efforts were of high value, and different factors were better understood. For instance, Adibhatla and Mohanty (2006) in a study dedicated to gravity drainage by surfactant flooding found that the adsorption of anionic surfactants on calcite surfaces decreased with a pH increase and a reduction in salinity. Another important finding was that IFT and wettability alteration were not linear functions of the surfactant concentration, meaning that wettability alteration was a more complex process (Adibhatla and Mohanty 2006). Mohanty and coworkers, also contributed with several studies of modelling and upscaling of different EOR processes that involved wettability alteration (Mohanty and Salter 1982, Mohanty and Salter 1983). Hirasaki and

Zhang (2004) conducted an experimental work based on wettability alteration of preferential oil-wet systems, and showed that the positive surface charge of calcite can be negatively charged through the presence of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$, a negative zeta potential was expected to promote water-wetness and the experimental work carried out validated that hypothesis (Hirasaki and Zhang 2004). However, a negative zeta potential alone cannot displace oil (Zhang et al. 2007).

The data provided by the studies made by Austad and coworkers focusing on EOR with acidic crude oil in chalk, consisted in the comparison of different surfactants, such as cationic, anionic and non-ionic, and their effect on chalk wettability (Austad et al. 1998, Standnes and Austad 2000, Standnes and Austad 2003). The experimental evidence suggested that especially at low temperatures (40 °C), the cationic surfactant C_{12}TAB was more effective than the other surfactants. Moreover, it did not lead to the creation of ultra-low IFTs. Hence, it allowed capillary forces to increase the oil recovery via wettability alteration. The efficiency of the C_{12}TAB was associated to sulfate, which later was found to work as a catalyst in the wettability alteration process (Strand et al. 2003). This fact marked the importance of the determining ions present in the aqueous phase of the studied system.

The effectiveness of surfactants was dramatically affected at high temperatures (Strand et al. 2003), low pH environments and salinity (Adibhatla and Mohanty 2006). Experiments at higher temperatures $T > 70$ °C (where the surfactants have reduced effect), led to the important finding of wettability alteration induced by water containing determining ions such as Ca^{2+} , Mg^{2+} and SO_4^{2-} . This discovery opened up a new way of understanding the role of the water chemistry and its effect on wettability alteration in carbonates (Strand et al. 2006). In the work conducted by Strand and coworkers, the effect of changing the sulfate concentration in a brine based on seawater (SW) composition was discovered (Strand et al. 2006). The oil recovery increased as the sulfate concentration in the imbibing fluid increased, this effect is summarized in Figure 11.

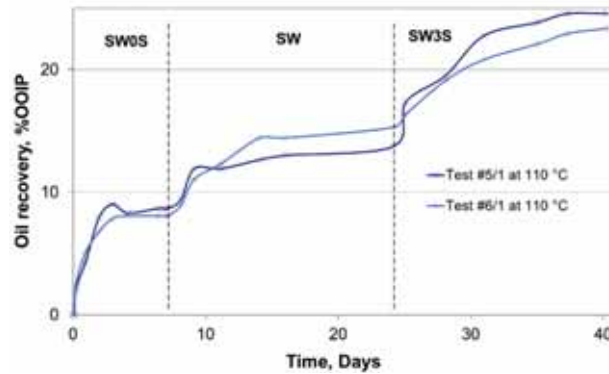


Figure 11. Spontaneous imbibition of a sequence of SW without sulfate (SWOS), SW, and SW with three times sulfate concentration (SW3S) into preferential oil-wet chalk cores at 110 °C. After Strand et al. (2006).

It was found that wettability alteration is basically triggered by chemical adsorption, and different types of surface active compounds can take part, including potential determining ions like Ca^{2+} , Mg^{2+} and SO_4^{2-} . All these ions are present in seawater. Hence, seawater injection in chalk can shift the mixed-wet state towards a more water-wet state, and for this reason seawater was then redefined as an EOR fluid. The refinement of this process is such, that no expensive chemicals are added, wettability alteration can take place without lowering the IFT and increasing the oil recovery; the technique was named Smart Water injection. A perfect example is the exceptional performance of seawater injection observed at Ekofisk. In this reservoir, the positive response to seawater indicated a special rock-brine interaction that improved the spontaneous displacement of oil (Austad et al. 2005), this means that seawater is a Smart Water in a chalk reservoir.

The description of the process is based on the symbiotic interaction of the determining ions, Ca^{2+} , Mg^{2+} and SO_4^{2-} , with the adsorbed carboxylic material onto the carbonate surface (Zhang et al. 2007). Sulfate act as a catalyst, lowering the ionic repulsion exerted on Ca^{+2} ions by the positive surface, by getting adsorbed on the chalk surface while available Ca^{2+} ions in the aqueous phase can react with the previously adsorbed carboxylic groups; triggering a wettability alteration process by desorption of the active components on the surface. It was argued by Korsnes et al. (2006) that by flooding seawater containing sulfate at elevated temperatures, Mg^{2+} can replace Ca^{2+} at the surface (Korsnes et al.

2006). This will lead to a higher concentration of the determining ion Ca^{2+} in solution; it is beneficial due to the importance of Ca^{2+} presence for the EOR Smart Water effect in CaCO_3 surfaces. The reactivity and rate of the wettability alteration process depends on the salinity, composition of the aqueous phase and the temperature of the system (Strand et al. 2006).

3.6.2 Sandstones and wettability alteration

Wettability alteration in sandstones is a major challenge due to their geochemical complexity. Generally, sandstone surfaces are negatively charged within the normal pH range of reservoirs. Their wettability can cover a broad range of values, from strongly water-wet to strongly oil-wet and therefore a careful evaluation of the initial wettability of the system is crucial in order to have a successful process of wettability alteration.

Wettability alteration of sandstones with surfactants entails numerous challenges that arise from their mineralogy. For instance, the presence of clays is highly linked to strong adsorption of surfactants onto the rock surface. Other factors like increasing salinity or generated surface acidity could promote the adsorption of surfactants onto the surface (Kwok et al. 1993). It was argued by Rao et al. (2006) that wettability alteration in water-wet systems can be positive if the wettability alteration goes on the direction of oil-wetness (Rao 2006). On the other hand, in strongly oil-wet reservoirs, a wetting drift towards a more water-wet situation can be beneficial. A research carried out by Seiedi et al. (2011), with atomic force microscopy, has showed two different wettability alteration trends, by using two Triton X-100 and C_{16}TAB on mica, Triton made the system more water-wet whereas the C_{16}TAB made the mica more oil-wet (Seiedi et al. 2011).

Therefore, wettability alteration by surfactants in sandstones can be beneficial if the surfactants are well chosen to execute the change in wetting needed. In general terms, the effect of surfactants in oil recovery is clearly positive but more research is needed to have better control of all variables affecting the oil recovery by wettability alteration.

It is well known that waterflooding is a common practice in sandstone reservoirs, and depending on the type of water injected, wettability alteration may occur.

As a consequence of this, parameters like relative permeabilities of oil and water can be modified, and therefore, oil recovery yields.

The Low salinity effect, LSE, was reported by Tang and Morrow (1997). The experiments performed on Berea sandstone cores indicated that oil recovery increased by spontaneous imbibition and waterflooding with a decrease in salinity (Tang and Morrow 1997). Necessary conditions to observed the effect in Berea sandstone cores were initially proposed by Tang and Morrow (1999). The main requirements were then described as follows.

- Significant presence of clay.
- Presence of connate water.
- Exposure to crude oil to create mixed-wet conditions.

The conditions above presented do not explain all the experimental results observed, and they are not sufficient for all types of sandstones; in some cases outcrop samples that met these requirements did not show the LSE effect (Morrow and Buckley 2011).

Today, it is generally accepted that the LSE is induced by wettability alteration towards a more water-wet condition. Enhanced oil recovery is observed because imbibition of water is able to reach previously unswept pores. Thereby, low salinity water is a specific type of Smart Water for sandstones (RezaeiDoust et al. 2009). This can be stated because the water chemical composition is the only parameter adjusted and no additional chemical are incorporated into the fluid. Furthermore, common characteristics are shared with the effect observed in carbonates. For example, no ultra-low IFTs are induced in a broad range of pH values and temperatures, and larger capillary action is promoted by the change in wetting towards a more water-wet state, leading to an improved sweep efficiency. Hence, low salinity water flooding is recognized as an EOR method that is driven by majorly wettability alteration. It is also important to note that IFTs obtained in LS brines are slightly higher than at higher salinities (RezaeiDoust 2011), see Figure 12.

Incremental oil recoveries have been reported when core floods are carried out with low salinity brines in cores containing clays (Tang and Morrow 1999). Moreover, several authors have referred to the existence of different salinity

thresholds in order to observe positive low salinity effects (Jerauld et al. 2006); increased recoveries using up to 5000 ppm have been regarded as LSE (Morrow and Buckley 2011). It has also been argued that divalent ions in LS brines have given mixed results (Zhang and Morrow 2006). Austad et al. (2010) have emphasized that a balanced presence of divalent ions in FW is a factor that can promote adsorption of polar components by influencing the pH of the system. Adsorption of polar organic components favors mixed-wet conditions, which are needed to observe LS effect. The author also argued presence of divalent ions in LS brines is not positive because it may hinder the pH rise needed to observe LS effects (Austad et al. 2010). Other authors have also pointed out the negative impact of divalent ions in FW (Lager et al. 2008).

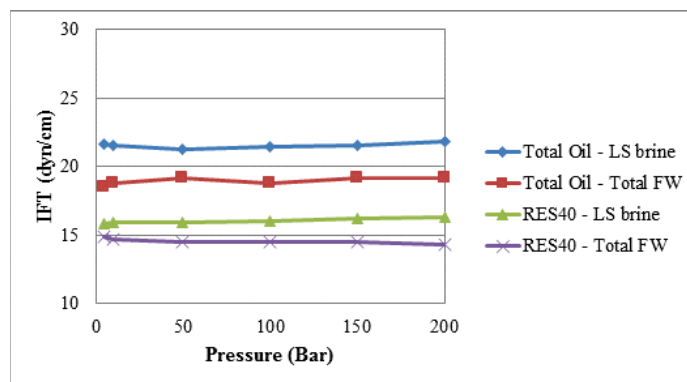


Figure 12. IFT as a function of pressure and salinity at 40 °C (RezaeiDoust 2011).

The number of publications about LSE have skyrocketed in the recent years. The high variability in results has allowed a proliferation of different mechanisms and most of them are not capable of explaining why in some cases the LSE is not taking place. Nevertheless, all the interest in the phenomena has led to a better understanding of the LSE as well as testing and deployment of the technology through inter-well trials (Seccombe et al. 2010) and recently to the full field implementation of low salinity injection in the Clair Ridge field in the North Sea by BP. This world leading project has a development cost of only 3 USD a barrel (Buikema et al. 2011), this is a strong evidence of the technique's cost efficiency. The first oil from the project is expected by the end of 2017.

3.7 Waterflooding as an EOR method

Standard waterflooding has the purpose of giving pressure support as well as improving the fluid flow of oil towards the producers, and the typical water used is formation water. In general terms, formation water is not expected to induce a significant change in wetting because it is already in equilibrium with the formation. Nevertheless, if the composition of the injected water is deliberately engineered to alter the wettability of the reservoir by changing the chemical composition, waterflooding can be then regarded as an EOR method.

Waterflood efficiency depends on the reservoir wettability and the brine composition of the injected water. When the wetting state of a reservoir is not optimum, it may be possible to improve its wetting in order to produce more oil by Smart Water flooding.

3.8 Smart Water definition

In order to define what Smart Water is, it is also important to ask the question: *How does Smart Water act in the porous media to produce EOR effects?*

To answer the question, the main effects on wettability and fluid flow properties must be described. Smart Water improves wetting properties of reservoirs, optimizing fluid flow and enhancing oil recovery in porous media during production by wettability alteration. Smart Water will also affect parameters associated to fluid flow in porous media such as relative permeabilities of oil and water and capillary forces by disrupting the established chemical equilibrium of the reservoir. Moreover, increased capillary forces created by Smart Water injection allow a better water imbibition into smaller pores improving sweep efficiency, and thereby inducing EOR effects, Figure 13. Smart Water is prepared by modifying the ionic composition of the water, no expensive chemicals are added, i.e., surfactants or polymers, it is a cost-effective technique (BP 2016), and it is more environmentally friendly than other water-based EOR methods.

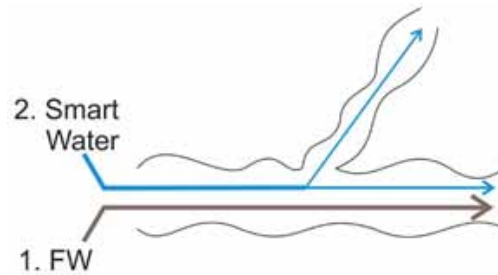


Figure 13. Scheme of how wettability alteration with Smart Water increases sweep efficiency due to increased capillary forces.

In short terms, Smart Water can be used to refer to a modified injection brine that can alter the reservoir wettability and improve oil recovery.

Yet, when the important consequence of using Smart Water is to improve oil recovery, the mechanism to achieve this purpose depends on the type of mineralogical formation that is targeted. Therefore, the chemical mechanisms in sandstones and carbonates are different. However, common features are also found. The literature covers several studies of Smart Water in both sandstones and carbonate involving wettability alteration. A major common aspect is that wettability alteration changes towards a more water-wet situation (Austad 2013).

The initial wetting of the reservoir is also an important factor. This property is established during millions of years within the reservoir, via chemical equilibrium of the present phases. Usually, the initial wetting is not optimum for oil recovery purposes, but the wettability can be improved by using Smart Water injection to favor oil production. Indirectly, initial wettability sets the limits for success of the waterflooding operation. For instance, if a system is completely water-wet, a Smart Water aiming to make the system more water-wet, can see its EOR potential substantially reduced. Thus, the Smart Water EOR potential has a strong link to initial wetting (Fathi et al. 2011).

The details of the chemical mechanisms behind the Smart Water EOR effects will be presented for sandstones and carbonates later, additionally the major differences and similarities will be discussed.

3.9 Mineralogical description of sandstones, carbonates and calcium sulfate minerals

Reservoir mineralogy is a critical parameter to understand when it comes to wettability issues and implications to Smart Water injection. The nature of the reservoir mineralogy will dictate the type of wetting mechanism and by consequence, the potential to observe EOR effects with Smart Water. A brief review on mineralogy of sandstones and carbonates is presented in this section.

3.9.1 Sandstones

By definition sandstones are clastic sedimentary rocks that are composed of clasts from 63 μm to 2 mm. Consolidated sand grains constitute the main structure of them and their pores can be empty, partially filled or completely filled. Particles of finer clastic material, cement or fluids can fill up the pore space.

Sandstones constitute around 15% of the sedimentary rocks. Their textures can record depositional setting, dispersal and transport mechanisms. They are also major reservoirs of ground water and hydrocarbons.

They are mainly composed of quartz, feldspars, rock fragments, accessory minerals, micas and clay minerals. Being monocrystalline quartz (SiO_2) grains the most abundant type of sandstone grain. In average, they contribute from 60 to 70 % of sandstone. This is due to the common presence of quartz in rock such as granite, gneiss and schist as well as for its high resistance to disintegration and decomposition. The sandstone classification is broadly divided in arenites and wacke. Arenites are Quartz arenites (Orthoquartzites), Feldspathic arenites (Arkosic) and Lithic/sublithic arenites; wackes are pooled together as wacke (Prothero 2004).

Typical quartz arenites consisted in average from 95% to 97% of SiO_2 , up to 1 % of Al_2O_3 and 1% of cementing material CaCO_3 . They constitute a third of the sandstone material on earth. Feldspathic arenites typically contain up to 50% of feldspar material and they contribute to approximately 20% of the total sandstone abundance on earth (Pettijhon 1975). Lithic and sublithic arenites have a varying presence of quartz that goes from 30% to 80%, other rock

fragments can go from 5% to 50%, and they constitute the most important sandstone family. Wackes have abundant clay presence and have quartz in the range from 50% to 70%, their abundance is close to 20% (Pettijhon 1975, Prothero 2004).

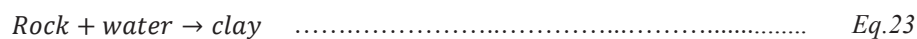
3.9.1.1 Micas

Micas are a group of phyllosilicate minerals that occurs in igneous, metamorphic and sedimentary regimes, their chemical composition is very similar. Micas appear in sandstone as silt and sand, the major micas are biotite, muscovite and chlorite, they are flake and discoidal shaped. Micas are detrital material, that was originated during weathering process of other rocks (Pettijhon 1975).

3.9.1.2 Clays

Clay minerals is a definition that includes several type of minerals from the hydrous aluminous phyllosilicates. They are generally abundant in sandstone, and clays are fine-grained with particle sizes lower than 2 μm . In order to be identified, they should be analyzed through X-ray diffraction or differential thermal analysis because of their fine grain size (Pettijhon 1975). Clay environments are limited by temperature and they are mostly at the upper layers of the earth crust. When temperatures are greater than 50 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$ they start to mutate into other minerals such as other type of clays, feldspars or micas.

The origin of clays lays on the simple interaction of silicate minerals and water. Therefore, they are by nature more hydrous than other minerals, *Eq.23*. And the range of forming temperatures is from 4 $^{\circ}\text{C}$ to high temperatures of approximately 400 $^{\circ}\text{C}$ under short thermal pulses caused by geothermal activity (Velde 1995).



Clay minerals are sheet-like structured, their main building blocks consists of tetrahedral or octahedral arrangements that are put together by sharing oxygen ions between Si or Al ions of the adjacent tetrahedral or octahedral (Worden and Morad 2003), see Figure 14.

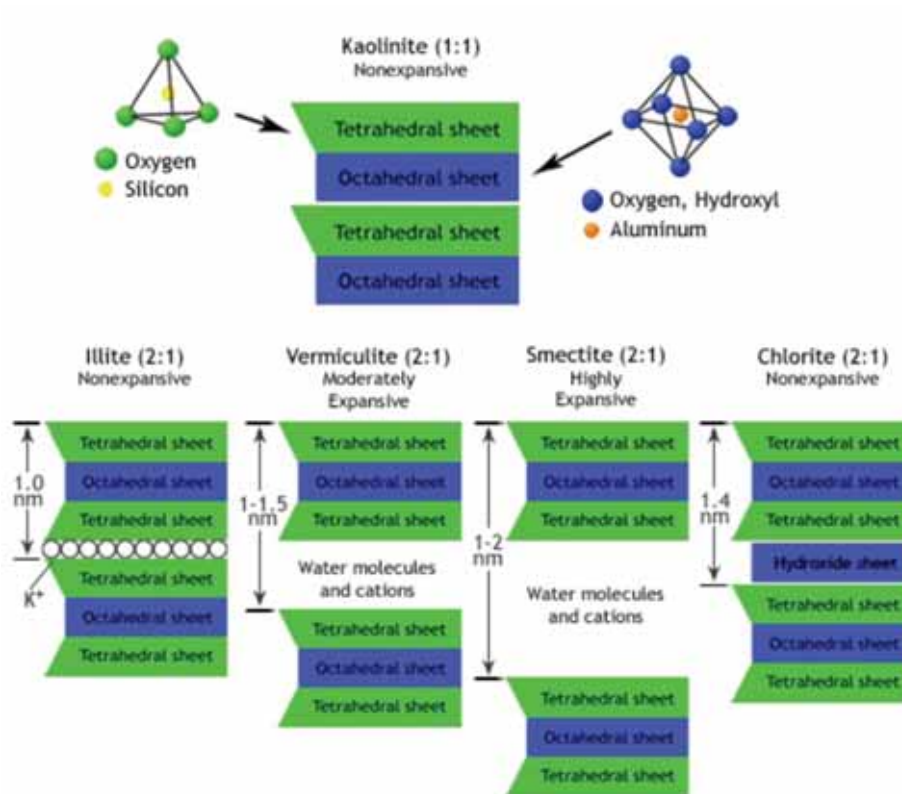


Figure 14. Overall Structure of 1:1 and 2:1 Clays, (Lorry 2016).

Most of the cations in the structures are silicon or aluminum, the number of oxygen that can surround a silicon ion is four. For reasons such as bonding orbital geometry and ionic size, the oxygen polyhedron will give shape to a tetrahedron. To achieve electrical neutrality, the bonding should be equal to that of the surrounding oxygens. However, the positive charge of silicon is four, while the charge of the total four oxygens is eight, but this situation is compensated by sharing the oxygen with other cations.

Aluminum, magnesium or iron form polyhedral structures with six oxygens instead of four. The counter ions of cations can be oxygens or hydroxyls. These structures are octahedral coordinated polyhedral units. Contrary to the tetrahedral, the octahedral linkages can have two to three cations. Therefore, dioctahedral or trioctahedral structures can occur. Al ions are

the major occupants of the space in between the tetrahedral and octahedral layers, however, other ions are demanded to charge balance the structure, among them iron, calcium magnesium and potassium are the most recurrent.

There are five major groups of clay minerals: kaolinite, illite, chlorite, smectite and mixed-layer varieties.

Kaolinite clays are made of one tetrahedral layer linked to one octahedral without interlayer cations. This type of structure is termed 1:1; O-H-O bonds connect them. The chemical formulation of Kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolinite has a tendency to form pseudo hexagonal plates that are found stacked (Worden and Morad 2003).

Illite has a high content of potassium in dioctahedral structures that are placed in between two tetrahedral layer; this type of structure is called 2:1. Bonds of the type O-K-O connect two opposing tetrahedral layers. The potassium cation is required for charge balance the present substitutions of silicon by aluminium. The O-K-O linkage reduces the swelling behavior due to the strong nature of the bond. The chemical formula of illite is given by $\text{K}_y\text{Al}_4(\text{Si}_{8-y}\text{Al}_y)\text{O}_{20}(\text{OH})_4$, with the y value being usually less than 2 (Worden and Morad 2003). Illite can take multiple shapes, such as flakes, filaments or hair like crystals.

Chlorite possess a 2:1:1 structure, made up of a negatively charged 2:1 structure, composed of a tetrahedral-octahedral configuration. However, differently to other clays, it has an octahedral positively charged layer made of cations and hydroxyl ion. Its chemical formula is $(\text{Mg,Al,Fe})_{12}[(\text{Si,Al})_8\text{O}_{20}] (\text{OH})_{16}$. Smectite is a 2:1 layered group with one octahedral in between two tetrahedral layers. Their cations present in between layer are exchangeable and can expose the history of its contact with aqueous mediums. As the ions in between the layers can become hydrated, this clay has swelling properties in contact with water but other organic fluids can cause the same effect. Montmorillonite is a good example of them. Its chemical formula is $(0.5\text{Ca,Na})_{0.7}(\text{Al,Mg,Fe})_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$.

Mixed-layer clays are a consequence of the interstratification of different mineral layers. Mixed minerals contain mostly smectite, illite-smectite and chlorite-smectite. The layer stacking is random, and this grade of disorder works as a way of classification in relation to the degree of disorder and the proportion

of illite present, common names are corrensite (chlorite-smectite) and allevardite (illite-smectite).

The main characteristic of clay minerals are the negative charges located at the edges or ends of the unit cells, this situation can lead to substitution of cations or to the interaction with the surrounding media to assure its charge balance. These sites can depend on pH conditions and are called variable charges (Velde and Meunier 2008). On the other hand, the so-called permanent charges depend on cation substitution within the layers. Both permanent and variable charges contribute to the cation exchange capacity of the clay minerals, CEC.

The impact of variable charges in the overall CEC is negligible in smectites but very important in kaolinite or illite (Velde and Meunier 2008). The reversible exchange of ions in the interlayer zone depends on the composition of the aqueous media. This property is denominated cation exchange capacity (CEC) and it is expressed in milli-equivalent per 100 grams of sample. The cations can be organized in series based on their replacing power, however, the definite position of a cation in a series will depend on the sort of clay and on the size of the ion replaced. There is a degree of attraction of different cations towards clay minerals, a typical behavior of replacing power is shown below (Yong et al. 2012). The main properties of clay minerals are summarized in Table 3.

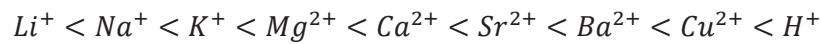
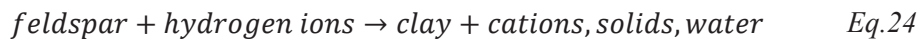


Table 3. Properties of main clay minerals (IDF 1982).

Property	Kaolinite	Illite	Chlorite	Smectite
Structure	1:1	2:1	2:1:1	2:1
Particle size (µm)	0.5-5	Large sheets up to 0.5	0.1-5	0.1-2
CEC (meq/100g)	3-15	10-40	10-40	80-150
Typical surface area BET (m ² /g)	15-25	50-110	140	30-80

3.9.1.3 Feldspars

Feldspars are a silicate minerals classification that occur in igneous rocks. Silicon and oxygen are the base constituents, but the presence of calcium sodium and potassium is a main characteristic of them. The relative abundance of these ions in dictates the type of feldspar studied. Feldspars contribute in the formation of clay minerals by a hydration process, where feldspars are the main initial mineral species. The chemistry of hydration is initially based on cation exchange mechanisms, and it can be described by *Eq.24* (Velde and Meunier 2008).



In general terms, feldspars are less abundant than quartz in sandstones, constituting between 10% and 15% of the sandstone. They are more easily decomposed than quartz. The main families of feldspars are K-feldspar, which is composed of orthoclase; sanidine, microcline, and plagioclase feldspars, which are sodium, or calcium rich feldspar such as albite or anorthite. The prevalence of K-feldspars is higher because they can resist decomposition better than plagioclases (Blum 1994, Crundwell 2015).

Feldspars appear to have reversible cation exchange activity, especially Na^+ can be exchanged with H^+ ions, this explains why albite is more susceptible of weathering in comparison to K-feldspars (Blum 1994). Additionally, cation occupancy is favored in the basic pH region (Blum 1994), Figure 15. They can be subjected to dissolution or changes at pH values lower than 6 or higher than 8.5 (Blum 1994). According to Stumm and Morgan (1996), feldspar have point of zero charge that ranges from 2 to 2.4, at neutral pH feldspars have a negative zeta potential (Stumm and Morgan 1996). Additionally, at the conditions studied by Oelkers et al. (2009), in the pH region of 1 to 10, the zeta potential is consistently negative, Figure 15.

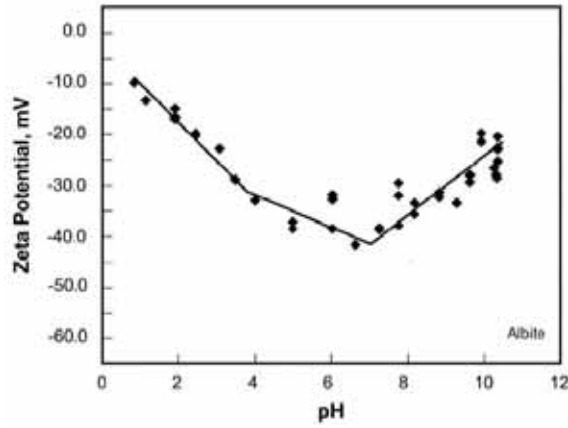


Figure 15. Effect on the zeta potential of albite in a solution of 0.1M NaCl at 25 °C (Oelkers et al. 2009).

The stability of feldspars is also temperature dependent. However, in the pH range from 5 to 9 the variation of dissolution rates is not very high. This is valid in a broad range of temperatures that can go from 3 °C to 300 °C (Gruber et al. 2016), see Figure 16.

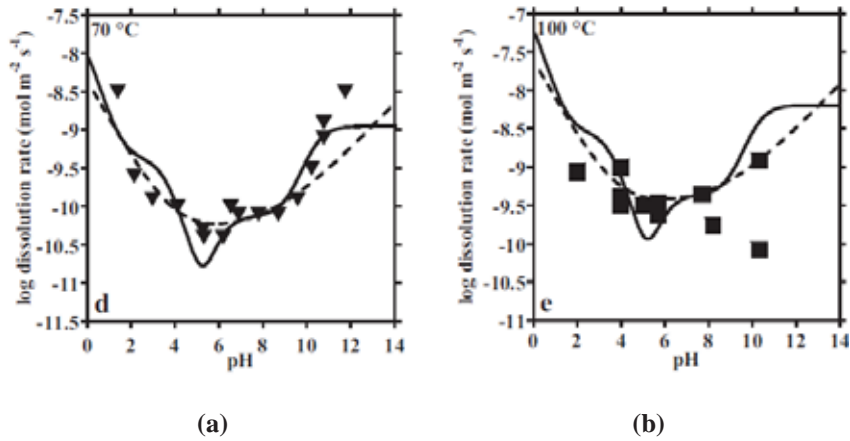


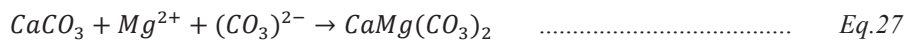
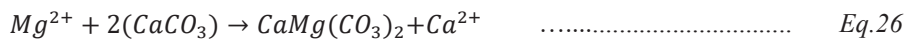
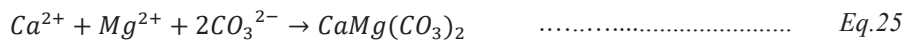
Figure 16. Change in log albite dissolution rate ($\text{mol.m}^{-2}.\text{s}^{-1}$) as a function of pH at (a) 70 °C and (b) 100 °C (Gruber et al. 2016).

3.9.2 Carbonates

Carbonates constitute approximately one tenth of the earth’s sedimentary shell. Their origin can be chemical or biochemical. The chemical origin comes from ions in solution that can precipitate and form solid minerals. Different organisms can extract components from seawater and build up shells or skeletons that later will be part of sedimentary rocks. Limestones are considered as clastic sedimentary rocks and dolomite is a chemical sedimentary rock that has its origins in the diagenetic alteration of limestone.

Carbonate minerals are made up by the combination of divalent ions (2+), with a high predominance of calcium and magnesium but iron, strontium, manganese and barium carbonates can be formed. The most abundant carbonates are calcite, aragonite and dolomite. The first two are polymorphs of CaCO₃, whereas dolomite comes from the substitution of magnesium for calcium.

For instance, any carbonate with magnesium content higher than 5% is regarded as a different mineral. Dolomite, which its chemical formula is CaMg(CO₃)₂ consists of alternating layers of calcium and magnesium that are separated by CO₃²⁻. In theory, dolomite have equal amounts of divalent ions but the average dolomite has a content of approximately 56% of calcium and 44 % of magnesium. Enormous obstacles are presented when trying to produce dolomite in laboratories, suggesting that only small amounts of primary dolomite is created naturally (Prothero 2004). Three main mechanisms have been suggested as summarized by Prothero (2004) in *Eq.25-Eq.27*.



The first one is the direct precipitation of dolomite from seawater, the second one involves replacement of calcium ions by magnesium ions, this include addition of magnesium and removal of calcium from the system and the third one is a dolomitization process involving dolomitizing fluids that provide magnesium cations and carbonate ions without being removed from the system.

Limestone formations have a relevant economic importance because they can bear oil and gas within their porous system. Nearly 80% of the oil production in the USA comes from carbonates and worldwide carbonates contribute with almost 50% of the oil production. Limestone is defined as a sedimentary carbonate rock with a content of calcite larger than 50% (Prothero 2004).

Chalk is a porous sedimentary carbonate rock made up of calcite. It is formed by accumulation of skeletal debris of calcite shells from microorganisms called coccolithophores. The typical base particles are calcite tablets with diameters ranging from 0.5 to 1 μm . These basic structures give shape to platelets which are put together in rings, such structures are called coccoliths and their average size diameters of these structures range from 3 to 15 μm (Standnes 2001, Prothero 2004).

3.9.3 Evaporites: Calcium sulfate minerals (Anhydrite, hemihydrate and Gypsum)

Evaporites are bedded sedimentary rocks that were crystallized from brines. They mainly consist of soluble ions. Among the most common evaporites are carbonates (calcite, aragonite, magnesite); sulfates (gypsum and anhydrite); and halides (halite, sylvite, and carnallite).

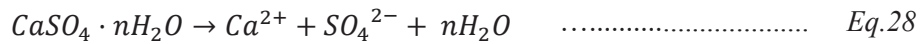
Calcium sulfate minerals such as anhydrite and gypsum are common marine evaporites. The chemical formula of anhydrite is CaSO_4 , which is the anhydrous form of calcium sulfate. On the other hand, gypsum is the di-hydrated form with the chemical formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Depending on the environmental conditions, anhydrite can mutate into gypsum and vice versa. Factors influencing this process are temperature, pressure and salinity of the solution. According to Posnjak (1938), the temperature threshold for this shift is 42 °C, and at higher temperatures anhydrite appears to be the stable form (Posnjak 1938). Moreover, there is also a transition from gypsum to the hemihydrate with a chemical formula of $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ at 97 °C. It was argued by Posnjak that within the region from 42 to 97 °C gypsum is metastable.

The solubility of the three different calcium sulfate phases is temperature dependent, Figure 17. Anhydrite has a low crystallization kinetics at

temperatures below 70 °C, this makes it difficult to get accurate estimates of the solubility below 42 °C, being the best estimates located in the region between 42 °C and 60 °C. Yet, there are clear trends that can allow the comparison of the different solubility of the phases. In the region from 0 to 200 °C the highest solubility is attributed to the hemihydrate, followed by anhydrite that is more soluble than gypsum from approximately 45 °C and upwards. Being gypsum the less soluble from 45 to 200 °C.

The solubility of the different calcium sulfate phases is described by the following equation.



Where:

- $n = 0$ For anhydrite
- $n = 0.5$ For the hemihydrate
- $n = 2$ For gypsum

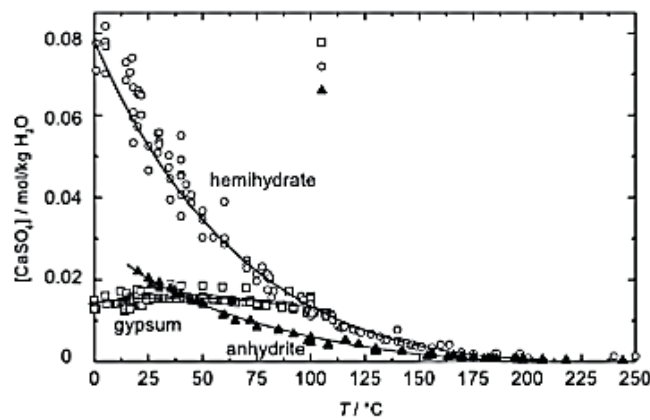
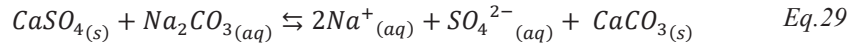


Figure 17. Literature data of solubility of gypsum, anhydrite and hemihydrate in the temperature range 0-200 °C at saturation pressure (Freyer and Voigt 2003).

In relation to EOR processes, the presence of dissolvable calcium sulfate is a factor that cannot be ignored, since depending on the type of formation it can be beneficial or problematic. For example, in alkaline flooding processes it has a negative impact since its dissolution triggers $CaCO_3$ precipitation (Lopez-

Salinas et al. 2011), as shown in *Eq.29*. Further implications of this process of dissolution will be discussed later in this thesis.



In carbonate formations, large amounts of anhydrite can be present in salt domes forming caprocks or reservoirs. Anhydrite constitute from 1 to 3% percent of salt domes. However, when halite is removed by water dissolution, anhydrite becomes upconcentrated and anhydrite is left as a layer accompanied by patches of gypsum (Saunders and Thomas 1996, Walker 1976). In an evaporite sequence, calcium carbonate is precipitated first, followed by calcium sulfate.

Anhydrite is also present in sandstone reservoirs as cementing agent that is usually located in the pore space or as oolite grains, the anhydrite distribution in sandstone reservoirs can be affected by cyclic dissolution and precipitation due to ground water streams. In a waterflooding operation, the evaluation of anhydrite presence is essential because gypsum hydration can occur, and increasing volume of the calcium sulfate deposition can cause formation damage (Collins and Wright 1985). Nevertheless, it seems that in cases where the calcium sulfate sources are present in low amounts it might not be detected by standard analysis, e.g., x-ray diffraction (Lopez-Salinas et al. 2011), therefore appropriate techniques should be implemented to have a proper quantification of dissolvable sulfate (Aksulu et al. 2012), i.e., ion chromatography. Other side effects of mismanagement of calcium sulfate minerals, is scaling. This problem is initiated by mixing of incompatible compositions of brines, which can generate scale problems that can end up with formation damage. It can also be an obstacle for implementation of EOR processes due to calcium or sulfate dissolution from anhydrite (Sharma et al. 2014). However, it seems that calcium and sulfate dissolution can be beneficial in Smart Water injection in carbonates (Austad et al. 2015), for these reasons, quantification of sulfate bearing minerals must be well managed to make it work in favor of a production project.

3.10 Smart Water EOR in sandstones

Based on the chemical attributes of sandstones and the chemisorption evidence found in the literature, it is easy to understand that Smart Water EOR in sandstones is a phenomenon that is strongly influenced by the pH of the system. The pH development depends on the rock, brine, crude oil interactions. A more detailed discussion on the topic is brought below.

3.10.1 Initial wetting

In clastic formations the presence of clays plays a significant role due to their large surface area and the presence of permanent localized negative charges. Due to these attributes clays show the highest affinity towards crude oil components, and for this reason they are the main wetting mineral in a clastic formation. The confirmation of clay presence from X-ray analyses are key in the evaluation of EOR potential of a sandstone reservoir. Adsorption of polar components on clay minerals is a pH dependent process, in the acidic region, $\text{pH} < 7$, basic material, R_3NH^+ , can be adsorbed onto the clay surface by electrostatic interaction, whereas the protonated acidic material can interact and get adsorbed via hydrogen bonding (Madsen and Lind 1998, Burgos et al. 2002).

Cations with an elevated replacing power, such as H^+ and Ca^{2+} will be also subjected to adsorption in such conditions. Calcium has an important role in initial wetting, because if Ca^{2+} concentration is high it may be able to displace some H^+ from the clay surface at the water-wet sites, leading to a pH drop that can increase the adsorption of polar components (RezaeiDoust et al. 2011), lowering the water wetness. The temperature can also increase the reactivity of divalent ions such as Ca^{2+} or Mg^{2+} , because the hydration number is reduced as the temperature increases (Zavitsas 2005). This effect will lead to higher levels of adsorption of Ca^{2+} on the clay surface.

Thus, the overall distribution of active surface species on the clay surface at a given reservoir temperature (T_{res}) will depend upon the pH conditions that will dictate the relative affinity of the species towards the clay. The oil wetness degree will be linked to the affinity of polar components in specific circumstances of temperature, pH, and composition/salinity of the brine, they are the components that will effectively initiate the wetting by oil on the surface.

When this occurs, the surface will become mix-wet (Austad et al. 2010, RezaeiDoust et al. 2011, Aksulu et al. 2012, Fogden 2012, Aghaeifar et al. 2015). This is analogue to what actually happened in oil reservoirs that were initially filled up with formation water and were successively invaded by crude oil. A requirement to obtain a mix-wet situation is to replace in this process the active cations already present on the surface by active polar components.

The processes of adsorption appear to be reversible (Austad et al. 2010, RezaeiDoust et al. 2011), this is in some way explained by the pH dependence of the concentration of polar organic components, R_3NH^+ and $RCOOH$, which decreases as the pH increases. As examples, the pH dependence of the fractions of the protonated basic component quinoline is shown in Figure 18, and the non-dissociated benzoic acid is shown in Figure 19. Protonated basic components and non-dissociated acids are the most active in adsorption onto negative clay minerals. When this fraction is lowered by a pH increase, it reduces adsorption onto surfaces, and a more water-wet system is then expected.

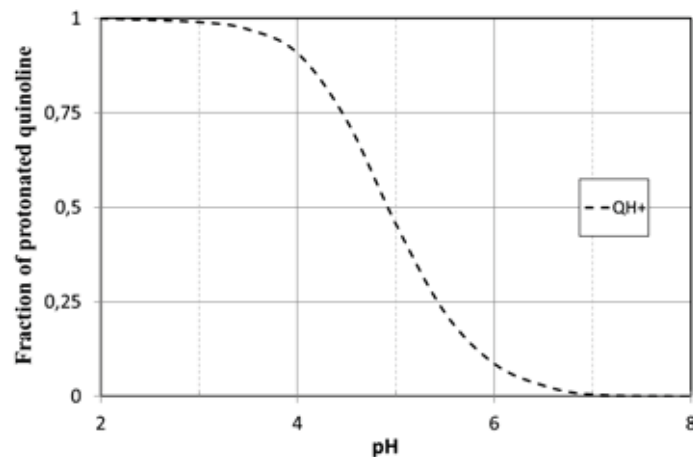


Figure 18. Fraction of protonated quinoline against pH. Re-drawn after (Burgos et al. 2002).

Characterization of the initial reservoir wetting can be addressed in function of the mineralogy, i.e., presence of clay and total amount, crude oil properties, i.e., especially acid number (AN) and base number BN values, formation water properties, i.e., salinity, pH and Ca^{2+} concentration and reservoir temperature.

Buckley and Morrow (1990), conducted a study about adhesion properties of 22 crude oils onto silica surfaces as a function of brine composition and pH. In the adhesion map, they observed characteristic pH values in the range of 6-7, above which, adhesion did not appear to happen at different salinity values. They concluded that pH was the key driver in the wetting process. It was also observed that deasphalted crude oil did not exhibit adhesion in the low pH range, confirming that pH effect on adhesion was primarily linked to surface active components in the crude oil (Buckley and Morrow 1990).

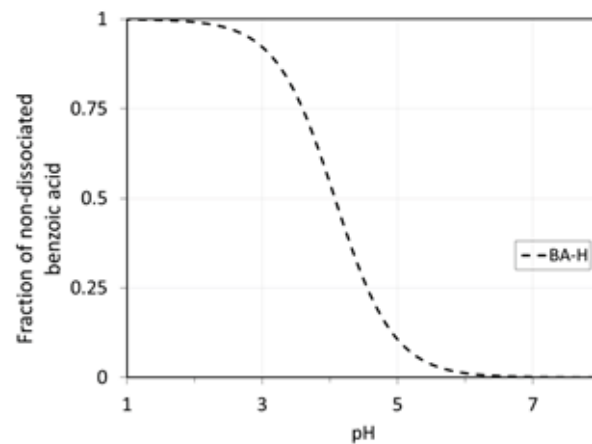


Figure 19. Fraction of non-dissociated benzoic acid against pH. Drawn after calculation with Marvin Sketch®.

3.10.2 Wettability alteration

The reversibility of the adsorption processes and the pH dependence are the bases of wettability alteration in sandstones. Wettability changes in either direction, towards oil-wet or water-wet states can be explained by a variability of the main properties of a specific system (RezaeiDoust et al. 2011, Fogden and Lebedeva 2012, Aghaeifar et al. 2015). For instance, the water wetness of a sandstone reservoir can be increased if any of the following changes occur:

- Increased concentration of Ca^{2+} in the FW
- Increased pH of the brine
- If T_{res} is increased

There are several published chemical studies about the reversibility of adsorption of polar active components on clays and silica surfaces and its pH dependence (Chorover et al. 1999, Burgos et al. 2002, RezaeiDoust 2011, Didier et al. 2015).

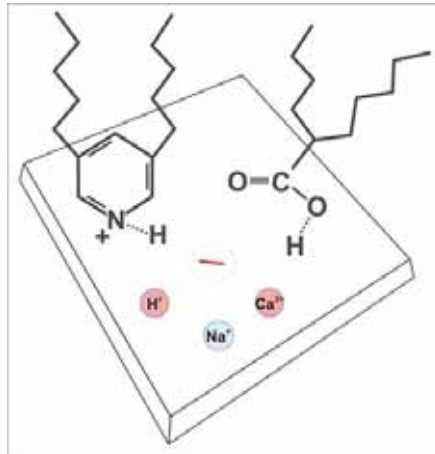


Figure 20. Competitive adsorption of ions and polar organic components onto sandstone surfaces.

Burgos et al. (2002) studied the adsorption of quinoline onto kaolinite as a function of pH and Ca^{2+} concentration at room temperature, and found that at a given pH the adsorption was larger at low Ca^{2+} concentrations, and adsorption was reported to decrease as the pH increased, at high and low Ca^{2+} concentrations. Likewise, Rezaeidoust et al. (2011) conducted an adsorption study of quinoline onto kaolinite as a function of pH and salinity, and proved that adsorption was reversible in the pH range of 5 to 9 at high and low salinities. They also found that at pH 2.5 the quinoline had shown low adsorption, even when the quinoline was fully protonated. This was explained by the increased activity of the H^+ ion which overcomes the affinity of the protonated quinoline.

Adhesion maps of crude oil on silica surfaces as a function of pH and brine composition presented the same trends in the pH region of 6 to 7 (Buckley and Morrow 1990, Didier et al. 2015). But adhesion did not occur at higher pH values, concluding that pH was the main factor behind the trends observed in wettability. Didier et al. (2015) backed up these results in a study using crude oil on two different types of sand. A striking observation was that adhesion of crude oil was enhanced in presence of a low salinity brine. These results contradict the

ionic models used to explain the LS effect, such as the double layer expansion, Gouy Chapman and DLVO theories, when pH changes are not included.

Madsen and Lind (1998) studied the adsorption of benzoic acid onto kaolinite. Their observations presented an increased adsorption of benzoic acid as the pH decreased from 9 to 5. Thus, the same trends apply for acidic polar components in relation to adsorption-desorption processes. This means that both acidic and basic polar components can influence wetting if present in crude oil. Experiments conducted at the Smart Water EOR laboratory at the University of Stavanger showed increased adsorption of quinoline onto illite at lower salinities and constant pH, Figure 21.

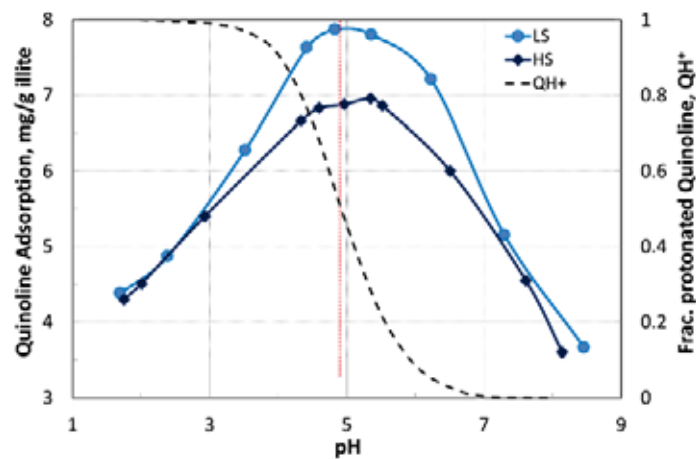


Figure 21. Quinoline adsorption and fraction of protonated quinoline vs pH. Re-drawn after Aksulu et al. (2012).

Fogden and Lebedeva (2012), carried out similar studies using crude oil onto kaolinite and the adsorption trend against pH was similar, i.e., highest adsorption was reduced as the pH increased, Figure 22.

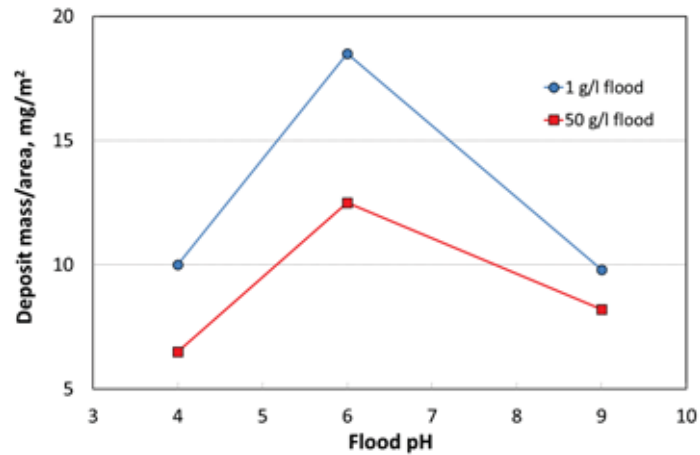


Figure 22. Adsorption of crude oil onto kaolinite, after Fogden and Lebedeva (2012).

3.10.3 Proposed low salinity EOR mechanisms in sandstones.

Understanding low salinity waterflooding is crucial to executing an adequate exploitation of the method. Numerous approaches have tried to explain the phenomena, however, some theories have large gaps that do not match the experimental evidence. The experimental work presented in the literature is vast but even today the community is using methods that are controversial. Some of the proposed mechanisms are included next.

3.10.3.1 Fines migration

Fines migration was proposed by Tang and Morrow (1999), and with this mechanism they attempted to explain the effect observed with a low salinity brine. The idea consisted in that at low salinities the electrostatic interaction between clay particles are higher than at high salinities, and this will lead to expansion of the double layer. As a result of this, clay particles will be detached from the rock surface, this explanation is based on the DLVO theory. If these particles were mixed-wet, the overall system would become more water-wet increasing oil recovery.

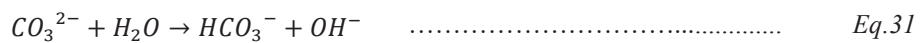
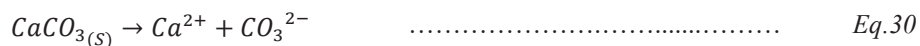
It was found that the fines were mainly kaolinite particles and that this effect was accompanied by a pressure drop increase. Furthermore, in this mechanism it was suggested that the release of particles can also block a part of the pore throats being responsible for the permeability reduction observed and in the worst case causing a serious damage to the porous media (Tang and Morrow 1999).

However, evidence for fines migration has not been observed in several experiments presenting LSE (Lager et al. 2008). The LS effect has been also observed in cores that did not contained any kaolinite at all (Cissokho et al. 2009). This mechanism does not explain the increased oil-wetness at a given pH with low salinity compared to a high salinity brine (Aksulu et al. 2012). Thus, fines migration is a mechanism that is not capable of explaining some of the important experimental observations reported in the literature.

3.10.3.2 pH variation

The effect of the pH has been object of attention in previous mechanisms because it has been reported in laboratory work and pilot tests (Tang and Morrow 1999, McGuire et al. 2005). McGuire et al. (2005) suggested that the effect behind the LSE is a similar effect to the one observed in alkaline flooding. It was explained by in-situ generation of surfactants; in theory, this will cause a reduction in interfacial tension promoting additional oil recovery.

Their simulation approach showed that the dissolution of kaolinite reduced the pH and dissolution of calcium carbonate explained the pH rise by the following equations.



The main drawback of the mechanism is that the activation of natural surfactants by the presence of polar components in the crude oil do not fit with the oil recovery experiments reported for alkaline flooding (Lager et al. 2008). Nevertheless, it is well known that a pH increment can make more water-wet sandstone and silica surfaces (Didier et al. 2015). Numerous tests performed by BP at reservoir conditions did not record the pH increment but displayed a

positive LSE, perhaps due to strong buffer effects (Webb et al. 2005, RezaeiDoust et al. 2011), other cases showed pH increments but no incremental recovery was seen (Reinholdtsen et al. 2011). Thus, the mechanism does not cover all aspects of wetting and the LSE experimental observations, nonetheless, it pointed out to a chemical mechanism, which is of high relevance in wetting processes.

3.10.3.3 Double layer expansion

A more physical approach was presented as a possible mechanism for the LSE, the double layer expansion effect (Ligthelm et al. 2009) was explained by an enlargement of the double layer as the low salinity invades the porous media, increasing the electrostatic forces that will eventually overcome the binding forces that were keeping the oil on the surface. This suggestion has a strong physical approach and it is in contradiction to the adsorption trend of polar components and crude oil exposed earlier in this thesis (Burgos et al. 2002, Austad et al. 2010, Fogden 2012). These simple facts make the mechanism questionable at constant pH conditions.

3.10.3.4 Multicomponent ion exchange

The multicomponent ion exchange mechanism (MIE) (Lager et al. 2008), suggested that multivalent cations present in the formation water will bond to polar compounds present in the oil phase forming organo-metallic complexes and promoting oil-wetness. During LS injection, MIE takes place, removing organic polar compounds and organo-metallic complexes from the surface and exchanging them with uncomplexed cations (Lager et al. 2008, Lager et al. 2008). Their claims were based on the fact that LSE does not occur when the formation water is stripped from divalent ions during the aging process. The adsorption mechanisms suggested by Sposito (1989), where the base to discuss the adhesion of crude oil onto the rock surface where Ca^{2+} acts as a sort of linkage between the negative surface charges of clay and crude oil. It was also claimed that the organic material should be removed by an ion exchange process (Sposito 1989, Lager et al. 2008).

The observations presented by Lager et al. (2008) showed a drop in the Mg^{2+} concentration in a larger extent than Ca^{2+} , and it was attributed to an exchange

mechanism. Nevertheless, it was argued by Austad et al. (2010) that these observations could be due to precipitation of divalent ions inside the core material. Furthermore, the experiments conducted by Cissokho et al. (2009) showed that the concentration of divalent ions is key parameter in the LSE (Cissokho et al. 2009).

3.10.3.5 The Smart Water LS mechanism

An adequate interpretation of the chemical evidence presented in the sections of initial wettability and wettability alteration in sandstones are covered by the Smart Water mechanism in sandstones. The mechanism of EOR LS injection in sandstones suggested by Austad et al. (2010), gives a leading role to the pH obtained from the interacting brines of the system and its impact on wettability (Austad et al. 2010), a schematic explanation of the Smart Water EOR LS mechanism is presented in Figure 23.

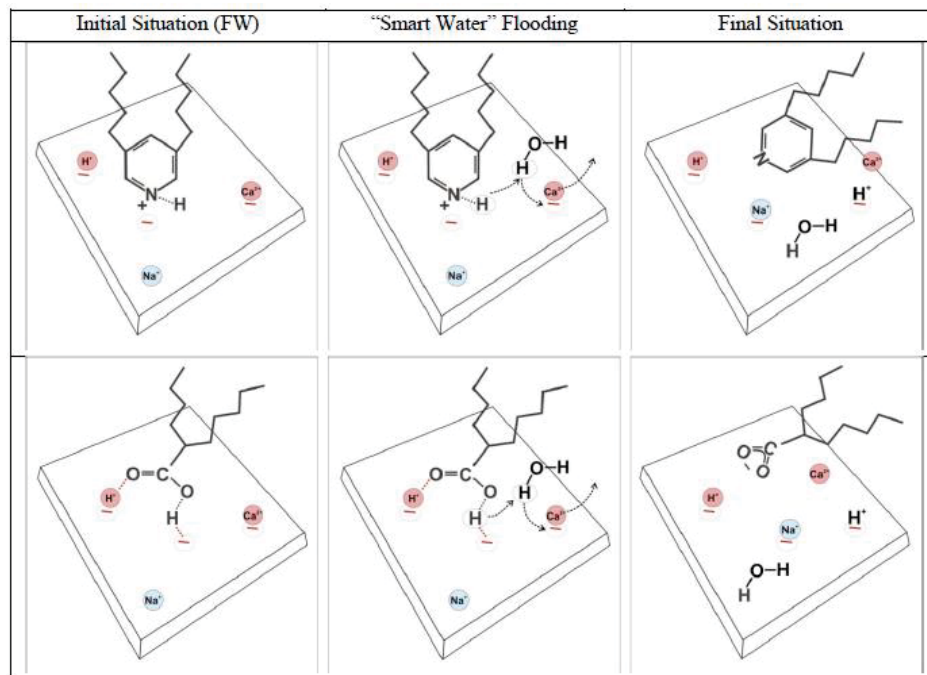
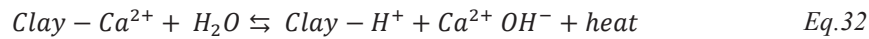
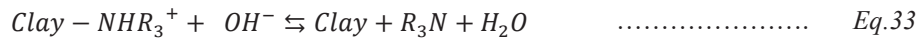


Figure 23. Smart Water mechanism with LS, the figure displays how adsorbed acidic and basic material onto clay minerals can be removed by an in-situ pH increase by desorption from the clay surface (Austad et al. 2010).

When a low salinity brine is injected, the equilibrium established with FW is disrupted, and as a result of this, desorption of cations from the surface takes place (Ca^{2+}) to reestablish equilibrium. This effect creates negative charges on the clay surface that must be charge balanced. At reservoir conditions, the H^+ ion has the largest affinity towards clay minerals, and by adsorption of an H^+ ion, the negative site located at the clay surface becomes charge balanced. The adsorbed H^+ ion is uptaken from water molecules, creating a local pH rise.



The local pH rise at the clay surface is the basis for the desorption of organic material from the clay surface. This is exemplified in the *Eq.33* and *Eq.34*. The whole description for basic and acidic material are shown in *Figure 23*.



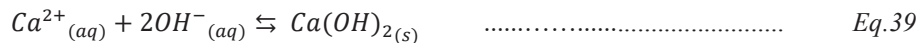
Note that the first step in the mechanism is exothermic, *Eq.32* (Aksulu et al. 2012) (Gamage and Thyne 2011). Temperature can thus affect desorption of Ca^{2+} . In addition, added Ca^{2+} in the LS brine or from $\text{CaSO}_{4(\text{aq})}$ can slow down the process described in *Eq.32*.

In reservoirs, the pH increase is negligible due to buffer effects. Mg^{2+} , Ca^{2+} , CO_2 and H_2S presence could buffer the pH by the following chemical aqueous equilibriums, *Eq.35-Eq.37*.



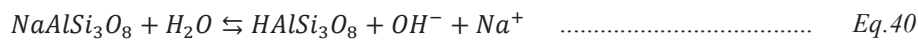
High salinity brines, with a high calcium concentration can have pH values close to 5.5 (RezaeiDoust 2011). The initial FW pH is influenced by FW composition, salinity, rock mineralogy, pressure, temperature and presence of sour gases such as CO_2 or H_2S . At the same time, these factors can influence the partition coefficient of CO_2 and H_2S in water.

Divalent ions can reduce the pH rise by precipitation of hydroxides, especially at elevated pH values. Thereby, they have the ability of reducing the potential to observe LS Smart Water effects.



In the reservoir, a chemical equilibrium is established among the different phases creating specific pH conditions, pressure and temperature. Depending on the initial conditions and wetting, adsorption of inorganic cations and polar organic components can take place onto the clay surface. A pH of approximately 5, favors adsorption of both non-dissociated carboxylic material and basic material onto clay minerals (Madsen and Lind 1998, Burgos et al. 2002).

Feldspars can also affect the pH of a system. For instance, reactive albite is capable of increasing the pH of a system by cation exchange. This occurs when it enters in contact with water as presented in *Eq.40* (Strand et al. 2014). When it comes to outcrop material containing reactive plagioclase, it is important to note that fresh water may have percolated sandstone formations and albite, $NaAlSi_3O_8$, could have been turned into $HAlSi_3O_8$. In such situation, and if FW is present, the protonated albite can produce acidic conditions. As shown in the chemical equilibrium of *Eq.41* (Strand et al. 2014).



Efficient characterization methods of the EOR potential are of high interest to the industry because they can save time and economic resources. Each of them can be advantageous in some aspects but disadvantageous in others. In the next sections some of these aspects are briefly explained.

3.10.3.6 pH screening

The pH screening is a method that aims to test the potential to observe low salinity Smart Water EOR effects in sandstones. It can be carried out relatively fast by using a 100% water saturated core at reservoir temperature, flooding it

with FW-LS-FW (Aksulu et al. 2012). The test can give information about the interaction between brines and the effective surface area exposed to brines in the porous media. It also provides information about initial wetting, LS potential (magnitude and speed) and reversibility of the process. What is also important from this test is that pore surface mineralogy is intact, and the brine interacts specifically with the effective area of the porous media.

In order to evaluate the LS EOR potential, during the injection, the pH should be plotted against pore volume injected, PV. An example is shown in Figure 24. Rock samples with potential to show LS EOR effects are characterized by an initial pH below 7. This is due to the fact that low pH values will favor the adsorption of polar components onto the rock surface creating mixed-wet conditions. Furthermore, the observation of a significant increase in pH as the HS brine is displaced by the LS brine is also a good indication of a positive potential. The pH increase in sandstone will generate the conditions for desorption of polar components and therefore changing the wettability towards a more water-wet state. Under such conditions, the Smart Water EOR effect may take place.

A typical pH screening result is shown in Figure 24. During the first FW-LS flood it was observed that desorption of Ca^{2+} from the clay surface is an exothermic process because the pH gradient decreases as the temperature increases, Figure 24. Provided that the concentration of active cations in the LS brine is low, desorption of Ca^{2+} will increase the pH, as the H^+ ions are adsorbed onto the negative site of the clay. Contrarily in the LS-FW flood, adsorption of Ca^{2+} will decrease the pH as H^+ is desorbed/displaced from the clay surface as the LS brine is switched to the FW brine. By observing the rates of change, adsorption of Ca^{2+} onto the clay is a fast reaction, while desorption is a much slower process, Figure 24.

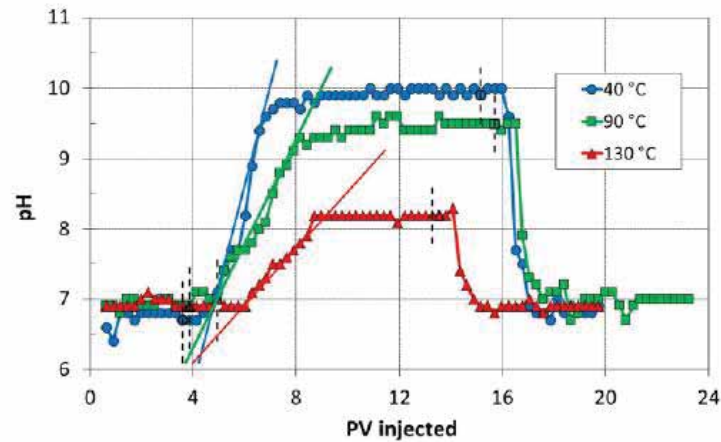


Figure 24. Change in the pH effluent versus PV injected in a reservoir core at temperatures ranging from 40 to 130 °C. Flooding sequence, FW-LS-FW. Injection switched is indicated by dashed lines. FW, 100 000 ppm NaCl and CaCl₂; LS 1000 ppm NaCl (Aksulu et al. 2012).

Therefore, the desorption rate of active cations as the LS brine invades the core material is highly affected by temperature. In cores where the clay contribution to pH changes is important, there is a decrease in the magnitude of the pH change with increasing temperature. Moreover, a reduced desorption rate of calcium from the clay is observed due to the exothermic nature of this process, see *Eq.32*. Therefore, it can be difficult to observe LS EOR effects at high temperatures, especially at $T_{res} > 100$ °C, compared at low temperatures $T_{res} < 100$ °C (RezaeiDoust et al. 2010, Gamage and Thyne 2011, Aghaeifar et al. 2015).

Minerals such as anhydrite or minerals of the feldspars type, i.e., plagioclase, if present in clastic rocks, can have influence on the development of pH when exposed to high salinity and LS brine. High temperature reservoirs may contain anhydrite, CaSO₄, which can dissolve in the presence of LS brine. Increased concentration of Ca²⁺ in the LS brine will shift the chemical equilibrium of *Eq.32* to the left, and the pH gradient will decrease. Furthermore, the presence of Ca²⁺ and Mg²⁺ in combination with a larger availability of hydroxyls (OH⁻), can lead to precipitation of Ca(OH)₂ and Mg(OH)₂ as shown in *Eq.38* and *Eq.39*. Therefore, Ca²⁺ and Mg²⁺ in solution have a large control of the ultimate pH observed in a Smart Water flood.

Feldspars/Plagioclase is a group of anionic polysilicates, which can be charge balanced with Al³⁺, Ca²⁺, K⁺, and Na⁺. Albite, NaAlSi₃O₈, is a common type of

plagioclase, and in some cases, at low salinities an alkaline solution can be observed due to the exchangeable Na^+ ion, as shown by *Eq.40* (Friedman et al. 1992).

As previously mentioned, the pH should remain below 7 during the high salinity flood or formation waterflood to confirm the absence of an alkaline environment that can cause too water-wet conditions. In the next step, which is the Smart Water LS flood, the pH gradient should increase due to the LSE triggered by the desorption of Ca^{2+} ions from the clay. As a last measurement, re-injection of HS/FW is recommended to test the reversibility of the process, which can be confirmed with a pH drop. The method itself can give information about the likelihood to observe LSE, however it cannot forecast the incremental recovery of a system since the oil phase is not present. In combination with an oil recovery test, it may serve as a tool to evaluate the LS Smart Water potential.

3.10.3.7 Adhesion tests

A rapid way to characterize crude oil-brine-rock interactions is to use adhesion maps as described by Buckley and Morrow (1990). They are useful because they show consistent trends for complex crude oil and brine interactions. They also provide a rapid way to characterize systems. Adhesion maps are susceptible to variations derived from temperature changes or high salinity concentrations. The method is less susceptible to problems related to evaporation of the fluids (Buckley and Morrow 1990).

Didier et al. (2015) proposed an improved protocol that will allow the equilibration of the studied system for different pH and salinities. The study aimed to evaluate the combined effect of salinity and pH on oil adhesion to sand grains and showed that at relatively low and very high pH values oil adhesion on to the substrate was stronger, while there was a zone of no adhesion in between the other two regions, Figure 25.

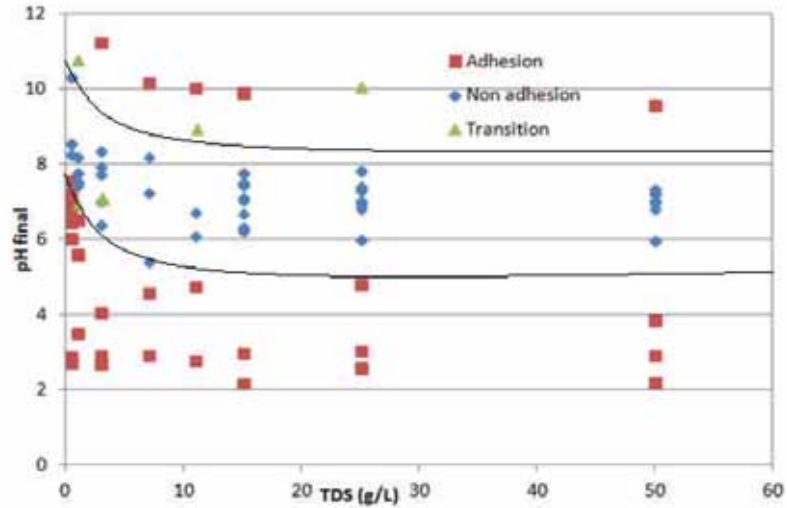


Figure 25. Adhesion of crude oil onto Fountain blue sand (Didier et al. 2015).

The drawback with this method is that mineral surfaces from crushed samples may not be representative for mineral pore surfaces in reservoir rocks. Hence, the crude oil-brine-rock interaction might be deviated from the ones occurring in a porous system. Furthermore, in the attempt of having a pure silica system the protocol does not include a reducing agent for the iron and manganese oxides which can influence pH changes (Didier et al. 2015). Tessier et al. (1979) used a reducing agent to have a complete dissolution of iron oxides in soil substrates and it can be convenient to control this type of side complexation reactions (Tessier et al. 1979).

3.11 Smart Water EOR in carbonates

Carbonates are definitely of huge importance because more than 60% of the world's oil is held in carbonate reservoirs (Schlumberger 2007). Broadly speaking the average recovery factor is 35% of OOIP, which is lower than the recovery in sandstones. This makes carbonate reservoirs an important target for EOR methods, especially for Smart Water injection. It promotes wettability modification towards a more water-wet condition, and at the same time enhances spontaneous imbibition of water into the reservoir matrix increasing oil recovery. Therefore, the method can be of interest in fractured carbonate reservoirs. A description of the major known factors affecting oil recovery when using Smart Water in carbonates are described next.

3.11.1 Initial wetting

Recall the earlier section about initial wetting, where it was stated that carbonates are on average oil-wet (Cuiec 1984). The final outcome of a Smart Water injection is highly influenced by initial wetting (Shariatpanahi et al. 2011). Thereby, It is important to correctly identify the initial wetting state of a carbonate system, and in order to do so, it is important to take into account the water film stability (Hirasaki and Zhang 2004). Water film stability is influenced by the zeta potential of the carbonate surface and the oil water interface, which is very often negatively charged by the presence of carboxylic material in crude oil at reservoir pH conditions. Instability caused by the interaction between the latter two causes adsorption of negatively charged polar components onto the carbonate surfaces creating initial wettability.

The acid number of a crude oil (Standnes and Austad 2000, Zhang and Austad 2005) is then an important parameter regarding wetting (Fathi et al. 2011). During geological time crude oil can be susceptible to changes in the chemical composition that can create polar components with higher or lower affinity toward carbonate surfaces. Therefore, substitution of the adsorbed material can take place in function of the degree of affinity. In some cases, the oil present in the reservoir may not be the oil that has initially wetted the reservoir. Thus, it is important to also take into account the history of the reservoir.

It has been described by Puntervold et al. (2007), that natural bases of crude oil are not very likely to co-adsorb with the carboxylic material onto the chalk surface due to steric hindrance. Moreover, they can form acid-base complexes reducing the adsorption of carboxylic material onto the chalk surface. Thereby, a higher BN does not imply more oil-wetness but rather the opposite.

Temperature is also important in carbonate reservoirs. There is a trend that shows more water-wet states as the temperature of the reservoir increases. This is due to that carboxylic material content decreases by decarboxylation, as the reservoir temperature increases, and CaCO_3 presence catalyzes this sort of reaction, which becomes only significant during geological time (Shimoyama and Johns 1972). Hence, a lower amount of acid in the crude oil leads to higher water-wetness (Standnes and Austad 2000).

Equally important, is the presence of sulfate, either in the brine of the system or in the carbonate formation in the form of dissolvable mineral species, i.e., anhydrite, gypsum. It is well known that SO_4^{2-} is a potential determining ion that can increase the water-wetness by being present in the aqueous media or by re-dissolution of the calcium sulfate present in the reservoir (Austad et al. 2015). Several studies have shown increased water-wetness with sulfate present in the FW or formation (Puntervold et al. 2007, Shariatpanahi et al. 2011).

3.11.2 Wettability alteration by Smart Water in carbonates

Several studies have proven that seawater can act as a wettability modifier in carbonates at high temperatures by increasing the water-wetness of the targeted systems (Austad et al. 2008, Puntervold et al. 2009, Fathi et al. 2011). Wettability alteration in carbonates with Smart Water can increase imbibition of water and at the same time, it could boost capillary action to improve sweep efficiency. The Smart Water wettability alteration in carbonates consists of a symbiotic effect among the determining ions Ca^{+2} , Mg^{2+} , SO_4^{2-} and the carboxylic material adsorbed onto the surface and the temperature of the system (Strand et al. 2006, Zhang et al. 2007, Gupta and Mohanty 2011, Puntervold et al. 2015). The mechanism and other important aspects of the wettability alteration processes in carbonates are explained next.

The mechanism of wettability alteration suggests that the potential determining ions, Ca^{2+} , Mg^{2+} and SO_4^{2-} are capable of influencing the surface charge of water-wet spots on carbonate surfaces to change the wettability of the rock (Zhang et al. 2007, Fathi et al. 2012).

The established chemical equilibrium of a system is disrupted by the injection of a brine with a higher concentration of potential determining ions. Then, the catalyst, SO_4^{2-} , is adsorbed onto the carbonate surface, lowering the density of positive charges. Due to this, less electrostatic repulsion allows the calcium ions to approach the surface and displace the carboxylic material adsorbed onto the surfaces via ion-bonding and finally altering the wettability of the surface.

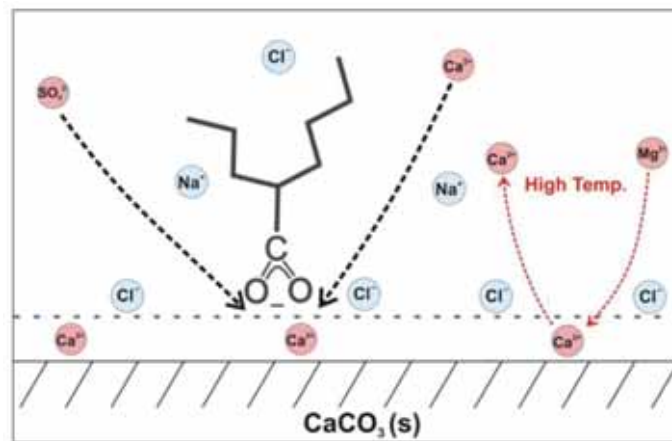


Figure 26. Schematic model of the suggested mechanism for wettability alteration induced by seawater. (a) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active species. (b) Mechanism when Mg^{2+} , Ca^{2+} and SO_4^{2-} are active species at higher temperature. Re-drawn after Zhang et al. (2007).

The main potential determining ions are Ca^{2+} and SO_4^{2-} , nevertheless Mg^{2+} can become slightly more reactive at higher temperatures, $>90\text{-}100\text{ }^\circ\text{C}$, because its hydration energy drops (Zhang et al. 2007, Austad et al. 2008, Shariatpanahi et al. 2010, Aksulu et al. 2012, Shariatpanahi 2012). In brines with similar ion composition to seawater, Ca^{2+} can be exchanged with Mg^{2+} at the carbonate surface, increasing the determining Ca^{2+} in solution to induce wettability alteration. Thus, Ca^{2+} and Mg^{2+} reactivities towards the carbonate surface are extremely important in a dynamic process involving wettability alteration, i.e., Smart Water flooding. Surface reactivity is responsible for the rate of the EOR

effect and the operational temperature range. Zeta potential measurements reported by Zhang (2006), indicated that Mg^{2+} ions increased the zeta potential of chalk to a more positive value than Ca^{2+} (Zhang 2006). However, in a dynamic process, i.e., core flood, the reactivity of Ca^{2+} towards the carbonate surface has been reported to be larger than the Mg^{2+} reactivity (Strand et al. 2006). This fact also reveals a drawback in techniques like zeta potential measurements, which are measured at static conditions to simulate dynamic wettability alteration processes. Another contribution of Mg^{2+} is to stabilize the sulfate ion. $CaSO_4$ solubility decreases as the temperature increases above 100 °C, but in presence of Mg^{2+} the solubility is enhanced by the formation of an ion pair between Mg^{2+} and SO_4^{2-} , lowering the activity of SO_4^{2-} in solution. This is also why seawater can be injected reservoir at high temperatures including reservoirs at 130 °C (Zhang et al. 2006).

It was later found that if the concentration of non-determining ions, e.g., Na^+ , Cl^- in seawater was reduced, a larger EOR effect could be observed. This was confirmed by spontaneous imbibition rates in chalk (Punternold and Austad 2008, Fathi et al. 2011, Punternold et al. 2015). Moreover, if in addition to the reduction of non-determining ions the brines were spiked with a higher concentration of sulfate, the catalyst for wettability alteration, a further increase in the EOR effect was obtained. Figure 27 shows the impact of modifying the chemical composition of the water in spontaneous imbibition from a chalk core.

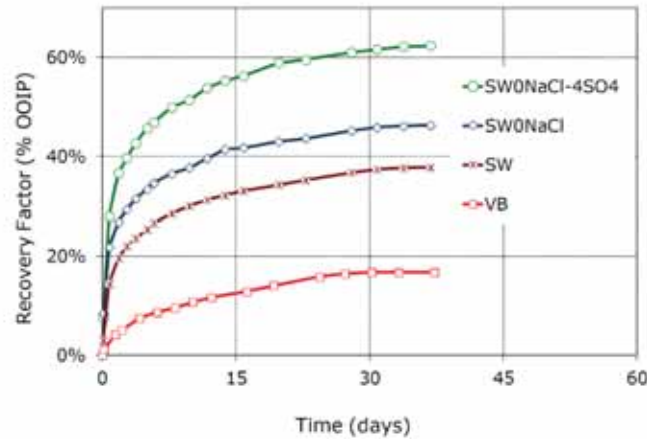


Figure 27. Spontaneous imbibition into oil saturated chalk core at 90 °C using VB, SW, and modified seawater: SW0NaCl, and SW0NaCl-4SO₄²⁻, $S_{wi}=10\%$, AN= 0,5 mgKOH/g (Fathi et al. 2011).

Thus, the Smart Water mechanism in carbonates is a wettability alteration process towards a more water-wet system that is influenced by an interplay of the determining and non-determining ions and the temperature.

3.11.3 Smart Water in dolomite

Limited work on dolomitic material is available in the scientific literature, but experimental observations have shown positive LS effects in dolomites (Romanuka et al. 2012) and dolomitic-limestone (Yousef et al. 2011). However, recent experiments suggest that the mechanism in dolomites has an important impact coming from the magnesium present in the dolomitic surfaces. This is highly related to the affinity of the negative charged carboxylic acids, R-COO⁻, which is larger toward Ca²⁺ than Mg²⁺ (Brady et al. 2012). There are indications of less strong interactions between the carboxylic material and the dolomitic surfaces compared with CaCO₃ surfaces. This characteristic may facilitate the shift to a water-wet system with a minor concentration of Ca²⁺, Mg²⁺ and SO₄²⁻ ions in the EOR fluids (Romanuka et al. 2012).

Contrary to the behavior observed in limestone or chalk, oil recovery by spontaneous imbibition with seawater, in dolomite cores at 70 °C, showed low EOR effects. However, significant EOR effects were observed by diluting SW

10 times, both in reservoir core material containing anhydrite and in outcrop core material without anhydrite present (Romanuka et al. 2012).

Shariatpanahi et al. (2016) conducted experimental work on dolomites and concluded that Smart Water injection is feasible in dolomite. The study also suggested that the adsorption of polar components in dolomites was weaker than in calcite. Moreover, EOR effects were observed in seawater diluted 10 times at 70 °C, while no effect was observed with formation water diluted 100 times without sulfate present (Shariatpanahi et al. 2016). It seemed that sulfate is required for wettability alteration to take place in dolomites.

3.11.4 Alternative mechanisms of wettability alteration in carbonate surfaces

Alternative ideas to the wettability alteration have been also suggested. A dissolution mechanism derived from studies of mechanical weakening in chalk (Omdal et al. 2009) was proposed by Hiorth et al. (2010). The analysis made with a geochemical model that coupled bulk aqueous and surface chemistry, led them to claim that mineral dissolution appeared to be the controlling factor for the improved oil recovery by seawater in chalk (Hiorth et al. 2010, Madland et al. 2011).

The work received criticism from Austad et al. (2009), who argued that oil production by wettability alteration increases as the concentration of Ca^{2+} increased, and due to the common ion effect, the addition of Ca^{2+} into the imbibing fluid will reduce chalk dissolution. Furthermore, Austad and co-workers presented a set of experimental data arguing that there was no correlation between the modelled dissolution of chalk and enhanced oil recovery (Austad et al. 2009).

Garcia-Olvera and Alvarado (2016), proposed an alternative EOR mechanism in carbonates, which was based on fluid-fluid interactions. It reported that the interfacial film between a Smart Water and crude can be more elastic than the film created with crude oil in presence of a high salinity brine (Garcia-Olvera and Alvarado 2016). The authors suggested that the elastic interface with Smart Water is more resistant to the interfacial film breakage, known as snap-off. By

suppression of the snap-off, the oil phase remains continuous increasing oil recovery.

However, the work overlooked the effect wettability alteration in carbonates as well as the effect of determining ions on which has been extensively documented by different authors (Yousef et al. 2011, Austad 2013). Moreover, the supposition of a water-wet state of all cores can be questionable because adsorption of polar components onto calcium carbonate surfaces occurs instantaneously (Hopkins et al. 2016).

3.11.5 Effect of calcium sulfate minerals on the Smart Water EOR effect

The detection of calcium sulfate minerals, i.e., anhydrite, gypsum as pore surface minerals is crucial for the right assessment of the EOR Smart Water potential in carbonates, because these minerals are a source of SO_4^{2-} and Ca^{2+} . As briefly mentioned earlier, their presence can affect the initial reservoir wetting by increasing the water-wetness, even at very low sulfate concentration in the formation water (Punternvold et al. 2007, Shariatpanahi et al. 2011).

In addition, the presence of these types of minerals can also positively affect the Smart Water EOR effect in carbonates, because re-dissolution of the calcium sulfate present in the reservoir can supply in situ SO_4^{2-} and Ca^{2+} . The fact of having an in situ source of potential determining ions can be crucial for the rate of the wettability alteration process. As SO_4^{2-} is adsorbed onto the carbonate surface (Strand et al. 2006), the concentration decreases in the imbibition front. This situation may lead to a slow wettability alteration process. However, if anhydrite dissolution takes place in the imbibition front, the wettability alteration is not dependent on the different rate of sulfate and the wettability alteration process can be faster. Austad et al. (2015) reported that in a group of limestone cores containing anhydrite, the dissolution of anhydrite increased as the salinity of the flooding fluid decreased. Thus, salinity reduction resulted in increased concentration of the active catalyst, and at the same time improved oil recovery by wettability alteration (Austad et al. 2015).

As the calcium sulfate solubility decreases as the temperature increases, and the optimal EOR conditions of temperature for Smart Water in CaCO_3 systems are

usually observed at temperatures above 90 °C (Strand et al. 2008), re-dissolution of calcium sulfate can be beneficial because Ca^{2+} , Mg^{2+} and SO_4^{2-} display a lower reactivity towards the CaCO_3 surfaces at lower temperatures. An additional supply of SO_4^{2-} and Ca^{2+} from dissolution of calcium sulfate minerals may compensate for the lower reactivity of these ions at low temperatures by providing a higher concentration of these determining ions. It is important to note that the availability of these ions coming from the formation will be readily available close to the surface.

During screening of Smart Water potential in carbonates, it is very important to evaluate the contribution of dissolvable sulfate into the injection fluids, especially for low salinity brines, as observed for dolomites (Romanuka et al. 2012, Shariatpanahi et al. 2016).

3.12 Main similarities and differences for Smart Water injection in sandstones and carbonates

Even knowing that wettability alteration mechanisms are chemically different for sandstones and carbonates, there are many aspects that are shared. The main similarities and differences will be discussed next.

Some of common features of the Smart Water EOR mechanisms for sandstones and carbonates can be extracted from the Smart Water definition. They are listed below.

- The injected Smart Water disturbs the established chemical equilibrium causing wettability alteration.
- Wettability alteration induce more water-wetness.
- Wettability alteration increase capillary forces and water imbibition.
- Improved sweep efficiency is observed.
- Smart Water is prepared by modifying the ionic composition according to the mineralogy.

Furthermore, the initial wetting of the reservoir is fundamental to observe EOR effects in both sandstones and carbonates. Systems that are very water-wet will present a poor Smart Water EOR potential, regardless of whether it is a sandstone or a carbonate reservoir. Therefore, mixed-wet conditions usually present a more favorable outlook for observing EOR effects in both lithologies.

It has been described for sandstones and carbonates the ionic Smart Water composition is the key parameters to tune. Ionic composition can be further optimized by studying the rock-brine interactions. A major issue is the proper identification of the important ions involved in each mechanism. An important point to highlight is that an approach only based on salinity is not sufficient to understand the complexity of such processes. For instance, the optimal Smart Water composition for CaCO_3 surfaces is obtained by the combination of a suitable concentration of potential determining ions and a reduction of the non-determining ions; see Figure 27. In the case of sandstones, the salinity has been the focus of attention, i.e., LSE. However, EOR effects have been reported at high salinities (RezaeiDoust et al. 2011, Torrijos et al. 2016). These facts,

suggest that is not the salinity what is important, but the chemical composition of the brines.

However, differences in the general reservoir chemistry dictate the interaction among the crude oil, brine and the rock. The main differences are attributed to:

- Mineralogy
- Surface charge
- Polar components in crude oil
- Formation water pH

Through the theory, it has been described that the charges of the mineral surfaces are generally opposed, negative for sandstones and positive for carbonates.

In addition, the FW pH of sandstones are mostly acidic while the carbonate FW pH are predominantly alkaline. This is extremely important because it will favor the presence of different microspecies of polar organic components. The type of charge of the polar components is crucial for wetting and wettability alteration processes. In sandstones, local pH increments control the relative concentration of species, favoring adsorption at low pH values of non-dissociated carboxylic acids and protonated bases, *Eq.21* and *Eq.22*. Likewise, adsorption will be reduced at higher pH values because the dominant species dissociated carboxylic acids and non protonated bases. On the other hand, in carbonate reservoirs the pH is buffered and predominately alkaline. Thereby, the dominant species will be the dissociated carboxylic acids and non protonated bases, this is also why carbonates appear to be more sensitive to acidic components (Hopkins et al. 2016).

Temperature has also shown different trends in initial wetting, for example carbonates tend to be more water-wet as the reservoir temperature increases (Hamouda and Rezaei Gomari 2006).

In summary, these different characteristics make it obvious that the wettability alteration mechanism by Smart Water must be different. A surface chemistry approach helps to acquire a better understanding of the systems, and improves the evaluation of the EOR Smart Water effects in a specific formation.

3.12.1 Low salinity water injection

It has been reported that the LSE in sandstones is controlled by the adsorption-desorption processes of polar compounds onto the sandstone surface (Madsen and Lind 1998, Burgos et al. 2002, Austad et al. 2010). Such processes are pH dependent, and the pH varies in function of the rock-brine interactions (RezaeiDoust et al. 2011, Brady et al. 2015, Didier et al. 2015, Shi et al. 2016). However, there is a lot of confusion about LS in carbonates. In order to observe LSE in carbonates with CaCO_3 surfaces, experimental results suggest that it is a requirement to have presence of determining ions (Austad et al. 2015). In several cases, the injected low salinity brines do not contain determining ions, but it is wrongly concluded that there was no sulfate. As formerly mentioned, sulfate can be added to the brine phase, if it is present as a dissolvable mineral. This simple but important fact has been very often overlooked, but it can clearly influence significantly the system's wetting (Austad et al. 2015).

Low salinity injection experiments conducted by Yousef et al. (2011), showed that improved recovery was observed by flooding carbonate reservoir cores with diluted seawater (Yousef et al. 2011). The results were in contradiction to these of Fathi et al. (2010) where diluted seawater gave low recoveries in chalk without anhydrite present (Fathi et al. 2010). Yousef et al. (2011) demonstrated that wettability alteration took place. X-ray computerized tomography (CT) scan was used, but presence of dissolvable anhydrite in the core material was not evaluated. Austad et al. (2015) performed a set of experiments in a similar material as the one used by Yousef et al. (2011) and found that the core samples contained anhydrite. The presence of dissolvable anhydrite acted as an in situ source of sulfate for the wettability alteration process with seawater and diluted seawater. It was concluded that a low salinity EOR effect could be observed in carbonates if extra sulfate was supplied by dissolution of CaSO_4 (Austad et al. 2015).

The results presented by Austad et al. (2015) are in line with what was observed by Fathi et al. (2010), which showed that, when the concentration of determining ions is diluted in seawater, there is no Smart Water effect in chalk cores, Figure 28. Diluted seawater brines with salinities less than 10 000 ppm were not successful in altering wettability of the chalk/limestone surfaces.

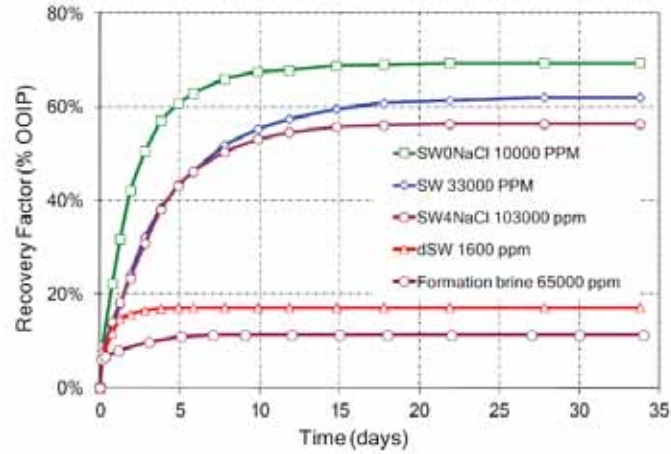


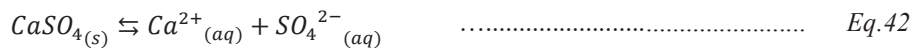
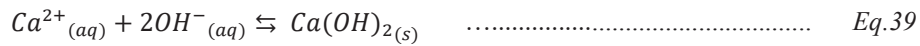
Figure 28. Spontaneous imbibition into oil saturated chalk cores at 120 °C using different imbibing fluids with different salinities, SW, SW0NaCl, SW4NaCl, dSW-1600 and formation brine, $S_{wi}=10\%$ (Fathi et al. 2010).

On the other hand LSE can be observed in dolomites as discussed in the work of Shariatpanahi et al. (2016), but again, it seems that a low content of non-determining ions, i.e., sodium and chloride ion, is an important attribute for the effect to happen (Shariatpanahi et al. 2016). So far, more research should be dedicated to fully understand the role of the potential determining ions in dolomite.

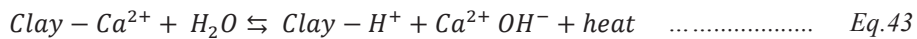
3.12.2 Calcium sulfate dissolution

It was mentioned earlier that dissolution of calcium sulfate can influence the initial wetting increasing the water-wetness of a system (Punternold et al. 2007, Shariatpanahi et al. 2011). Additionally, it can be a source of potential determining ions during Smart Water injection (Austad et al. 2015). These observations are mainly influenced by the in situ availability sulfate and calcium. Sulfate was identified as the catalyst in the Smart Water mechanism in carbonates, and calcium is also a potential determining ion in this process (Zhang et al. 2007). Thereby, the accurate detection of dissolvable calcium sulfate (Lopez-Salinas et al. 2011) is crucial to have control of the factors that may influence wetting in carbonates (Austad et al. 2015).

Contrary to carbonates, dissolution of calcium sulfate during LS Smart Water injection in sandstones represents a negative influence. In this case the contribution of sulfate has a minor impact, but calcium can affect substantially the performance of the process. It can consume the alkalinity needed to trigger the LS Smart Water mechanism. This is caused by the interaction of calcium ion with the hydroxyls present in the aqueous media, *Eq.39*, and calcium can be made available by re-dissolution of calcium sulfate, *Eq.42*. This chemical equilibrium can lead to precipitation of $Ca(OH)_2$, buffering the pH.



Furthermore, the immediate availability of calcium can slow down the Ca^{2+} desorption process from clay, a critical part of the LS EOR mechanism in sandstones. By displacing the chemical equilibrium described in *Eq.32* to the left, the increase in pH is lowered potentially influencing the oil recovery.



Therefore, calcium availability from re-dissolution of trace minerals is negative for Smart Water EOR effects in sandstone because it can affect negatively the pH development and the calcium desorption from the clay surface.

4 Experimental

The materials and methods used in the experimental work of this thesis are summarized in this section. A detailed extended version is included in the different papers incorporated in this work.

4.1 *Materials*

Crude oil and reservoir/outcrop core material were provided by Total E&P. All brines were prepared according to specific brine compositions. Mineralogical analyses were both carried out in-house as well as being supplied by Total E&P.

A condensed version of materials and methods is presented below. Note that the nomenclature may differ from the papers for adaptation purposes.

4.1.1 *Core material*

The core material was divided in sandstones and carbonates, sandstone cores were mostly outcrops with varied characteristics, while the carbonate cores were reservoir samples.

4.1.1.1 *Sandstones cores*

Two sets of outcrop sandstone cores have been used locations in the USA. The first set of outcrop material was composed by cores termed as Briar Hill, Boise, Cedar Creek, Idaho Gray, Leopard, and Sister Gray. A North Sea reservoir sandstone core provided by Talisman Norway was also used; it was termed Y-24.

Total E&P provided the outcrop core material together with mineralogical data composition and cation exchange capacities (CEC). In addition to the provided data, BET, specific surface area measurements, porosities and permeabilities were determined.

The physical properties are given in Table 4 and mineralogical data is presented in Table 5.

Experimental

Table 4. Physical properties of the first set of sandstone cores.

Core #	PV, (ml)	Porosity (ϕ), %	Permeability k^* (mD)
Briar Hill-1	16.7	19	609.7
Briar Hill-4	18.3	22	639.5
Boise-4	24.5	29	1170
Cedar Creek-1	13.8	16	10.9
Cedar Creek-3	16.6	19	13.6
Cedar Creek-4	18.1	22	28.8
Idaho Gray-4	22.4	30	971.2
Leopard-4	15.9	19	294.5
Sister Gray-4	16.5	19	102.4
Y-24	12.8	15	38.6

*Permeability to water (LS 1000 ppm NaCl) at 20 °C.

Table 5. Main mineralogical composition of the first set of sandstones cores from USA.

Mineral	Briar Hill	Idaho Gray	Leopard	Cedar Creek	Boise	Sister Gray	Y-24
Quartz	91.88	39.65	93.90	74.63	40.72	82.21	72.40
Kaolinite	4.50	6.00	2.50	5.00	5.00	7.00	8.30
Chlorite	-	-	-	-	-	-	1.15
Illite	0.00	0.00	0.00	0.00	0.00	0.00	6.70
Smectite/Illite R0-R1	0.00	0.90	1.20	3.60	0.70	0.60	-
Albite	0.00	29.00	0.50	7.50	29.00	1.43	7.30
Microcline	2.50	22.00	1.20	8.00	22.00	7.00	2.25
Calcite	0.00	0.20	0.07	0.60	0.35	0.40	0.85
Dolomite	0.05	0.70	0.00	0.00	0.50	0.00	0.45
Others	1.07	1.55	0.63	0.67	1.73	1.36	0.6
Total clays and micas	4.50	6.90	3.70	8.60	5.70	7.60	15.00

*This includes smectite (Illite) R0 (Disordered) and/ or R1 (ordered two layers) and/or smectite.

4.1.1.2 Total outcrop sandstone

Another series of outcrop sandstone cores have been used, and were supplied by Total E&P. This outcrop core material has previously been used in several

Experimental

parametric studies, giving highly reproducible results (Austad et al. 2010, RezaeiDoust 2011, RezaeiDoust et al. 2011). Physical properties are shown in Table 6 and mineralogical properties in

Table 7. The core material has a significant amount of reactive albite with approximately 30 wt %. All cores come from the same block, containing ≈ 10 wt % clay. The major clay present is illite contributing to almost 8 wt %. All cores showed quite similar physical and chemical properties.

Table 6. Physical properties of outcrop sandstone cores with reactive plagioclase.

Core #	Pore volume (ml)	Porosity (ϕ), %	Permeability k^* (mD)	BET (m ² /g)
B-01	16.3	20.4	n/a	1.81 ± 0.02
B-21	23.3	20.8	48.4	
B-22	23	20.5	135.1	
B-24	22.5	19.9	22.3	
B-25	23.6	21.0	50.2	
B-26	22.5	19.9	34.6	

Table 7. Main mineralogical composition of outcrop sandstones cores with reactive plagioclase.

Mineral	B01	B21,B22	B24,B25,B26
Quartz	58.2	56.2	57.0
Albite	30.4	32.9	32.0
Chlorite	1.9	1.7	1.7
Illite	8.4	8.1	8.2
Kaolinite	0.0	0.0	0.0
Calcite	0.3	0.3	0.3
Others	0.8	0.8	0.8

The total outcrop core material has a heterogeneous pore size distribution, as shown by Figure 29.

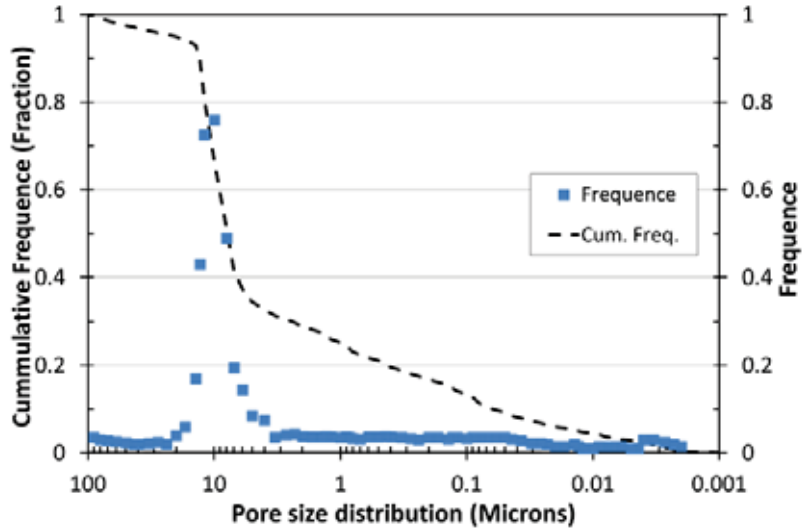


Figure 29. Pore size distribution of a core from the same block as the tested core material. Data submitted by TOTAL E&P.

It shows a peak at about 10 μ m, and with a significant contribution of pores down to 0.01 μ m.

4.1.1.3 Reservoir carbonate cores

Core material from a limestone reservoir with T_{res} of 65 °C was used in a study that involved characterization and evaluation of the Smart Water EOR potential in a carbonate reservoir. The cores were characterized based on mineralogical, physical, and surface chemical properties; core properties are presented in Table 8 and Table 9.

Experimental

Table 8. Physical properties of reservoir carbonate cores

Core #	Pore volume PV, ml	Porosity (ϕ), %	Permeability k, mD
10D	10.2	13	1.1
10E	8.7	11	26.2
14B	5.1	7	0.9
14C	8.4	11	2.5
15A	8.0	10	1.0
17A	6.7	10	1.0
29B	4.4	7	0.8
37A	8.0	10	0.9
37C	12.1	15	15.4

Table 9. Elemental composition of carbonate reservoir core samples (At % = mole %). The data is obtained from EDS analyses of small rock samples from the cores.

Core #	Ca (At %)	Mg (At %)	S (At %)	Si (At %)	Al (At %)	Rock
10D	56.00	35.43	2.24	5.19	1.14	Dolomitic-limestone
10E	51.65	41.08	1.51	1.79	3.97	Dolomitic-limestone
14B	91.43	2.03	0.00	5.67	0.87	Limestone
14C	90.48	1.50	1.24	1.32	5.46	Limestone
15A*	95.80	1.15	0.40	1.47	1.18	Limestone
17A	96.99	1.05	0.35	0.58	1.03	Limestone
29B	86.41	0.69	1.34	5.02	6.54	Limestone
37C	90.73	3.21	1.57	2.03	2.46	Limestone

*Mineralogical analysis conducted in the neighbor core of 15D.

4.1.2 Brine composition

All chemicals used to prepare the brines were reagent grade and delivered by Merck laboratories. Deionized (DI) water was used for the brine preparation with a total organic content T.O.C <5 ppb and resistivity of 18.2 M Ω cm. The brines were filtered prior to use using a 0.22 μ m, millipore membrane filters.

The following set of brines was used in the experimental section dedicated to the sandstone outcrops from USA, Table 10.

Experimental

Table 10. Brines used with sandstone outcrops and core Y-24.

Ions	FW1 (mM)	d ₂₀ FW1 (mM)	FW (mM)	LS (mM)
Na ⁺	480.1	24.0	1540	17.1
K ⁺	12.5	0.6	-	-
Ca ²⁺	10.6	0.5	90	-
Mg ²⁺	57.6	2.9	-	-
Cl ⁻	629.0	31.5	1720	17.1
TDS, (mg/l)	35 604	1780	100 000	1000
pH	5.3	5.6	5.5	5.7
μ @25 °C, (cp)	1.07	1.01	1.18	1.01
μ @60 °C*, (cp)	0.56	0.51	0.63	0.60

* Test temperature.

The brines used in the experimental part dedicated to the outcrop core material containing reactive plagioclase are described in Table 11.

Table 11. Brines used in the total outcrop cores.

Ions	FW (mM)	LS (mM)	nSW (mM)	NaCl ₂₅ (mM)	FW (25 000 ppm CaCl ₂) (mM)	(40 000 ppm NaCl) (mM)	LSP (mM)
Na ⁺	1540	17.1	402	427.8	-	684.5	17.1
K ⁺	-	-	10	-	-	-	-
Ca ²⁺	90	-	0.1	-	225.3	-	-
Mg ²⁺	-	-	0.2	-	-	-	-
Cl ⁻	1720	17.1	411	427.8	450.5	684.5	17.1
pH	5.5	5.7	8	5.7	7.1	5.8	7.8
TDS, (mg/l)	100 000	1000	24 350	25 000	25 000	40 000	1000

All brines used with the carbonate reservoir cores are summarized in Table 12.

Experimental

Table 12. Brines used for the experimental section of carbonates.

Ions	FWR (mM)	SW0Na4S (mM)	d ₂₀ SW (mM)	d ₁₀ SW (mM)
Na ⁺	1516.0	194.0	22.5	45.0
K ⁺	89.0	10.0	0.5	1.0
Ca ²⁺	305.0	12.0	0.6	1.2
Mg ²⁺	90.0	44.0	2.2	4.4
Cl ⁻	2382.0	125.0	26.2	52.4
SO ₄ ²⁻	0	96.0	1.2	2.4
HCO ₃ ⁻	13.0	-	-	
TDS mg/l	138 058	20 240	1668	3336
pH	6.0	8.0	7.0	7.0
Density, g/ml	1.0941	1.0154	0.9991	1.0008

4.1.2.1 Polymer solution

The polymer used was HPAM which is a hydrolyzed polyacrylamide, Flopaam 3630S from SNF Floerger. It had a hydrolysis degree of 25–30% and a molecular weight of 20 million Da. The LS polymer solution (LSP) used in this study was prepared by dissolving 0.1 wt % of HPAM in 1000 ppm NaCl brine. The viscosity of the LSP solution at 25 °C was 13.3 cp at a shear rate of 100 s⁻¹.

4.1.2.2 Cationic surfactant C₁₂TAB

The cationic surfactant was used in Smart Water study on reservoir carbonates. The surfactant was used because it is a very efficient wettability modifier in carbonates. In some of the experiments, after the last spontaneous imbibition with the chosen Smart Water brine, a 1 wt % of dodecyl trimethyl ammonium bromide, also known as C₁₂TAB was added to the Smart Water brine. The surfactant is a very efficient wettability modifier in carbonates, but does not decrease substantially the IFT (Strand 2005). Typically, measured values of IFT were 1-2 mN/m.

4.1.3 Crude oil

Stabilized crude oils were used in this work. Prior to use, the Total oil and RES 40 oil were centrifuged for 1 hour at a high rotation speed and afterwards filtered with a 5 µm Millipore filter. The crude oil used with the carbonate cores; denoted “Reservoir crude oil” was stabilized but not filtered. Crude oil properties are given in Table 13.

Table 13. Crude oil properties.

Crude oil sample	AN mg KOH/g	BN mg KOH/g	Density g/cm ³	Viscosity cp @20 °C
Total oil	0.10	1.80	0.846	17.6
Reservoir crude oil	0.37	0.27	0.825	4.0*

* Measured at reservoir temperature (65 °C).

4.2 Methods and analyses

The main experimental and analytical methods used in the experimental work are briefly described as follows.

4.2.1 Core flooding

The core flooding set up consisted of computer controlled system, Gilson HPLC pump, stainless steel piston cells, a Hassler core holder, an oven and a glass burette. The experiments were performed with a confining pressure of 20 bar and a back pressure of 10 bar.

4.2.2 Core restoration

4.2.2.1 Mild core cleaning

The core exposed to crude oil were initially mildly cleaned with: (1) Kerosene until a clear effluent is observed; (2) Heptane to displace kerosene; (3) 4 PV of LS brine for sandstone cores or distilled water for carbonate cores to displace FW and easily dissolvable salts; each flood was carried out at a rate of 0.1 ml/min.

4.2.2.2 Initial water saturation

Initial FW saturation, was established using the desiccator technique in line with the procedure described by Springer et al. (Springer et al. 2003). The core was saturated with diluted FW brine. The water molecules were evaporated in the desiccator until the desired S_{wi} of correct concentrated FW brine was reached. The core was then equilibrated for 72 hours to get an even ion distribution. Subsequently, the core was placed in a core holder, and shortly evacuated to remove gas from the pores prior to oil saturation.

4.2.2.3 Crude oil saturation

The core with initial S_{wi} was initially saturated with crude oil and then flooded 2 PV of crude oil in each direction at 50 °C. The oil-flooded core was aged in a steel aging cell at the respective test temperature, for 14 days.

4.2.2.4 pH screening test

Mildly cleaned sandstone cores were exposed to pH screening tests to evaluate the chemical interaction between pore surface and injected brines (Aksulu et al. 2012). Effluent samples were collected, and pH and density were plotted against PV injected.

4.2.2.5 Oil recovery test

Oil recovery test by viscous flooding was performed on restored cores. The restored core was mounted in the core holder with a back pressure and confining pressure of 10 and 20 bar respectively. The system was left overnight to achieve thermal stability at the actual test temperature. The core was successively flooded with various brines at constant rate. The cumulative oil produced was monitored, as well as pH and salinity of the produced water.

4.2.2.6 Spontaneous imbibition tests

Spontaneous imbibition (SI) was performed on restored carbonate cores. After the aging process, the cores were placed in a glass Amott imbibition cell surrounded by the imbibing fluid. The SI test was performed at the designated temperature. Cumulative oil production was monitored and plotted against time

until a recovery plateau was reached. In order to test capillary forces, 100% heptane saturated cores were spontaneously imbibed at room temperature using deionized water as imbibing fluid.

4.2.3 Analyses

A brief description of the analyses carried out during this work is included below.

4.2.3.1 pH measurement

The pH in brines and produced water was measured using the pH meter seven easy™ from Mettler Toledo. The electrode semi micro-pH was used. The repeatability of the measurement was +/- 0.01 pH units at room temperature.

4.2.3.2 Density measurement

The density of brines, oils and produced water samples were measured using a density meter DMA-4500 from Anton Paar.

4.2.3.3 AN and BN determination

Representative samples of the stabilized reservoir crude oil were analyzed for the amount of acidic and basic polar components, mg KOH/g. The analyses were performed by potentiometric titration. The methods used were developed by Buckley and Fan (REF) modified versions of ASTM 664 and ASTM 2895. AN (mg KOH/g) and BN (mg KOH/g) measurements were carried out using a Mettler Toledo DL55 auto-titrator. The reproducibility of the analyses was better than 0.02 mg KOH/g oil added.

4.2.3.4 Viscosity

Brine and crude oil viscosities were determined using the rotational rheometer Physica MCR 302 from Anton Paar.

4.2.3.5 Surface area

BET surface area measurements were carried out in a TriStar II PLUS instrument from Metromeritics®, using small pieces of representative core material.

4.2.3.6 Brine composition analyses

Effluent brine samples were collected during different core experiments. The brine samples were diluted prior to the analysis with the assistance of the trilution™ LH system from Gilson. The chemical analyses of both anions and cations were performed using an ion chromatograph, DIONEX ICS-3000. Ion concentrations were calculated based on external standard method.

4.2.3.7 Qualitative sulfate analysis

Ba²⁺ ions were added to detect the presence of sulfate in effluent samples. Ba²⁺ ions will form a white precipitate, BaSO₄ (S).

4.2.3.8 Scanning Electron Microscope (SEM), EDAX

A ZEISS SUPRA 35VP environmental Scanning Electron Microscope was used to collect images of rock surface, from small rock samples collected from the reservoir cores. Elementary analyses of the same rock sample were taken using an EDAX detector.

Experimental

5 Results and discussion

This thesis aims to contribute with applicable concepts that can give a better understanding of the Smart Water EOR mechanisms. The objectives were addressed by studying the potential application of Smart Water in both sandstones and carbonates systems. A broader picture of the factors behind the Smart Water EOR mechanisms was obtained by studying both limitations and possibilities of the aforementioned processes.

In relation to sandstones, the pH development at the mineral surfaces plays an important role, not only by indicating the initial wetting state of a system but also by describing the evolution of the wettability alteration process. Systematic attempts to expand the knowledge associated to rock-brine interactions, temperature and injection strategies has been made.

For carbonates, the Smart Water EOR effect has been tested in supposedly non-favorable temperature conditions. A full characterization of the reservoir material has contributed to acquire important insights linked to the potential to improve oil recovery.

The results presented have addressed the evaluation of the Smart Water EOR and the performance of the method in specific reservoir systems. The approach takes into account the mineralogical complexity, which is regarded as a controlling parameter in Smart Water EOR processes. The parameters that lead to the selection of a Smart Water brine composition are the mineral composition, surface reactivity between the brines and the knowledge previously gained on Smart Water EOR processes in both Carbonate and Sandstone reservoirs.

5.1 Linking low salinity EOR effects in sandstones to pH, mineralogy and water composition

The initial pH of a crude oil-brine-rock system is dependent on FW composition, mineralogy and crude oil. The effect of pH on initial wetting and the potential for EOR by wettability alteration was studied in sandstone core material.

Main results and discussion

Six different outcrop sandstone systems were used. The amount of relevant minerals, type of clays and plagioclase/albite, were determined by using two different experimental techniques; x-ray powder diffraction and fluorescence. By using the two techniques, the amount of clay minerals and types of feldspars, microcline/albite, was determined for each outcrop system, the mineralogy is given in Table 14.

Table 14. Mineralogical data, from SPE paper 154209 (Winoto et al. 2012).

Property	Briar Hill	Idaho Gray	Leopard	Cedar Creek	Boise	Sister Gray
Clays & micas (Mass %)	4.50	6.90	3.70	8.60	5.70	7.60
Kaolinite (Mass %)	4.50	6.00	2.50	5.00	5.00	7.00
Smectite/Illite (Mass%)	0.00	0.90	1.20	3.60	0.70	0.60
Albite (Mass%)	0.00	29.00	0.50	7.50	29.00	1.43
Microcline (Mass %)	2.50	22.00	1.20	8.00	22.00	7.00
BET (m ² /g)	0.36	0.53	2.00	5.12	0.5	0.80
CEC (meq/100g)	0.00	1.02	1.00	3.02	0.70	0.60

The total clay content was quite low and varied between 3.7-8.6 wt%. The major clay present was kaolinite. Two of the outcrops, Idaho Gray and Boise, contained a large amount of feldspars, 29 wt% albite and 22 wt% microcline.

5.1.1 Relationship between initial pH and initial wetting

It is important to point out, that regardless of the complexity of the sandstones mineral composition, the pH of the effluent created in a non-buffered aqueous media, will summarize the rock-brine interactions that could influence pH and the initial wetting when crude oil is introduced. Initial pH values above 7 may indicate a high degree of water-wetness (Reinholdtsen et al. 2011), whereas lower values will favor conditions for adsorption of polar organic molecules on pore surface minerals to obtain mixed-wet conditions. It was previously described in Figure 8 that at high pH values, polar organic components with acidic and basic functional groups represented by carboxylic acids or heterocyclic nitrogen compounds will be dissociated and deprotonated. As the sandstone mineral surfaces are negatively charged, the affinity of these polar components present in crude oil is low. Electrostatic repulsion does not allow

adsorption of negatively charged or non-charged R_3N polar components onto the sandstone surface and therefore the system will appear to be water-wet.

In the study by Winoto et al. (2012), poor LS effects were observed in the same outcrop sandstone systems. The average LS recovery for LSE for outcrop sandstone was also lower than typically observed for reservoir cores (Winoto et al. 2012). In the work conducted by Winoto et al. (2012), the composition of formation water used, FW1, was based on a seawater composition, Table 10. This composition is not a typical formation water. In seawater, calcium concentration is rather low compared to magnesium. In formation waters, calcium concentration is typically 5 to 15 times higher than magnesium (Houston 2007, Lee and Neff 2011, Li 2013). The low salinity brine ($d_{20}FW$) used in Winoto's work was made by diluting FW1 20 times.

5.1.2 pH screening tests on outcrop cores

A series of pH screening tests were performed on the same outcrop sandstones as used by Winoto et al. (2012). The flooding sequence in the pH screening tests was FW1- $d_{20}FW$ -FW1. The bulk pH of FW1 and $d_{20}FW$ are quite similar, 5.3 and 5.6, respectively. The pH values observed in effluent samples that differ from the bulk pH are directly linked to rock-brine interactions (Piñerez et al. 2016). An example from Sister Gray is shown in Figure 30. A summary of the pH screening tests made in all cores is presented in Table 15.

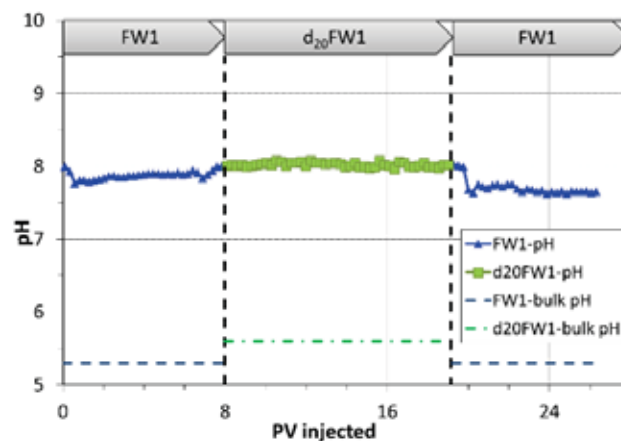


Figure 30. pH screening for a Sister Gray core at 60 °C, flooding sequence FW1- $d_{20}FW$ -FW1.

Main results and discussion

As previously discussed, initial core pH below 7 will favor adsorption of polar components. The pH screening results for all outcrops were poor in that aspect. Only one core, Cedar Creek, gave a pH value below 7 during formation water flooding. The high pH values observed, indicate a high potential to obtain very water-wet conditions (Buckley and Morrow 1990, Reinholdtsen et al. 2011).

Table 15. Initial water saturation and tertiary LS EOR effects from SPE paper 154209 (Winoto et al. 2012) and pH screening test results from this study (initial pH and Δ pH).

Initial water saturation and tertiary LS EOR effects (Winoto et al. 2012).						
	Briar Hill	Idaho Gray	Leopard	Cedar Creek	Boise	Sister Gray
S_{wi} % PV*	26.9	22.0	43.4	42.0	22.0	28.1
ΔR_t^{**} (%OOIP)	3.65	3.27	1.05	0.74	1.09	0
pH screening tests conducted in this work						
Initial pH	7	7.3	7.2	6.6	7.2	8
Δ pH	0	0.5***	0.5***	0.5	1.0***	0

* S_{wi} : Initial water saturation (Winoto et al. 2012).

** ΔR_t : Amount of oil recovered in the tertiary LS EOR process (Winoto et al. 2012).

*** The pH increment was not stable during the LS flooding (decreasing trend).

The combination of rather low clay content, which is the main wetting material, and unfavorable FW composition, gave a too high initial pH and a low potential of adsorption of polar organic molecules on to the rock surface. This could explain why all the tested cores behaved quite water-wet, showing a low LS EOR potential (Winoto et al. 2012).

5.1.3 Potential for observing Smart Water EOR effects

In order to observe Smart Water LS EOR effects in sandstone cores, it is crucial to establish initial low pH with the FW brine. Also a pH increment is needed for wettability alteration during Smart Water injection. This pH increase is controlled by an exchange of H^+ at the clay and/or feldspars surfaces as the salinity and ion composition in the injected brines is changed. Thus, the potential of wettability alteration increases as the pH change observed is larger, steeper and sustained as Smart Water is introduced in the system.

The pH screening tests performed on the same outcrop sandstone systems with the same brines used by Winoto et al. (2012), confirmed high initial pH with

FW1 and small pH changes during d₂₀FW1 injection, confirming the low potential of the systems to observe LSE, Table 15.

The initial pH was ± 7 . The pH gradients observed during d₂₀FW1 injection are characteristic for systems with low LS EOR potential. For instance, in the Briar Hill and Sister Gray cores there was no pH rise at all. The cores Idaho Gray, Leopard and Cedar Creek presented only a pH increment of 0.5 pH units, but they lacked stable pH values during the LS flooding. Only one core reached 1 pH unit increment, but the pH decreased steadily afterwards.

The conditions set by the used brines and the mineralogy of this set of cores, steady state conditions triggering wettability alteration by continuously exchanging cations and H⁺ at the clay and/or feldspars surfaces was not observed. This was partly caused by the low concentration of Ca²⁺ in FW1, ≈ 11 mM, Table 10. Therefore, a large gradient of Ca²⁺ between the rock surface and the aqueous media was not present upon the use of the diluted FW, d₂₀FW1. This did not create beneficial conditions to induce a pH increment, Eq.32. Furthermore, as the initial pH with FW1 did not either favor conditions for adsorption of polar organic material onto mineral surfaces, the rock-brine system did not promote conditions for observing substantial LS EOR effects.

In summary, the results from the pH screening test are in agreement with the small tertiary LS EOR effects seen by Winoto et al. (2012) As previously discussed, initial core pH below 7 will favor adsorption of polar components. The pH screening results for all outcrops were poor in that aspect. Only one core, Cedar Creek, gave a pH value below 7 during formation water flooding. The high pH values observed, indicate a high potential to obtain very water-wet conditions (Buckley and Morrow 1990, Reinholdtsen et al. 2011), Table 15.

5.1.4 Effect of formation water composition on initial pH core wettability and EOR potential

The work by Winoto et al. (2012) using different outcrop sandstone material with a given brine system showed low EOR effects. The pH screening tests confirmed low pH changes that are needed for wettability alteration. Furthermore, high initial pH was observed, promoting quite water-wet initial conditions.

The observed pH values are mainly caused by the rock-brine interactions. A high initial pH does not favor initial adsorption of polar components onto to the rock. Thereby an important question to ask is: “*Can another brine with a typical formation water composition create initial conditions favoring the adsorption of polar organic components?*” A formation water brine with higher calcium concentration and salinity than FW1, was used, FW, Table 10.

The Cedar Creek outcrop core system was chosen to evaluate the effect of FW composition on initial pH and the pH change by introducing a LS injection brine. The total clay content in the Cedar Creek cores were ≈ 8.6 wt. %, and contained also a considerable amount of feldspars, 15.5 wt. %. Two pH screening tests were performed, one using the Winoto brine system, FW1 and d_{20} FW1, and a second brine system with FW-LS. The pH scan for the core is shown in Figure 31.

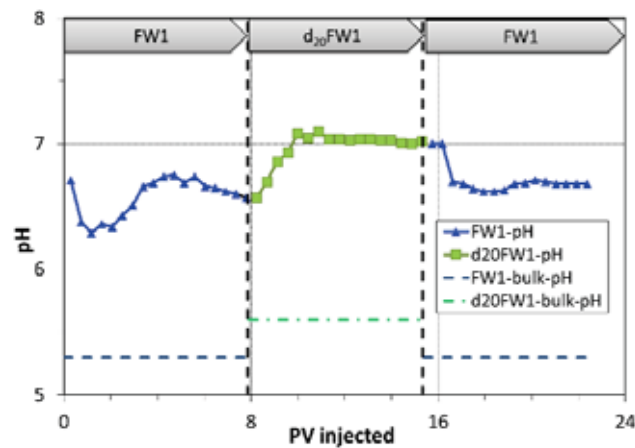


Figure 31. pH screening for the Cedar Creek core-4 at 60 °C, flooding sequence FW1- d_{20} FW1 - FW1.

This was the only outcrop system where the effluent pH using FW1 was below 7, with an average pH value of 6.6. The increase in pH as the flooding fluid was changed to the LS brine, d_{20} FW1, was only 0.5 pH units. The pH remained stable at ≈ 7 during the LS flooding. The small pH gradient corresponds to the low LS EOR effect, 0.74% of OOIP, observed by Winoto et al. (2012), Table 15.

Main results and discussion

Using the brine system of Winoto, the initial pH was high and the pH gradient during low salinity flooding was rather small to promote larger Smart Water EOR effects. Furthermore, the formation water ion composition used by Winoto does not have a typical FW ion composition with a high Mg^{2+} concentration in relation to a low Ca^{2+} concentration.

Therefore, another Cedar Creek core was tested in a pH screening test at 60 °C. This time a formation water, FW, with 100 000 ppm salinity and 90 mM Ca^{2+} was used. The LS brine used contained 1000 ppm of NaCl. This brine system will create a larger Ca^{2+} gradient. The brine compositions are given in Table 10. The result from the pH screening test is shown in Figure 32.

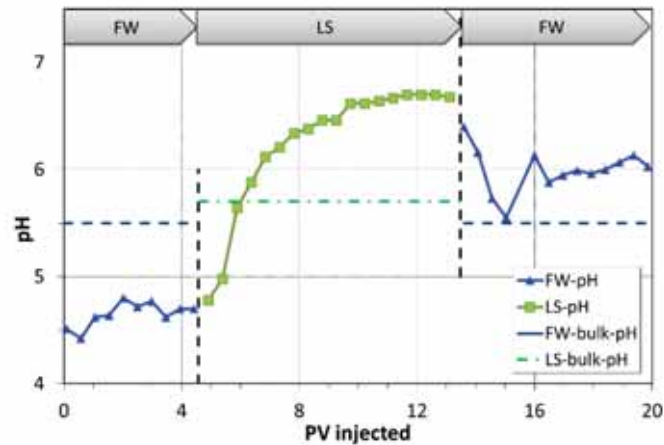


Figure 32. pH screening of a Cedar creek-3 core using 100 000 ppm FW and 1000 ppm LS. Test temperature 60 °C.

The pH scan using FW and LS appeared quite different from the observations when using FW1 and d_{20} FW1 brine. With the FW-LS system, the initial pH was lowered from 6.6 to 4.7. A lower initial pH will increase the concentration of protonated species and improve the adsorption of polar components when a crude oil is added to the rock-brine system. Additionally, with a pH gradient (Δ pH) of 2.0 during LS injection, favorable conditions for desorption of polar components are present, compared to Δ pH of 0.5 observed when using the FW1- d_{20} FW1 brine system.

Main results and discussion

The lower initial pH observed can be explained by presence of feldspars in a protonated/hydrolyzed form, as shown by *Eq. 41*, which could be observed with higher Ca^{2+} and Na^+ concentrations.

The imposed pH gradient by using the LS containing 1000 ppm brine of NaCl is also an evidence of ion exchange at the clay/minerals surface. However, it was also noticed that the pH gradient did not increase beyond 7. This can affect the speed and degree of wettability alteration during the Smart Water EOR injection. Laboratory studies have shown that wettability also take place at pH values below 7 (Buckley and Morrow 1990, Didier et al. 2015).

Using FW with higher Ca^{2+} concentration should favor better initial conditions regarding initial wettability. Following this idea, an oil recovery test was carried out using Cedar Creek cores. The crude oil used have previously shown reasonable LS EOR effects in previous oil recovery experiments. The Total oil has a high BN and a lower AN, Table 13. The Cedar Creek core was restored with $S_{wi}=0.2$ with FW, saturated and aged in crude oil. The oil recovery test was performed by successively flooding the core with FW-LS brines, Figure 33.

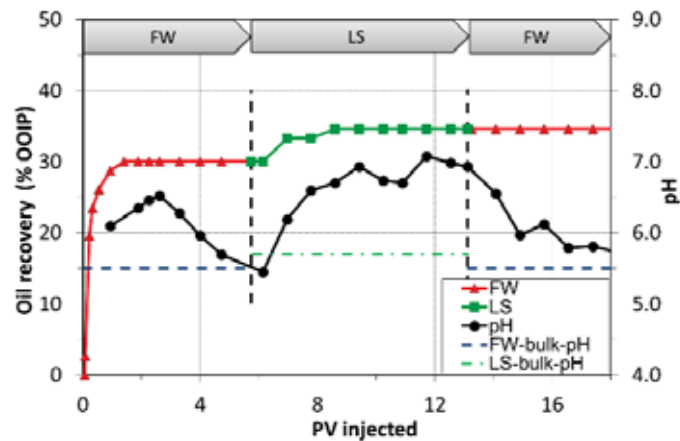


Figure 33. Oil recovery for Cedar creek core-1 at 60 °C. The restored core with $S_{wi}=0.2$ was successively flooded with FW-LS-FW at a rate of 4 PV/D.

30% OOIP was produced during FW flooding. First produced water had a pH of 6.1, indicating positive initial conditions for adsorbing polar components

Main results and discussion

onto the mineral surface. After 6 PV the injection fluid was changed to LS. A rapid increase in pH was observed with a ΔpH of 1 pH unit. A significant increase in oil recovery was also observed, with an ultimate recovery of 35% OOIP, corresponding to a 5 % OOIP increased recovery.

Based on the observed results, an interesting question is: “*Can FWI with cation composition equal to seawater act as a LS fluid when injecting it into a reservoir with high FW salinity?*”

Knowing that Ca^{2+} is a key cation in the exchange of cations at the clay surfaces and due to the low concentration of Ca^{2+} in FW1 (only 11 mM), it should be possible to observe a pH gradient when injecting FW1 in a core with high clay content. A reservoir sandstone core, Y-24, was used for this purpose; containing 16 wt. % clay minerals and 10 wt. % feldspars, Table 5.

Core Y-24 was mildly cleaned prior to the pH screening tests. The core was successively flooded with FW- FW1- $\text{d}_{20}\text{FW1}$ at 60 °C, Figure 34.

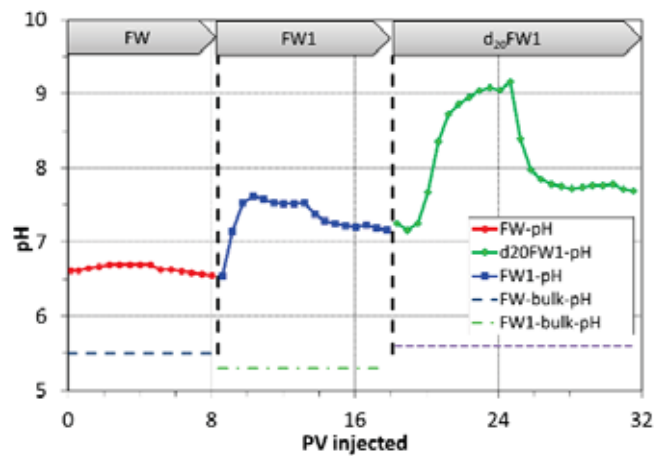


Figure 34. pH scan of the core Y-24 (high clay content about 16 wt%) 60 °C, injection sequence FW- FW1- $\text{d}_{20}\text{FW1}$.

The initial pH using FW was about 6.6, giving favorable initial conditions for adsorption of polar components. When the injection brine was change to FW1, the pH increased 1.0 pH unit.

Using the diluted brine, d₂₀FW1, the pH increased nearly 2 pH units, with an ultimate peak at 9.2. If it is believed that the pH change is the parameter controlling initial wettability and wettability alteration in sandstone reservoirs, a brine based on the SW composition increased the pH somehow and is not favorable as formation water brine, 20 times diluted FW1 showed more promising behavior as a LS EOR brine used in a reservoir core.

The dynamic stability of the pH during a waterflood is also an important issue to study, Figure 34. The pH stability is dependent on the type and amount of the minerals exposed on the pore surface, and controlled by their cation exchange capacity, which is crucial to create and maintain favorable conditions of adsorption of polar components with FW, and desorption of polar components with a Smart Water brine. Equally important, is mineral dissolution, which can induce buffer effects that affect the pH development during the waterflood. Awareness of all these factors is advisable to obtain a more reliable evaluation of the Smart Water EOR potential in sandstone reservoirs.

5.1.5 The salinity effect of Smart Water

There is a general acceptance that typical LS brines are brines with salinities below 5000 ppm (Morrow and Buckley 2011). However, an analytical perspective only based on the salinity can exclude relevant information about the effect of the ion composition in the LS brines. The main purpose of this work was to evaluate if salinity is the main factor limiting the Smart Water EOR effect in sandstone.

The total outcrop core system has been used in this study. The outcrop sandstone contains ≈10% clay and 30% feldspar, Table 7. FW is used as formation water. The crude oil used was Total crude oil, Table 13. Typical LS EOR effects for crude oil-brine-rock system in tertiary mode is presented in Figure 35.

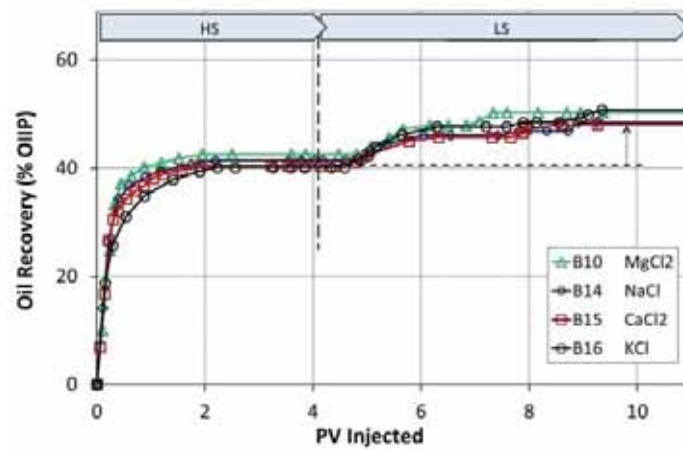


Figure 35. Oil recovery tests performed on Total outcrop system at 40 °C. LS EOR effect using 4 different LS brines, $\approx 7\%$ OOIP (RezaeiDoust et al. 2011).

As observed, the outcrop system shows very good repeatability with ultimate recovery of 40% OOIP during FW flooding, and also very good reproducibility of tertiary LS EOR effects using different LS brines with salinities close to 1000 ppm. The effect of salinity of the Smart Water EOR brines was tested using the same Total Outcrop system.

An oil recovery test on the core B-25 was performed with $S_{wi}=0.2$. The core was restored saturated and aged in crude oil. The core was successively flooded with FW- NaCl_{25} at 60 °C, Figure 36. The oil recovery during FW injection reached a plateau of 35% of OOIP. After 8 PV of FW injected, the injection brine was changed to NaCl_{25} , which is a 25 000 ppm NaCl brine. The pH of first produced water was 6 and increased slightly. The pH increased to pH 7.2 during the NaCl_{25} flooding. At the same time gradual increase of 10 % of OOIP was observed, even though the salinity of the Smart Water brine was 25 000 ppm.

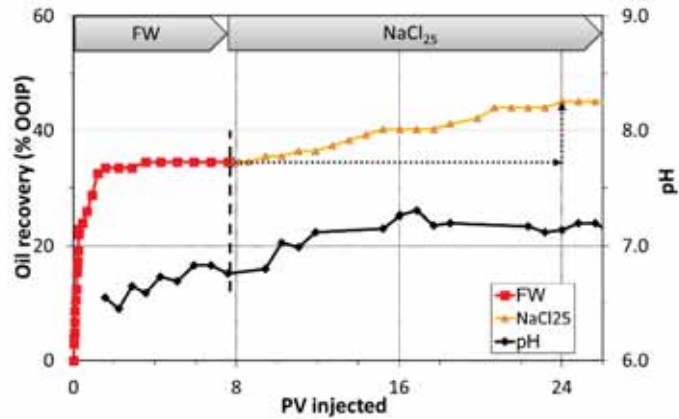


Figure 36. Oil recovery on core B-25 at 60 °C, restored with $S_{wi}=0.2$, saturated and aged in crude oil. Injection sequence FW (100 000 ppm)-NaCl₂₅ (25 000 ppm) at injection rate of 4 PV/D. Bulk pH are 5.5 for FW and 5.7 for NaCl₂₅.

In addition, a lower pH gradient was observed with NaCl₂₅ resulted in quite high numbers of PV needed to reach the plateau.

A lower pH gradient with 25 000 ppm brine could be explained by the high NaCl concentration. High Na⁺ concentration will reduce the contribution of alkalinity from the reactive plagioclase (Strand et al. 2014), as described by Eq.40.

The Smart Water EOR potential using 40 000 ppm of NaCl brine has previously been tested at 40 °C in core B-01, Figure 37 (RezaeiDoust et al. 2011).

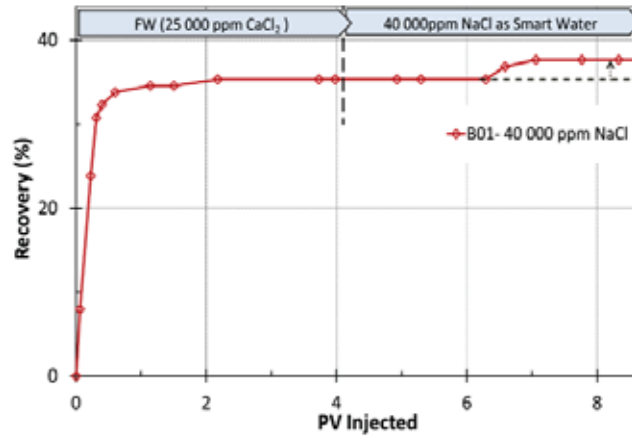


Figure 37. Oil recovery test performed with the outcrop B-01 at 40 °C, injection sequence FW (25 000 ppm CaCl₂)-Smart Water (40 000 ppm NaCl), flooding rate of 4PV/D (RezaeiDoust et al. 2011).

The oil recovery plateau with formation water, FW (pure 25 000 ppm CaCl₂ solution), was 35% OOIP. When the 40 000 NaCl brine was injected, the oil production increased but the extra oil of 3% OOIP was dramatically delayed and observed after 2 PV injected of 40 000 ppm NaCl brine.

With a very high Ca²⁺ concentration in the formation water, the Ca²⁺ concentration need to be reduced before the wettability alteration took place. A gradient in Ca²⁺ concentration between rock surface and the bulk Smart Water fluid must be created, before any EOR effect could be observed.

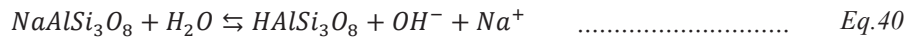
By injecting NaCl₂₅ brine, a 10 % OOIP improved oil recovery was observed for this rock-FW-crude oil system in tertiary mode. This recovery is in line with recoveries observed with 1000 ppm LS brines. Injecting the 40 000 NaCl brine improved oil recovery 3% OOIP. The experimental results confirm that it is not the salinity of the EOR fluid that is important, but rather the ion composition, and especially the Ca²⁺ concentration. These experimental results agree well with the suggested pH induced wettability alteration mechanism proposed by Austad et al. (Austad et al. 2010). The speed of oil production in tertiary mode and ultimate oil recovery are both influenced by the concentration of Ca²⁺ in the FW, the salinity of the Smart Water brine (presence of NaCl) and by the resulting pH gradient. Smart Water brines with salinities below 5000 ppm are

still a good choice because dilution of brines also reduces the concentration of divalent cations like Ca^{2+} .

5.2 Temperature Smart Water EOR effect in cores with feldspar minerals

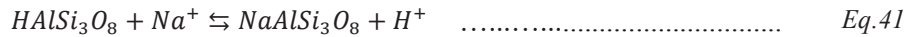
Previous published work has indicated reduced Smart Water EOR potential at high temperatures (Gamage and Thyne 2011, Aksulu et al. 2012). This could be explained by increased reactivity of Ca^{2+} ions and reduced Ca^{2+} desorption from the clay surface as the temperature increases (Aghaeifar et al. 2015), Ca^{2+} desorption is a temperature dependent process as observed in Eq.32.

As observed in the previous presented results, the pore surface minerals play an important role controlling both the reservoir pH and pH changes during Smart Water injection. Reactive albite influences initial wetting and the pH development during LS flooding of reservoir cores (Reinholdtsen et al. 2011, Strand et al. 2014). Reactive Albite, $\text{NaAlSi}_3\text{O}_8$, behaves as shown in Eq.40.



In the presence of LS brines with lower Na^+ concentration, Na^+ from albite could be substituted by H^+ , increasing the pH of the system. Na^+ ions are not strongly hydrated by water (Burgess 1978). Therefore, the ion exchange process should not be very temperature dependent.

When an outcrop rock is exposed to fresh percolating water, albite could be transferred to its protonated form HAlSi_3O_8 . When this rock is exposed to high salinity brines with high Na^+ concentration, the pH will decline displacing the chemical equilibrium of Eq.41 to the right. Note that Eq.41 is technically the same chemical equilibrium presented in Eq.40.



Shortly, when plagioclase minerals are present at the pore surface, it could influence the reservoir pH, giving lower or higher values depending on its exchangeable cations and the salinity of the brines.

5.2.1 Kinetic description and the pH development

Pore surface minerals-brine interactions were investigated in a dynamic flooding process on a core containing reactive plagioclase. A pH screening test was carried out on core B-21 at 60 °C, Figure 38.

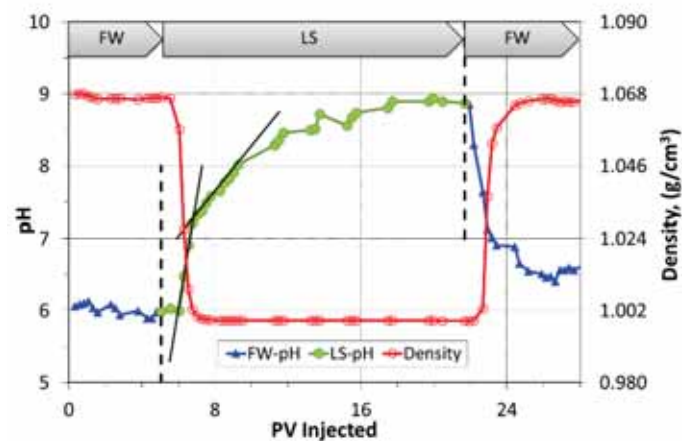


Figure 38. pH screening test at 60 °C on Total outcrop core B-21, containing 30% plagioclase. The core was saturated 100% with FW and successively flooded with FW-LS-FW at a rate of 4 PV/D. Bulk pH values are 5.5 for FW and 5.7 for LS.

During FW injection, the effluent pH stabilized at pH 6. When the injected fluid was changed to LS brine, a fast increase in pH was observed. The speed of change decreased and the pH stabilized close to pH 9.

A steady state situation/equilibrium was established as the pH reached 9. The result indicates different kinetic regions for the pH change. A possible explanation is that the faster region is controlled by exchange of easily accessible cations on the clay and albite surfaces, with protons, H^+ , from water. The slower region is more controlled by the exchange of cations from less accessible minerals (Velde 1995), or from minerals present in the smaller and low permeable pores, i.e., cations in-between the layers of illite.

It was also noticed, that the desorption of Ca^{2+} or Na^+ from the minerals, and increase pH was a much slower process compared to the salinity gradient observed. The adsorption of ions and reduction of pH during LS-FW flooding was as expected a much faster process.

The pH screening test confirms that the core material containing plagioclase could have both low initial pH with FW promoting mixed-wet conditions, and high pH during a Smart Water injection promoting wettability alteration.

5.2.2 Temperature effect on pH

To confirm the temperature dependency in core material containing feldspar minerals, a pH screening test was performed on core B-21. The core was successively flooded with FW-LS-FW at 60, 90 and 120 °C. The pH of the eluting brine was logged. The results are shown in Figure 39.

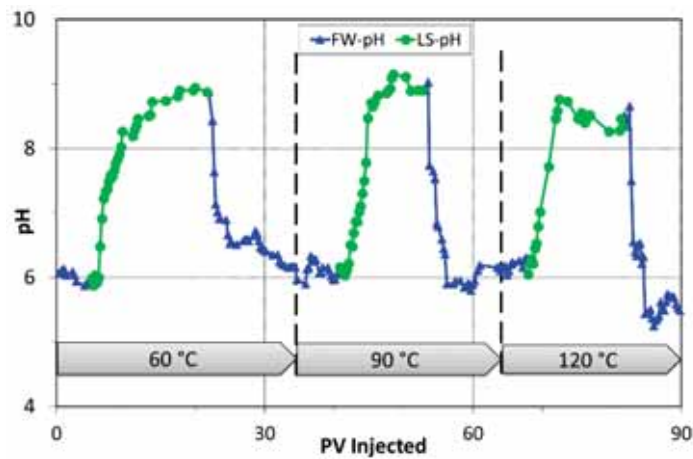


Figure 39. pH screening tests on core B-21. Mildly cleaned and 100% brine saturated core was successively flooded with FW-LS-FW at a rate of 4 PV/D. pH in effluent samples was recorded. Tests were performed at 60, 90, and 120 °C. Bulk pH values are 5.5 for FW and 5.7 for LS.

Initial acidic conditions were observed during FW flooding at all temperatures. This initial conditions could promote adsorption of polar components giving mixed-wet initial conditions. The pH increased as the LS was injected. The pH increments were large at all temperatures, with a $\Delta\text{pH}\approx 3$.

Based on the results from the pH screening tests, cation exchange at mineral surfaces present in the core material promotes the favorable conditions for observing Smart Water EOR effects observed at temperatures from 60 to 120 °C. An acidic environment is created with FW, while during LS flooding it is observed a large and rapid change in pH toward alkaline conditions.

It is important to recall that acidic initial conditions in presence of formation water must occur in order to obtain mixed wet conditions. If an initial alkaline environment is predominant with FW, it will make the rock too water-wet giving a negligible LS EOR response. An example for non-beneficial initial conditions is the Snorre pilot in the North Sea (Reinholdtsen et al. 2011, Skrettingland et al. 2011), The reservoir core material with high plagioclase content turned to be a system with poor potential for LS injection due to alkaline initial conditions in presence of a formation water with a salinity of 35 000 ppm.

5.2.3 Temperature effect of Smart Water EOR effects in cores with plagioclase

In order to investigate temperature effects on oil recovery from cores containing plagioclase minerals, two oil recovery test were performed.

The oil recovery test at 60 °C was performed on core B-21. The oil recovery test at 120 °C was performed on core B-22. Both cores were restored with $S_{wi}=0.20$, saturated, flooded and aged with Total crude oil at the test temperature.

The cores were successively flooded with FW and LS brine at a rate of 4 PV/D. The oil recovery was logged against PV injected. The pH of produced water was also monitored. During the core at 60 °C the oil recovery plateau of 40.1% of OOIP was reached after 2 PV of FW injected, Figure 40.

The first produced water sample had a pH of 6.0 indicating initial conditions that promote mixed-wet conditions. After 4 PV injected, the flooding fluid was changed from FW to the LS brine. The produced water pH increased and a tertiary LS EOR effect was observed. The oil recovery gradually increased to a plateau of 49.3% OOIP after 12 PV injected.

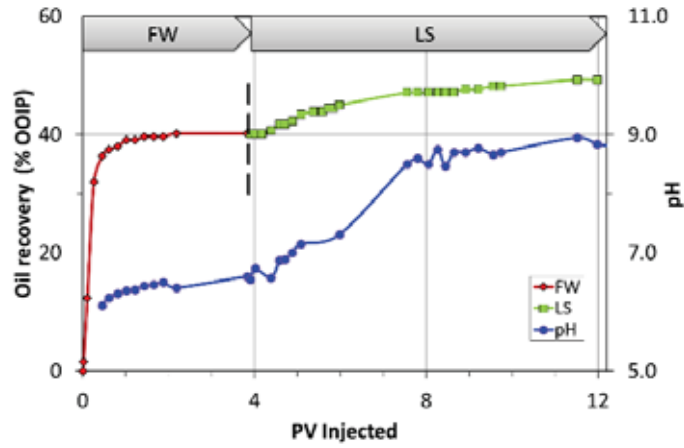


Figure 40. Oil recovery test on core B-21 at 60 °C. The core was restored with $S_{wi}=0.20$, saturated and aged in crude oil. The core was successively flooded with FW-LS at a rate of 4 PV/D. Bulk pH values are 5.5 for FW and 5.7 for LS.

The oil recovery test at 120 °C was performed on the outcrop core B-22, Figure 41.

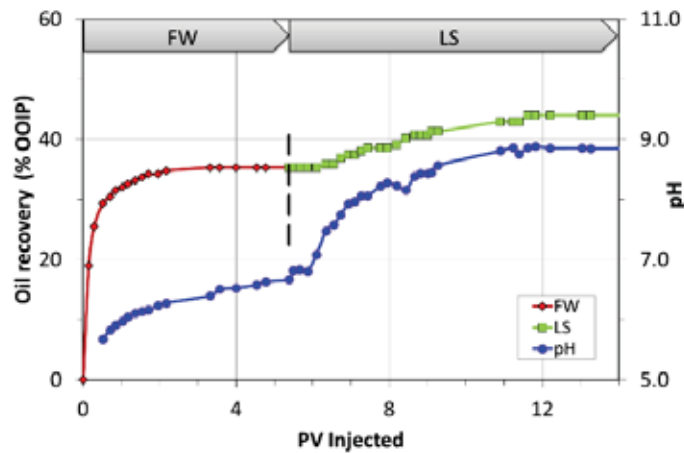


Figure 41. Oil recovery tests on core B-22, core with $S_{wi}=0.20$ saturated and aged in crude oil. The core was successively flooded with FW-LS at a rate of 4 PV/D tested at 120 °C. Bulk pH values are 5.5 for FW and 5.7 for LS.

Main results and discussion

The secondary oil recovery plateau with FW was 35.3 %OOIP. This could be explained by a difference in mobility ratio or more water-wet conditions at 120 °C compared to 60 °C.

During the LS flooding both the pH and the oil recovery increased. The oil recovery plateau of 44.0 %OOIP was reached after 12 PV injected. The LS EOR effect is the same range as observed at 60 °C.

The pH development during water injection was quite similar at both temperatures, Figure 42. The pH was generally lower compared with the observed values from the pH screening tests. This could be explained by buffer effects of the crude oil, and the fact that water-wet sites are available at mixed-wet conditions, reducing the full rock-brine interaction observed in the pH screening test at 100 % S_{wi} .

The pH increased slightly during FW flooding in both cores. A less water-wet rock surface will influence the dynamic equilibrium achieved at a given injection rate.

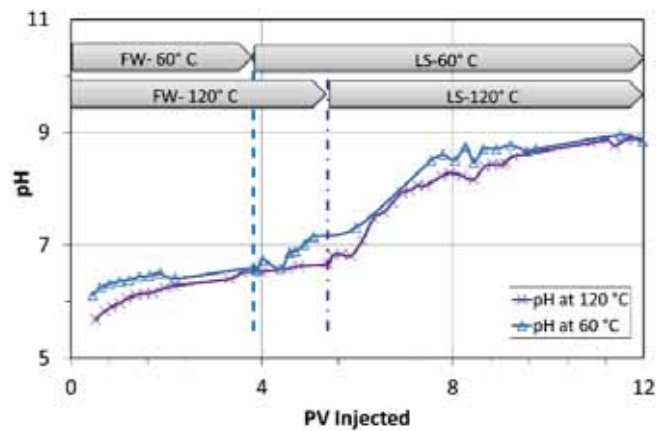


Figure 42. Comparison of pH profiles during oil recovery tests at 60 °C and 120 °C. Both cores were successively flooded with FW-LS at a rate of 4 PV/D. Bulk pH values are 5.5 for FW and 5.7 for LS.

The pH screening tests for this rock system containing plagioclase minerals, showed a high pH gradient during both LS injections at low and high temperatures.

Main results and discussion

It is important to notice that increase in oil recovery is synchronized with the increase in pH at 60 and 120 °C, confirming the strong relationship between the LS EOR effect and the induced pH gradient. The oil recovery tests at 60 and 120 °C confirmed both high pH gradients during LS flooding at both temperatures and LS Smart Water EOR effects. A summary of the main results during the oil recovery tests is shown in Table 16.

Table 16. pH gradients from pH screening tests, oil recovery and the observed LS EOR effect.

Temperature (°C)	Δ pH (FW-LS) pH scan	Δ pH (FW-LS) Oil recovery	LS EOR effect (% of OOIP)
60	3.0	2.3	9.2
90	3.0	-	-
120	2.7	2.2	8.7

A strong link between salinity changes and pH changes during waterflooding has also been pointed out previously by Vaidya and Fogler in work related to Berea sandstone cores (Vaidya and Fogler 1992).

Pendant drop IFT measurements performed on equilibrated crude oil-brine systems, confirmed only minor IFT effects using the same crude oil-brine system. The measurements were performed using different temperature and constant pressure, Table 17 (RezaeiDoust 2011).

Table 17. IFT as a function of temperature at 50 bars of pressure (RezaeiDoust 2011).

Temperature (°C)	IFT (mN/m) Total oil-FW brine	IFT (mN/m) Total oil-LS brine
40	19	21
80	19	21
100	19	19
130	21	21

The viscosity ratio between crude oil and FW is more favorable than the viscosity ratio between crude oil and LS brine at 60 and 120 °C. This clearly shows that the extra oil recovered during the LS brine injection cannot be linked to viscous forces, the extra oil produced has to be linked to increase water-

wetness that induce positive capillary forces and improved microscopic sweep efficiency.

Table 18. Viscosities of crude oil and brines at different temperatures.

Temperature (°C)	Crude oil (cp)	FW (cp)	LS (cp)	Viscosity ratio (μ_o/μ_{wFW})	Viscosity ratio (μ_o/μ_{wLS})
25	17.60	1.18	1.01	14.92	17.43
60	4.59	0.63	0.60	7.29	7.65
120	2.02	0.29*	0.23*	6.97	8.78

In summary, the presence of plagioclase minerals seems to be a key parameter for observing high pH and high LS EOR effects at both 60 and 120 °C. The oil recovery results are in agreement with the rock-brine interactions observed in the pH screening tests.

5.3 Smart Water Injection strategies in sandstones

Positive conditions to induce wettability alteration and low salinity Smart Water EOR effects in tertiary mode have been presented and discussed. However, the process to create the conditions and displace extra oil, and observe a substantial Smart Water EOR effect might take time, as seen in Figure 36 and Figure 37. Therefore, it is important to define: “*what could be the best injection strategy to reduce the EOR response time?*” This is crucial because an optimal injection strategy could both increase the oil production and at the same time reduce operation costs.

5.3.1 LS-Slug injection in sandstones with reactive plagioclase

In the previous work it was seen that the LS-EOR effect was synchronized with the pH increase observed during the LS injection. *What would be the consequence of a limited LS-slug injection regarding the EOR effect?* The slug volume should be large enough to increase the pH which dictates the wettability alteration process.

Main results and discussion

Based on the results from core B-21, Figure 40, $\approx 50\%$ OOIP extra oil was recovered after 2 PV of LS injection, and this could be an appropriated slug volume.

A total outcrop core B-24 was prepared for an oil recovery at $60\text{ }^\circ\text{C}$ in the same way as core B-21. The secondary oil recovery with FW was 39.0% OOIP, Figure 43, i.e., quite similar as observed in core B-21.

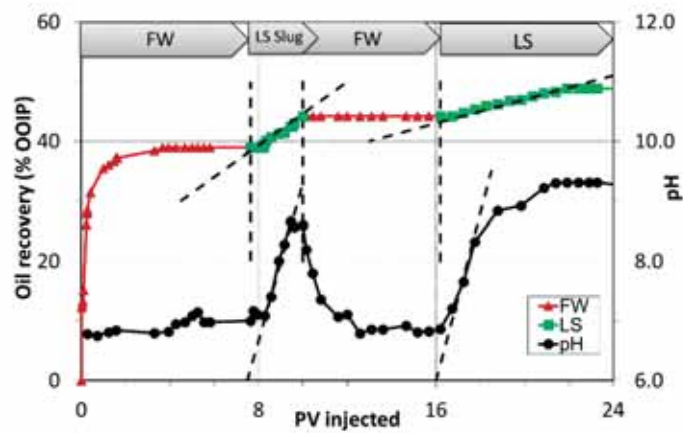


Figure 43. Oil recovery test for core B-24 at $60\text{ }^\circ\text{C}$. The restored core with $S_{wi}=0,2$ was saturated and aged in crude oil, the core was successively flooded at a rate of 4 PV/D with FW-LS (2PVs) - FW - LS. Bulk pH values are 5.5 for FW and 5.7 for LS.

After 8 PV of FW, a LS slug of 2 PVs was injected. The oil recovery increased to 44.3% OOIP, corresponding to a LS EOR effect of 5.3% of OOIP. The pH in the first produced water was, 6.4, and the pH increased rapidly by 2 pH units to 8.8 during the LS brine flooding.

After the LS slug, FW was again injected. The oil recovery immediately stopped, and the pH in the produced water rapidly decreased. The pH stabilized at 6.8 after 16 PV.

Once again, the LS brine was reinjected. The pH increased rapidly back to 8.9, but the observed LS EOR production became slower as seen by the production slopes in Figure 43. After the fast pH increase, the pH slowly increased to 9.3. The oil recovery plateau of 49.0% OOIP was achieved after 2 PV injected.

A plausible explanation for the observed behavior is linked to the heterogeneous pore distribution in the core material, as illustrated in Figure 29. A general illustration of the process is presented in Figure 44.

During the secondary flooding with HS brine, at mixed-wet conditions, the oil present in the larger pores will be mobilized and the residual oil saturation after flooding with a high salinity brine, HS, becomes $(S_{orw})_{HS}$, Figure 44(a). No wettability alteration takes place, and smaller pores are bypassed.

The LS brine slug, with lower viscosity and unfavorable mobility ratio compared to the HS brine should follow the same water paths as the HS brine. As wettability modification takes place in both the larger pores and together with induced spontaneous imbibition from the smallest pores generating the highest P_c . A decrease in the residual oil saturation from $(S_{orw})_{HS}$ to residual oil saturation after the low salinity slug (LS1) $(S_{orw})_{LS1}$, are observed Figure 44(b).

A new injection of HS brine will of course follow the pores with the highest water saturation, i.e., the larger pores. Simultaneously the pH will decrease and stop the wettability alteration process. No oil is produced, and the oil saturation remains the same, $(S_{orw})_{LS1}$, Figure 44(c). Injection of a new LS brine gave a fast pH response in the larger pores, similarly to the first LS slug.

The LS EOR effect in the second LS slug are mainly produced due to wettability alteration and spontaneous imbibition into bypassed pores. This time the larger bypassed pores with lower P_c will contribute with most of the extra oil. The oil saturation will decrease to the final residual oil saturation obtained during the LS injection $(S_{orw})_{LS2}$, Figure 44(d).

The residual oil saturations for the experiment in figure Figure 43 changed in the following way; $(S_{orw})_{HS} > (S_{orw})_{LS1} > (S_{orw})_{LS2}$.

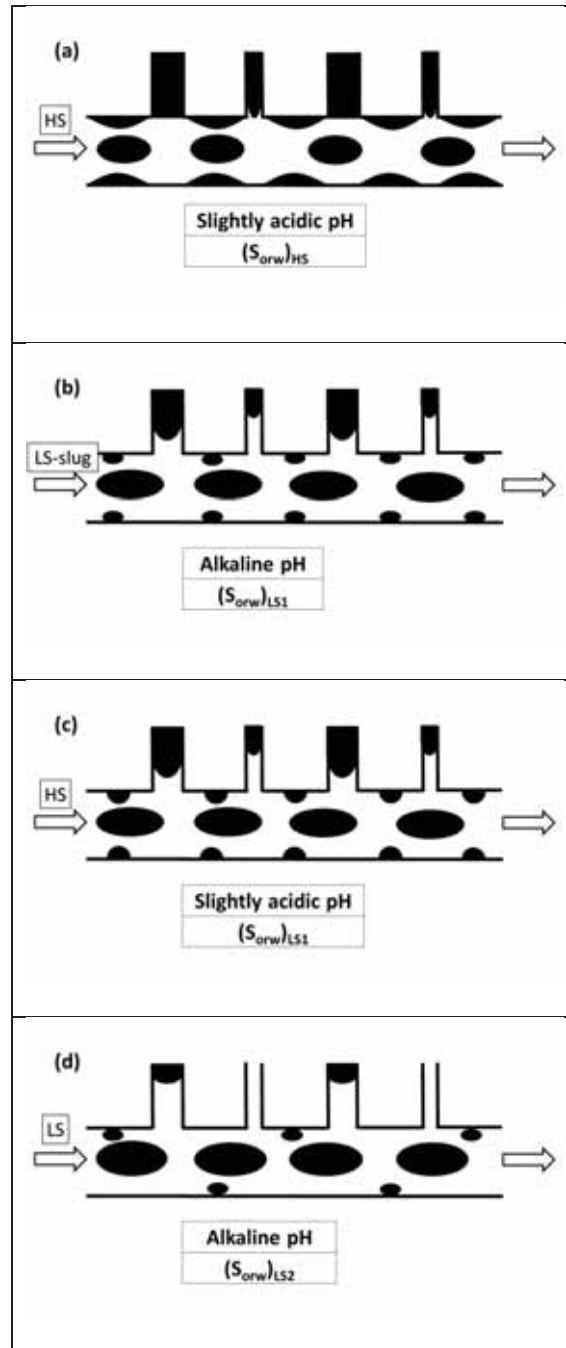


Figure 44. Mobilization of oil from a porous medium, controlled by pore size distribution and wettability alteration from mixed-wet conditions toward more water-wet conditions.

In the slug experiment in Figure 43, about half of the tertiary LS EOR effect was produced after 2 PV injected. Additionally, 6 PV of LS brine must be injected to reach the EOR recovery plateau. According to the discussion above, a fast tertiary LS EOR response can only be obtained if the LS brine redistributes oil in the pores pre-flooded with HS brine. Some of this redistributed oil could be mobilized by viscous forces after wettability modification. The response time for extra oil from bypassed pores by spontaneous imbibition and improved microscopic sweep efficiency is dependent on the pore size and the induced P_c during the wettability alteration process. This oil can contribute to a large fraction of the total EOR effect.

For the present crude oil-brine-rock system 50% of the extra oil was produced with a short response time, 2 PV. The remaining 50% was produced with a longer response time, 6 PV. It therefore appears that the pore size distribution as seen in Figure 29 will have a great impact on the response time of the LS EOR effect.

The suggested LS Smart Water EOR mechanism in mixed-wet core material is based on wettability modification towards more water-wet conditions. Some of the redistributed oil during LS injection could be trapped due to increased capillary forces in the porous system. If, however, the mobilized oil bank is larger than the amount of oil trapped because of increased capillary forces, a positive LS EOR effect will be observed.

5.3.2 Secondary LS EOR effect

To displace FW or secondary injected brines with Smart Water is a EOR process that is delayed, especially in tertiary mode when the water saturation with “non-optimized” water is higher. In the slug experiment, Figure 43, the first extra oil during the first LS flooding was observed after ≈ 0.6 PV injected.

New oil recovery tests were performed using the same total outcrop system. Two oil recovery experiments were performed on the same core to confirm the reproducibility of the experiment.

Main results and discussion

The outcrop core B-26 was prepared in the same way as the two previous cores used for tertiary LS studies. The restored core B-26 was immediately flooded with the LS brine. The results represented in Figure 45.

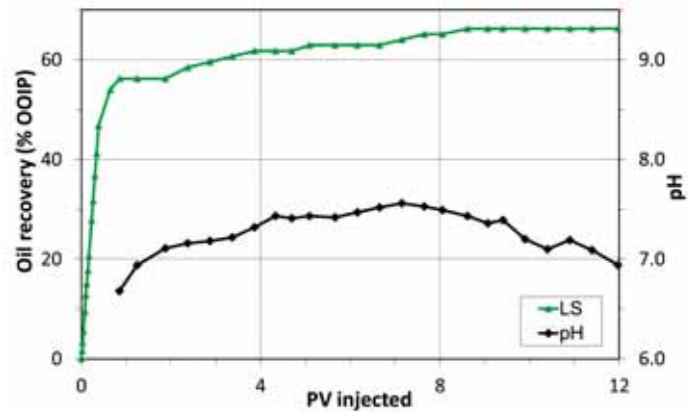


Figure 45. Oil recovery test at 60 °C from core B-26 after the first restoration. A secondary LS brine injection was performed at a rate of 4 PV/D. Bulk pH value for LS is 5.7.

The oil recovery increased rapidly and the first produced water was observed after 46% OOIP produced. The oil recovery continued and reached a recovery of 56% OOIP after 1 PV injected. Steadily extra oil was observed and 60% OOIP were obtained after 3 PV, with an ultimate increase to 67% OOIP after 8.6 PV injected. The efficiency of the EOR LS effect is dramatically larger when performed in secondary mode. The LS oil recovery in secondary mode is compared with the LS oil recovery in tertiary mode in Figure 46.

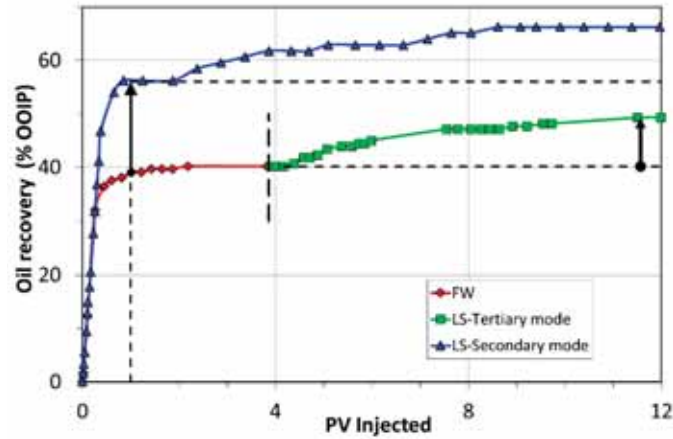


Figure 46. Comparison LS injection in secondary and tertiary mode in sandstone. Core B-21 was used to test LS in tertiary mode, core B-26 was tested in secondary mode. The arrow indicates the production after 1 PV injected. Bulk pH values are 5.5 for FW and 5.7 for LS.

After 1 PV injected the LS EOR recovery is 17% OOIP higher than during 1 PV of FW injection. The secondary LS EOR recovery after 1 PV is still 7% higher than the ultimate tertiary LS recovery after 11 PV injected.

The results are in agreement with Hamon (2015), who summarized the results from more than 500 studies, and reported that injection of LS brine in secondary mode give an augmented oil recovery effect in comparison with injection of an HS brine (Hamon 2015). Incremental oil with LS brine can be observed at an early stage of the process, for instance at water breakthrough or briefly afterwards. A faster and increased response was observed when LS was directly injected in to the core, as seen in Figure 45.

The pH in the produced water increased but only reached a maximum value of 7.5 after 4 PV injected. Stronger buffer effects from the polar organic components can explain this behavior, which in secondary mode are stronger at the beginning of the process due to a larger oil saturation. As the oil saturation is reduced, upconcentrated polar components in the oil droplets disconnected by snap-off can explain the buffer effect observed in the later stages, Figure 45.

5.4 Smart Water as a platform for other EOR methods

After identifying significant differences in the recovery yield in relation to different injection strategies for Smart Water EOR injection, it is important to evaluate the combination of Smart Water with other EOR methods.

The Smart Water changes the rock surface wetting from mixed-wet towards more water-wet conditions, which induces positive capillary forces, P_c , and improve the microscopic sweep efficiency. During this process, less oil is strongly attached to the rock surface. This redistribution results in more oil in trapped in the middle of the pores, but due to increased capillary entrapment the oil is still immobile.

As this oil is not mobilized by water, other methods can help to contact and expel the oil out of the porous media, improving macroscopic sweep efficiency. At the same time, LS brines increase the selection of EOR chemicals like polymers and surfactants. It also increases the stability and improve the performance of these chemicals at reservoir conditions. This could improve the cost efficiency of the EOR chemicals.

After the first LS experiment on core B-26, the core was mildly cleaned and restored. In the second oil recovery test, B-26-R2, the core was first flooded with LS brine, followed by a LSP in tertiary mode, Figure 47.

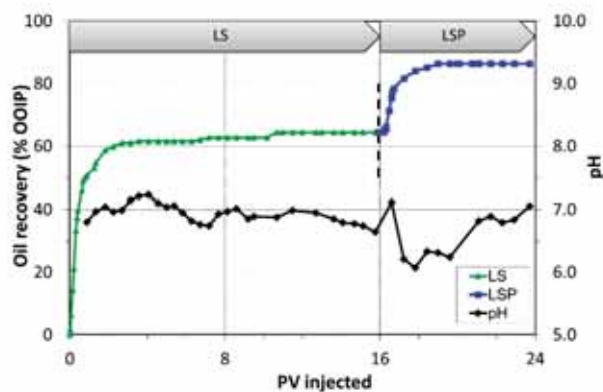


Figure 47. Oil recovery test from core B-26-R2 at 60 °C by secondary injection of LS brine, followed by a LSP flood. Bulk pH values are 5.7 for LS and 7.8 for LSP.

The secondary LS injection showed reproducible recovery results as observed in the first recovery test, Figure 45. When oil recovery plateau of 65% OOIP was reached after 10.6 PV, 1 wt % of HPAM polymer was added to the LS brine, named LSP. By injecting LSP in tertiary mode, a fast oil recovery response was observed, with ultimate oil recovery of 86% of OOIP.

Oil recovery from Total outcrop systems with no wettability alteration gives ultimate recovery of 40% OOIP. Secondary injection of LS brine induced wettability alteration, which increased microscopic sweep efficiency and redistributed oil inside the core giving an 65% OOIP.

Combining LS and polymer was highly efficient, improving macroscopic sweep efficiency with 21% OOIP extra oil, leaving the core with an extremely low final $S_{or}=0.14$.

A possible explanation is that most of the residual oil is trapped in the middle of larger pores due to high water wetness after the LS flood. This trapped oil is easily mobilized because the LSP solution decrease the mobility ratio creating a more stable displacement front increasing microscopic and macroscopic sweep efficiency.

5.5 Impact of carbonate mineralogy on Smart Water EOR effect

Mineralogy plays a crucial role for the right selection of the Smart Water composition. In sandstone, clays, feldspars and calcium sulfate minerals influence the initial wetting of a system as well as the wettability alteration processes by Smart Water.

Likewise, the Smart Water wettability alteration process in carbonates is similarly influenced by mineralogy. Depending on whether the carbonate is mainly formed by calcite or dolomite minerals, the Smart Water can have a different chemical composition (Fathi et al. 2011, Romanuka et al. 2012, Shariatpanahi et al. 2016). Besides this, calcium sulfate minerals are capable of influencing the initial wetting in carbonate rocks (Punternvold et al. 2007) and be a source of potential determining ions like Ca^{2+} and SO_4^{2-} which is the catalyst for the wettability alteration process (Shariatpanahi et al. 2011, Austad et al. 2015). Additionally, oil mobilization by wettability alteration is dependent on chemical reactions taking place between oil components, brine constituents, and the rock surface. In the following experimental work performed on a reservoir carbonate system at low temperature, it is shown that the Smart Water effect is highly influenced by mineralogy, brine composition, and temperature.

The Smart Water EOR potential was evaluated in cores from a carbonate reservoir with a reservoir temperature of 65 °C. A selected group of cores was screened for mineralogy, capillary forces, surface reactivity and presence of initial calcium sulfate and hydrocarbons. Oil recovery tests by spontaneous imbibition were performed. Among the cores, limestone and dolomitic limestone material was detected. Initial dissolvable sulfate was present in all cores.

All reservoir cores were mildly cleaned and restored with initial water saturation of 10%, $S_{wi}=0.1$, established using the formation water termed FWR, Table 12. The cores were saturated, flooded and aged in the stabilized crude oil termed Reservoir crude oil, Table 13. The oil recovery tests were performed by spontaneous imbibition, SI. The cores were initially imbibed with the formation water, FWR, and when the production plateau was reached, the imbibing fluid was changed to the suggested Smart Water to observed any wettability

alteration and increased oil recovery. Some of the cores were subjected to final imbibition stage using at the end Smart Water containing 1 wt % of C₁₂TAB. Oil recovery was logged against time.

5.5.1 Smart Water EOR effects in limestone reservoir cores at low temperature

The purpose of this study was to test the potential of the Smart Water EOR in a limestone reservoir at low temperature.

For CaCO₃ surfaces the presumably best known Smart Water is seawater depleted in Na⁺ and Cl⁻ ions, and spiked with four times sulfate (SW0Na4S) (Fathi et al. 2011), especially at low temperature (Punternold et al. 2015). At high temperatures, a high sulfate concentration can lead to CaSO₄ precipitation. Reducing Na⁺ and Cl⁻, increases the relative concentration of the ions Ca²⁺ and SO₄²⁻ that are important for wettability alteration. Increased SO₄²⁻ concentration, i.e., catalyst concentration, can compensate for low reservoir temperature (Fathi et al. 2011).

There is an increased SO₄²⁻ reactivity towards the CaCO₃ surface as temperature increases (Strand et al. 2006). Hence, a major drawback for Smart Water at low temperatures is that SO₄²⁻ is less reactive. By spiking the Smart Water brine with SO₄²⁻, the lower reactivity of SO₄²⁻ observed at low temperatures can be compensated by an increased amount of the catalyst in solution (Punternold et al. 2015). Moreover, at low temperatures the solubility of calcium sulfate minerals is larger than at higher temperatures (Carlberg and Matthews 1973). For this reason, the presence of initial calcium sulfate in the formation can be beneficial for the wettability alteration process triggered by Smart Water injection (Austad et al. 2015).

As the temperature for this carbonate reservoir was low, an optimized Smart Water composition should be a modified seawater brine, depleted in Na⁺ and Cl⁻ with 4 times sulfate, SW0Na4S; the composition is detailed in Table 12. Examples of oil recovery tests by spontaneous imbibition in reservoir limestone cores are presented next.

Mildly cleaned and restored reservoir cores 14C, and 29B, were successively imbibed at 65 °C with FWR and the Smart Water brine termed SW0Na4S, Figures Figure 48 and Figure 49.

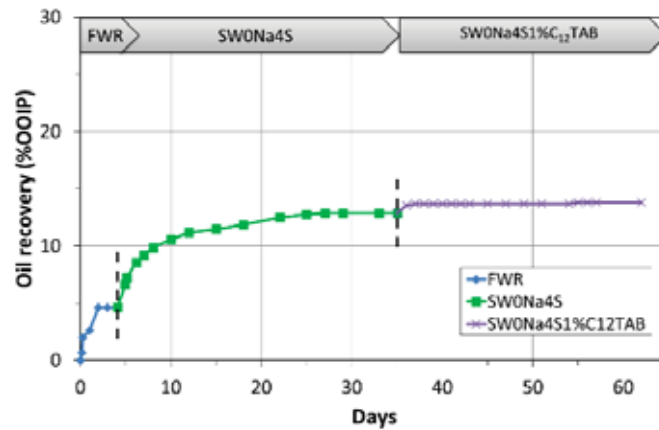


Figure 48. Spontaneous imbibition test at 65 °C in the limestone core 14C after first restoration. The core was initially imbibed with FWR, followed by the Smart Water (SW0Na4S) and (SW0Na4S) +1 wt % C₁₂TAB.

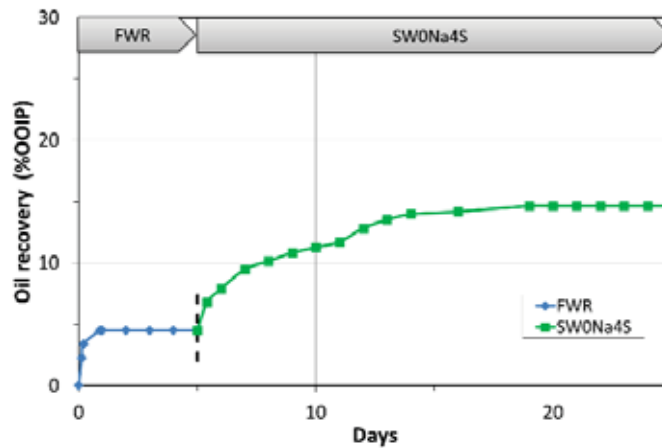


Figure 49. Spontaneous imbibition test at 65 °C in the limestone 29B. The core was initially imbibed with FWR, followed by the Smart Water (SW0Na4S).

In both cores spontaneous imbibition by FWR gave an oil recovery close to 5% OOIP, showing reproducible results. By changing the imbibition brine to

SW0Na4S, both cores experienced an increased oil recovery up to $\approx 13\%$ OOIP for core 14C and $\approx 15\%$ OOIP for core 29B due to wettability alteration. A 1 wt % of the cationic surfactant $C_{12}TAB$ was added to the imbibing brine SW0Na4S to test if there are still an alteration potential. Only a minor increased of $\approx 1\%$ OOIP was observed, Figure 48.

The chosen Smart Water responded positively in all tested cores at $65\text{ }^{\circ}\text{C}$ in their first restoration. The results gave useful evidence of Smart Water EOR effects in reservoir limestone cores even at $65\text{ }^{\circ}\text{C}$, which previously was considered as a non-optimum temperature to observe Smart Water EOR effects (Zhang and Austad 2006, Fathi et al. 2011, Austad 2013).

When oil recovery tests were performed on the same cores after a second restoration, the EOR effect was in general poorer. This observation can be explained by a reduction in the dissolvable calcium sulfate caused by previous experiments and core cleaning. A sulfate reduction in the effluent was observed qualitatively and in some cases quantitatively. It is well known that the presence of dissolvable calcium sulfate will affect the initial wetting giving a more water wet behavior and thereby affecting the EOR potential with Smart Water (Shariatpanahi et al. 2011). If anhydrite is absent, less water-wet initial conditions can be created during core restoration. Additionally, calcium sulfate dissolution during Smart Water injection may contribute with both calcium and sulfate ions in the imbibing front, which is adsorbed onto the rock surface but also needed to induce wettability alteration. However, a quantification of this contribution is difficult, especially at pore scale. The slow wettability alteration process from 115-25 days indicates a lack of critical minimum concentration of sulfate in the imbibing front.

In summary, 7 cores were tested, and the incremental oil recovery ranged from 1.8 to 10.1 % OOIP for the pure limestone material. Variation in different samples under similar conditions were observed, see Table 19. However, the results were most likely also influenced by the heterogeneity in the physical properties, Table 8.

5.5.2 Impact of the brine composition on EOR from limestone reservoir cores

In the previous section increased oil recovery by wettability alteration was observed using the Smart Water brine SW0Na4S in limestone cores 14C and 29 B, Figure 48 and Figure 49. It has been reported that diluted seawater can improve oil recovery by wettability alteration in dolomites (Shariatpanahi et al. 2016).

The mildly cleaned and restored core 14B, Figure 50, was successively imbibed with FWR and a 20 times diluted seawater termed d_{20} SW at 65 °C.

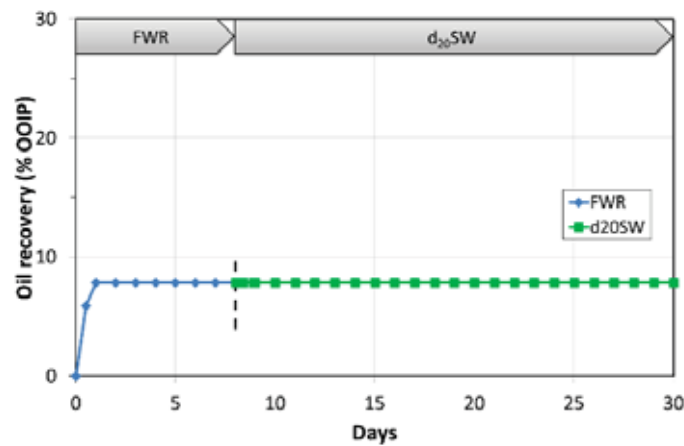


Figure 50. Spontaneous imbibition tests at 65 °C on limestone core 14B, first restoration. FWR and d_{20} SW were used as imbibing brines.

Spontaneous imbibition by FWR gave an oil recovery close to 8% OOIP. However, when diluted seawater, d_{20} SW, was used as imbibing brine, no wettability alteration took place, Figure 50.

This observation is in line with the work by Fathi et al. (2010), They observed that at CaCO_3 surfaces an adequate concentration of Ca^{2+} and Mg^{2+} ions are needed in the Smart Water brine to observe an EOR effect (Zhang et al. 2007). It is known that Ca^{2+} and SO_4^{2-} are responsible for wettability alteration, and a diluted brine has low amounts of these ions.

As observed in Table 12, in d_{20} SW the sulfate, calcium and magnesium concentrations are quite low, 1.2, 0.6, and 2.2 mM respectively. Furthermore,

the limestone cores used with low CaSO_4 content did not contribute with enough calcium and sulfate from dissolvable minerals to induce wettability alteration.

5.5.3 Smart Water EOR effect in dolomitic reservoir cores

Referring to recent studies on Smart Water in dolomitic material, where diluted seawater brines were able to alter wettability. The carbonate reservoir system studied, also consisted of a dolomitic limestone zone, and it was decided that the Smart Water brine to be used in the received dolomitic reservoir cores should be seawater diluted 10 or 20 times, $d_{10}\text{SW}$ or $d_{20}\text{SW}$.

It is well known that SO_4^{2-} gets adsorbed on to carbonate surfaces (Strand et al. 2006). Thus, in a process of spontaneous imbibition, a lack of SO_4^{2-} in the imbibition front can occur, reducing speed or potential of Smart Water EOR effects. However, if dissolvable calcium sulfate is present, low salinity brines will dissolve it faster, releasing Ca^{2+} and SO_4^{2-} ions in situ, in the imbibing front diluted SW brines such as $d_{20}\text{SW}$ and $d_{10}\text{SW}$ could appear more effective as the salinity increases in dolomitic material.

The mildly cleaned and restored core 10E with $S_{wi}=0.1$, was successively imbibed at 65 °C with FWR followed by 20 times diluted seawater termed $d_{20}\text{SW}$. Spontaneous imbibition by FWR gave an oil recovery of 6% OOIP. When diluted seawater, $d_{20}\text{SW}$, was introduced extra oil recovered of 10% OOIP was produced, Figure 51. At the end, a 1 wt % of C_{12}TAB was added to Smart Water brine $d_{20}\text{SW}$, to test its remaining potential for wettability alteration.

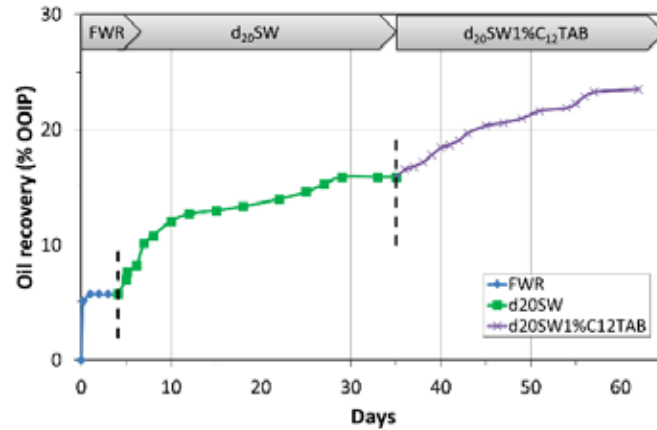


Figure 51. Spontaneous imbibition test at 65 °C on a dolomitic limestone core 10E, first restoration. FWR, d₂₀SW and d₂₀SW 1 wt % C₁₂TAB were used as imbibing fluids.

The cationic surfactant C₁₂TAB, is an efficient wettability modifier in carbonates but does not reduce the IFT drastically. This helps to preserve capillary forces. Another important characteristic is that C₁₂TAB is catalyzed by sulfate (Standnes and Austad 2003). The net recovery increase with C₁₂TAB was ≈8 % OOIP, while the ultimate oil recovery was ≈24 % OOIP. The results showed that there was more room to further improve the wettability alteration process after using d₂₀SW. Furthermore, the positive effect with surfactant points to presence of enough sulfate in the system for the C₁₂TAB to act as a wettability modifier. The sulfate partially comes from CaSO₄ dissolution, as sulfate was detected in a post-cleaning of the core.

In connection to temperature and the Smart Water EOR effect in dolomites, it is important to mention that this piece of work and other in-house experiments have shown positive effects within the range of 65 to 115 °C (Punternold et al. 2017). The temperature versatility of Smart Water in dolomites can provide an important operation flexibility during the implementation of the technique in pilots or in full field projects.

5.5.4 Impact of the brine composition on EOR from dolomite reservoir cores

The Smart Water composition SW0Na4S used in pure limestone at low temperature, 65 °C, was also tested in a dolomitic-limestone core.

The dolomitic limestone core 10D was restored and imbibed with FWR followed by SW0Na4S, Figure 52.

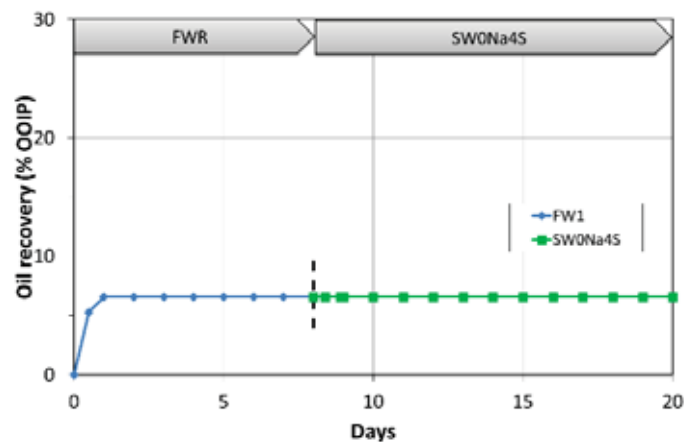


Figure 52. Spontaneous imbibition tests at 65 °C on core dolomitic limestone core 10D, first restoration.

Spontaneous imbibition with FWR gave a recovery of 6.5% OOIP, switching to SW0Na4S gave no extra oil.

The result confirms EOR effects in dolomitic surfaces by low salinity brines. Perhaps the salinity of SW0Na4S is too high to be an effective wettability modifier, Table 12. For this reason, it is important to dig deeper into the understanding of the role of potential determining ions in the wettability alteration process in dolomites (Romanuka et al. 2012).

In summary, wettability alteration did not take place using SW0Na4S at 65 °C in a dolomitic limestone reservoir core, however a diluted seawater $d_{20}SW$, did induce wettability alteration, and an EOR effect of 10 % OOIP was observed.

5.5.5 Overview of the evaluation of the Smart Water EOR potential in a carbonate reservoir.

From a research perspective, the EOR potential of Smart Water was confirmed to be positive for the targeted reservoir. All experimental techniques used contributed with valuable information that served as important input parameters to evaluate and provide the right Smart Water composition. Oil recovery tests at 65 °C using the selected Smart Water brines were performed in the different core materials. Consistent trends were observed. For instance, EOR effects in cores restored for first time were larger compared with EOR effects after a second restoration. This observation was equal in both limestone and dolomitic material. The presence of initial dissolvable sulfate can impact both the initial core wettability (Shariatpanahi et al. 2011), and is also important for triggering the Smart Water wettability alteration process. Nevertheless, the amount of dissolvable calcium sulfate is usually lowered in a second restoration due to the flooding history. Figure 53 summarizes the Smart Water EOR effects after the first restoration in both limestone and dolomitic cores.

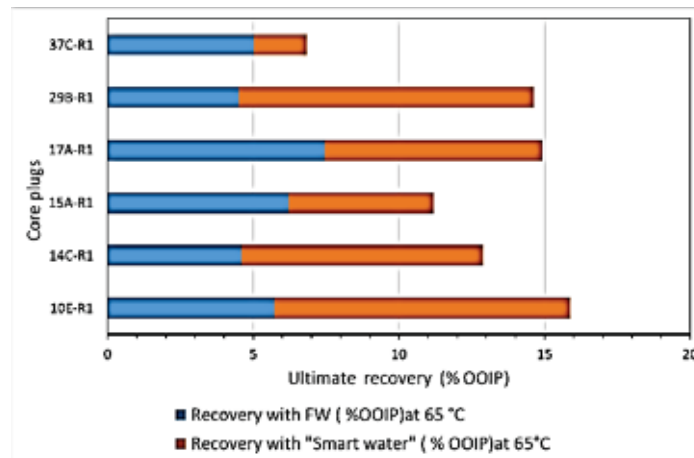


Figure 53. Summary of oil recovery tests in first restoration including both dolomitic limestone and limestone cores.

Different brine compositions were successfully proposed, based on previous research. For the dolomitic material, diluted seawater brines, $d_{20}SW$ and $d_{10}SW$, were the most efficient brines, and the recovery increased as the dilution

Main results and discussion

increased. Whereas for the limestone cores, the best brine was a modified SW brine with salinity of 20 240 ppm, SW0Na4S.

When the proposed Smart Water did not match the targeted mineralogy, as observed in the oil recovery tests on cores 10D-R1, 14B-R1 and 37A-R1, Table 19. The explanation was orientated towards salinity thresholds for dolomite and lack of dissolvable calcium sulfate in the limestone system (Romanuka et al. 2012).

Table 19. Summary of oil recovery tests.

Core #	Mineralogy	“Smart Water” 65 °C	FW Recovery (%OOIP) at 65 °C	ΔR_1 <i>Smart Water</i> (% OOIP) at 65 °C	Ultimate recovery (%OOIP)
10D-R1	Dolomitic	SW0Na4S	6.55	0.00	6.55
10E-R1	Dolomitic	d ₂₀ SW	5.72	10.17	15.89
10E-R2	Dolomitic	d ₁₀ SW	3.81	2.54	6.35
14B-R1	Limestone	d ₂₀ SW	7.84	0.00	7.84
14C-R1	Limestone	SW0Na4S	4.60	8.29	12.89
14C-R2	Limestone	SW0Na4S	5.27	2.63	7.90
15A-R1	Limestone	SW0Na4S	6.22	4.98	11.20
17A-R1	Limestone	SW0Na4S	7.46	7.46	14.92
29B-R1	Limestone	SW0Na4S	4.50	10.14	14.64
37A-R1	Limestone	d ₂₀ SW	5.96	0.00	5.96
37C-R1	Limestone	SW0Na4S	5.02	1.83	6.85
37C-R2	Limestone	SW0Na4S	3.65	2.74	6.39

It is well known that low temperatures can be a constraint in a Smart Water wettability alteration process in carbonates. 65 °C has previously been considered as a too low temperature to observe Smart Water EOR effects. A major remark is that in this study EOR effects were observed in both dolomitic and limestone core material at 65 °C, confirming that Smart Water injection in carbonates has an EOR potential also at lower reservoir temperatures.

6 Concluding remarks

The importance of the reservoir mineralogy has been highlighted throughout this work. Mineralogy influences both initial wettability and the Smart Water wettability alteration process. A good understanding of the crude oil and brine interactions with the pore surface minerals is crucial to evaluate the potential for observing Smart Water EOR in both sandstone, and carbonate reservoirs. Furthermore, the selection of a favorable Smart Water brine composition depends on a good interpretation of mineral properties in combination with the components in crude oil influencing reservoir wettability, as well as the formation water and the Smart water ions that dictate both the initial reservoir wettability and the wettability alteration process.

Throughout this work, similarities and differences in initial wetting and wettability alteration processes in sandstones and carbonates have been presented. Conclusions and future work are presented below.

6.1.1 Mineralogical impact on the Smart Water EOR effect

The pore surface mineralogy plays a crucial role, from reservoir characterization to how wettability processes take place. Not only the main minerals influence the Smart Water EOR process, but also trace minerals less abundant in the formation, i.e., calcium sulfate, could have a huge impact. In principle, due to different mineralogies, crude oil compositions and brine compositions, it appears to be discernible that the Smart Water EOR mechanisms should be completely different. The main differences between the Smart Water EOR mechanism in sandstones and carbonates are presented in this work, based on experimental evidence and the reservoir chemistry characteristics of each system.

The ability for polar components in the crude oil to adsorb or desorb from the pore surfaces are deeply linked to the type and distribution of minerals to cause the adequate initial wetting condition needed to observe Smart Water EOR effects.

Concluding remarks

Furthermore, it has been observed that trace minerals can influence the Smart Water EOR effect, i.e., calcium sulfate minerals. Which can be positive in carbonates if they act as a source of the Smart Water ions, or be negative in sandstones if the pH increment needed to induce wettability alteration and increased oil production, is lowered due to reduced Ca^{2+} desorption from the sandstone mineral surfaces.

- Wettability alteration with Smart Water at CaCO_3 surfaces is highly dependent on the availability of Smart Water ions to desorb acidic polar components. The process seems to be controlled by the diffusion of Ca^{2+} and SO_4^{2-} ions in the porous media. This becomes clear when studying the rates of wettability alteration in spontaneous imbibition experiments, where it normally takes several days to reach a production plateau.
- In sandstones, the Smart Water wettability alteration is pH controlled. The pH is quickly transported through the aqueous phase, and the wettability alteration in sandstones is a faster process compared to what has been observed in carbonates. The limiting factor is the desorption rate of calcium from the clay surface which are slower in comparison to acid-base reactions, and that finally releases the polar organic components from the surface. Calcium desorption can be slowed down by increasing brine salinities or dissolution of minerals like CaSO_4 or CaCO_3 from cementing material.
- The presence of calcium sulfate compounds can influence the Smart Water EOR effect in both carbonates and sandstones. In carbonates, calcium sulfate minerals will contribute with SO_4^{2-} ions in the FW, reducing the adsorption of acidic polar components promoting a more water-wet reservoir. The presence of calcium sulfate is also beneficial, since dissolvable sulfate can be a source of Smart Water ions. For sandstones CaSO_4 has a negative impact because it could be a source of Ca^{2+} . Increased Ca^{2+} concentration can influence the pH by precipitation of $\text{Ca}(\text{OH})_2$ as well as reducing the calcium desorption rate at the clay surfaces needed for the wettability alteration process.

6.1.2 Sandstones

Experimental work was performed to improve the understanding of the chemical processes influencing initial wetting and wettability alteration by Smart Water in sandstones. The effect of formation water and Smart Water composition on the Smart Water EOR potential in sandstone was tested. Temperature effects on the smart water EOR response in sandstone cores containing plagioclase minerals were also investigated. Furthermore, injection strategies of Smart Water were studied in order to optimize Smart Water EOR efficiency.

It is crucial to understand why EOR effects by wettability alteration are observed in some cases but not in others. Once the crude oil–rock–brine interactions are better understood, the EOR state by Smart Water could also be improved.

- The experimental work showed that when the initial pH due to rock–brine interactions is high, > 7 , the potential for EOR by wettability alteration with Smart Water was reduced. In order to observe Smart Water EOR effects, it is required that the initial wetting is mixed-wet.
- Formation water composition based on seawater gave high initial pH and low adsorption of polar components onto the rock surface. Formation water with more representative ionic composition gave reduced pH at a level that could favor adsorption of polar organic components giving initial mixed-wet conditions. By injecting a LS brine with low Ca^{2+} concentration, a beneficial pH gradient was observed. Oil recovery tests confirmed a significant improvement in the LS EOR effect.

The effect of Smart Water composition with high salinities was tested.

- Smart Water EOR effects were observed in tertiary mode using a 25 000 ppm NaCl brine. At higher salinities, a lower pH gradient was observed, resulting in a slower response. Previous experiments have confirmed tertiary EOR effects even at 40 000 ppm NaCl brine.

Concluding remarks

- The results obtained in this work, confirm that it is not the salinity of the EOR fluid that is important, but rather the ion composition, more explicitly the Ca^{2+} concentration in the interacting brines.

Protonated plagioclase minerals in contact with high saline FW can induce beneficial initial conditions by creating an acidic environment, favoring adsorption of polar components. These minerals also contribute with increase pH in presence of a LS brine. The temperature effect on Smart Water EOR was studied on outcrop sandstone cores containing plagioclase.

- In the temperature range of 60 to 120 °C, the pH gradient as the FW was displaced by LS brine, was not affected significantly, and oil recovery tests in tertiary mode confirmed similar LS EOR effects of 9 % OOIP.

Injection strategies for implementing Smart Water EOR brines were studied.

- During the LS-Slug injection, a large dependence between EOR response on pH development was observed. A pH increase gave correspondingly increased oil recovery. As soon as the LS-slug was followed by FW injection, the pH dropped and the oil recovery stopped. LS reinjection increased again the pH and the oil recovery was resumed, but at a lower production rate.
- The total EOR potential of the system was retained with a similar incremental oil to a continuous tertiary LS injection. The result confirms the need of a continuous steady state situation to maintain high pH values to maintain appropriate conditions to observe the LS EOR effect.

LS injection in secondary mode was also tested giving overwhelming results.

- Secondary LS injection was dramatically more efficient than tertiary LS injection, giving a fast oil recovery of approximately 56 % of OOIP compared to only 39% OOIP with FW after 1 PV injected. Ultimate recoveries were 17% OOIP higher with LS in secondary mode than tertiary mode.

A tertiary polymer flooding was performed after the LS injection in secondary mode.

- A fast response in oil recovery was observed. The oil recovery increased from 66% OOIP to 86% of OOIP. Wettability alteration during LS injection towards more water-wet conditions, redistributed the oil attached on the mineral surfaces, which was easily mobilized when lowering the mobility ratio.

6.1.3 Carbonates

Smart Water EOR potential for a fractured carbonate reservoir at a low temperature, 65 °C, were evaluated. It is well known that low reservoir temperatures in carbonates can be a limiting factor for observing Smart Water EOR effects. The Smart Water brine compositions were optimized based on core mineralogy. The major conclusions drawn from this work were:

- Smart Water EOR effects were observed in both dolomitic-limestone and pure limestone reservoir cores at 65 °C, confirming that wettability alteration in carbonates also has a potential at reservoir temperatures previously considered to be low.
- The largest EOR effects were observed at the first core restoration. The amount of dissolvable sulfate was higher in the first restoration and could explain the lower EOR effects observed in the second restorations.
- The Smart Water compositions were successfully proposed based on core mineralogy. For limestone, the most effective brine was modified seawater spiked with sulfate, SW0Na4S. In the case of the dolomitic-limestone, 20 times diluted seawater, d₂₀SW was the most effective brine. Switching brines gave no EOR effects. In the case of limestone, this was due to lack of enough Smart Water ions present in the d₂₀SW brine, and for the dolomitic limestone the salinity of the brine SW0Na4S (20 240 ppm) could have been too high.

6.2 Future work

The experimental work provided has contributed to expanding the understanding of the Smart Water EOR processes, but it has also indicated a way forward to improve the knowledge of the topic. Some suggestions are set below.

The pH screening tests performed on sandstone cores summarizes the overall interactions between the surface minerals and the injecting brine. However, the contribution from the individual minerals are needed when Smart Water EOR potential should be evaluated for larger reservoir zones and not only linked to single cores.

The importance of initial wetting has been highlighted through all this work for both sandstones and carbonates. The Smart Water EOR effect is induced by wettability alteration towards more water-wet conditions. To be able to predict Smart Water EOR potentials, it is necessary to be able to estimate the initial wetting of the reservoir. Thus, studies targeting the effect of different minerals on initial wetting would surely contribute to reaching an improved understanding of Smart Water EOR method, which is crucial for further implementation in the field.

The Smart Water EOR processes in dolomites is not fully understood yet. The effect of CaSO_4 minerals, Ca^{2+} and SO_4^{2-} in the LS brine should be further described.

Water-wet reservoirs will normally have large S_{or} due to increased capillary entrapment of oil. By optimizing the ion composition, it may be possible to find a “Smart Water” composition that modifies the reservoir wettability toward less water-wet conditions, inducing further S_{or} reduction.

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Paper I

**Linking low salinity EOR effects in sandstone to pH,
mineral properties and water composition**

Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand, Tor
Austad, Gérald Hamon and Stanislaw Wrobel

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Recovery Conference, April 9-13, 2016, Tulsa, Oklahoma, USA.*

Paper I

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Paper II

Optimizing the low salinity water for EOR effects in sandstone reservoirs - composition vs salinity

Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand and Alireza Rezaeidoust

Paper Tu-SBT2-11, proceedings of the 78th EAGE Conference & Exhibition 2016, 30 May - 2 June 2016, Vienna, Austria.

Paper II

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Paper III

Impact of temperature on the low salinity EOR effect for sandstone cores containing reactive plagioclase

Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand, Tor Austad, Vinh Vuong Tran and Kaia Olsen

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Paper III

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Paper IV

An experimental study of the response time of the low salinity EOR effect during secondary and tertiary low salinity waterflooding

Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand, Tor Austad, Hajar I. Abdullah and Kaia Olsen

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Paper IV

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Paper V

**Enhancing oil recovery from dolomitic reservoirs–
investigation of temperature limitations**

Tina Puntervold, Skule Strand, Iván Darío Piñerez Torrijos, Paul
Hopkins and Tor Austad

Conference manuscript.

Paper V

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Paper VI

Evaluation of the Smart Water EOR potential in a carbonate oil reservoir

Iván D. Piñerez Torrijos, Tina Puntervold, Skule Strand and Tor Austad

Technical report.

Paper VI

Evaluation of the Smart Water EOR potential
in a carbonate oil reservoir

Experimental results

This report is a part of the PhD project funded by Total E&P
and in collaboration with the University of Stavanger:

“Enhanced oil recovery from sandstones and carbonates with Smart Water”

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Evaluation of the “Smart Water” EOR potential in a carbonate oil reservoir

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EXPERIMENTAL WORK

This is a compilation of the most important data registered during the experimentation done in this study. It includes the general screening test performed and all the oil recovery tests carried out.

WORK METHODOLOGY

Experimental work review

The reservoir material consisted of 46 core plug samples, which initially were visually characterized to obtain comparable results in the different experiments. 18 of these samples were subjected to mineral analyses through EDAX and SEM. Different sections were selected to perform 3 surface reactivity tests and spontaneous imbibition and drainage tests with heptane and water to test capillary forces before and after trying to induce a wettability change with seawater at 130° C. Finally, 12 different oil recovery tests by spontaneous imbibition were run to test the response from different brines. Furthermore, different ionic catalysts were tested in chalk cores by spontaneous imbibition tests. A total of 57 individual experiments were carried out using different techniques.

Work performed

- Catalysts for wettability alteration. Experiments using chalk cores and spontaneous imbibition tests were designed to test if different chemical ions could act as catalysts in the water-based wettability alteration by seawater. The background for this work was a paper published by Gupta et al. (Gupta et al. 2011), showing that phosphate was a better catalyst than sulfate in wettability alteration by a so-called seawater brine. Three different possible catalysts were tested; phosphate, borate and sulfate.
- Carbonate reservoir core plug characterization. Physical and chemical characterization of the carbonate reservoir core plugs were performed using different analytical techniques in order to design a specific “Smart Water” composition for different zones of the targeted reservoir; SEM images, EDX analysis, surface reactivity tests, batch tests for sulfate presence, spontaneous imbibition/drainage tests were part of the initial screening tests.
- Oil recovery tests from carbonate reservoir core plugs. Oil recovery tests using spontaneous imbibition were carried out to test the “Smart Water” compositions proposed. The reservoir rocks that were selected for these experiments were core plugs with similar properties to facilitate the interpretation of the results.

METHODS

Core flooding set up

The flooding set up consisted of a computer controlled system, a Gilson HPLC pump, stainless steel piston cells, a Hassler core holder, an oven and a glass burette. The experiments were performed with a confining pressure of 20 bar and with a back pressure of 10 bar.

Core restoration

Mild cleaning

The cleaning procedure was carried out in a Hassler core holder subjected to a confining pressure of 15 bar to assure axial flow of the cleaning fluids through the core. A mild cleaning was performed for each core in order to try to preserve the initial reservoir wetting of the core material (Hopkins et al. 2015). This procedure consists of (1) Kerosene injection until a clear effluent is observed; (2) Heptane injection to displace kerosene; (3) 4 to 5 PV of distilled water injection to displace formation water (FW) and easily dissolvable salts. Each flood was carried out at a rate of 0.1 ml/min. During the cleaning stage and after displacing the heptane with water a qualitative analysis of sulfate presence was carried out. A group of effluent water samples were collected and tested with BaCl_2 for sulfate presence and some samples were analysed for sulfate content by ion chromatography.

Initial water saturation

Initial FW saturation, $S_{wi}=0.1$, was established using the desiccator technique in line with the procedure described by Springer et al. (Springer et al. 2003). Once the target weight of the core was reached, it was left to equilibrate for 72 hours to assure a homogeneous distribution of the initial brine in the core. The core was then placed in a core holder and briefly evacuated prior to oil saturation.

Crude oil saturation

After establishing S_{wi} , the reservoir cores were saturated and flooded with 2 PV of crude oil in each direction at 50°C (due to the high viscosity of the crude oil at room temperature) using a Hassler core holder with a confining pressure of 20 bar. Subsequently the cores were wrapped with teflon tape to avoid unrepresentative adsorption of polar components, that can prevent spontaneous imbibition, on the outer surface of the core. Aging time was two weeks at reservoir temperature 65°C.

The chalk cores were subjected to the same procedure, but the aging temperature was 90°C.

Spontaneous imbibition/drainage

Capillary forces

Spontaneous imbibition tests were carried out at room temperature using standard Amott cells made of glass. A core saturated with heptane was placed in the Amott cell, distilled water was used as imbibition fluid, and the test was carried out for 5 days. The tests were done after the mild cleaning and also after flooding with hot seawater at 130°C. The reason was to verify any induced capillary forces after seawater injection.

The spontaneous drainage experiments were conducted after the second spontaneous imbibition tests using water as the resident fluid and heptane as the imbibing fluid.

Oil saturated cores

The restored core containing crude oil was immersed in formation water in an Amott glass cell and placed into an oven at reservoir temperature (65 °C). The first imbibing brine was formation water, followed by the EOR fluids proposed in the different cases.

Surface reactivity tests

A core was mounted into a Hassler core holder, and a confining pressure of 20 bar and a backpressure of 10 bar were applied throughout the experiment. The brine injection rate was 0.1 ml/min and the test temperature was 25 °C.

The experiment was based on the methodology proposed by Strand et al. (Strand et al. 2006b). Two brines based on the composition of seawater were used to study the surface reactivity of the cores. One brine was prepared containing sulfate and a tracer, thiocyanate ions, (SW 1/2T), and the other brine was prepared without both sulfate and tracer (SW 0T). 3 PV of SW 0T were injected through the core followed by 3 PV of SW 1/2T. Effluent samples were collected and analysed for sulfate and thiocyanate by ion chromatography. Sulfate affinity to the surface is determined by the delay in sulfate concentration relative to the tracer concentration.

ANALYSES

Quantitative sulfate analysis

BaCl₂ was used to detect sulfate presence in the effluent samples during the stage of distilled water in the mild cleaning process. If sulfate is present in the water sample, there will be visible precipitation of BaSO₄ upon addition of BaCl₂.

Brine composition analysis

Effluent brine samples collected during flooding were stored at 4 °C and diluted with DI water, using the trilion™ LH system from Gilson, prior to their analysis. The sample ion concentrations were analyzed with an ion chromatograph DIONEX ICS-3000.

Scanning Electron Microscope (SEM), Energy Dispersive Analysis X-Ray (EDAX).

A ZEISS SUPRA 35VP SEM was used to collect images of the rock surface of a group of targeted samples. 15 kV were used as the energy source of the mentioned device, and the coupled EDAX tool to the SEM was used to determine the elementary composition of the samples studied.

Acid and base number determination

A Mettler Toledo DL55 autotitrator was used to measure the acid number (AN), and base number (BN) of the crude oil samples used in this study.

Viscosity and WAX Precipitation Point Measurement

A Modular Compact Rheometer MCR 302 from Anton Paar® determined the viscosity and the wax precipitation point of the crude oil at different temperatures and strains.

The wax precipitation point for the reservoir crude oil was determined by using two different methods. One of them consisted in plotting the viscosity against temperature, and the software automatically detected the precipitation point. The second method involved a relationship between the storage modulus, the loss modulus and phase angle against the temperature.

MATERIALS

Core plugs

Limestone cores

A preliminary characterization of the cores was performed by visual inspection. The cores were classified according to a score based on how layered they were, presence of fractures, vugs and their general mineral homogeneity. Porosities ranged from 7 to 15 % and permeabilities varied from 0.8 to 26.2 mD. Table 1 contains the main properties of the carbonate reservoir cores used in this study.

Table 1. Main properties of the limestone cores.

Core	Test	Length cm	Diameter cm	Pore volume ml	Φ Porosity %	k Permeability mD	S_{wi} %
10D	<u>Oil recovery and surface reactivity test</u>	7.1	3.8	10.2	13	1.1	10
10E	<u>Oil recovery</u>	7.1	3.8	8.7	11	26.2	10
14B	<u>Oil recovery and surface reactivity test</u>	6.6	3.8	5.1	7	0.9	10
14C	<u>Oil recovery</u>	7.1	3.7	8.4	11	2.5	10
15A	<u>Oil recovery</u>	7.1	3.8	8.0	10	1.0	10
17A	<u>Oil recovery</u>	7.0	3.8	6.7	10	1.0	10
29B	<u>Oil recovery</u>	5.7	3.8	4.4	7	0.8	10
37A	<u>Oil recovery and surface reactivity test</u>	7.0	3.8	8.0	10	0.9	10
37C	<u>Oil recovery</u>	7.1	3.9	12.1	15	15.4	10

Chalk cores

The chalk cores used in this work were taken from the same block of the Stevns Klint quarry. This core material is well known for its high reproducibility (Frykman 2001), and the main core properties are given in Table 2.

Table 2. Main characteristics of the chalk cores

Core	Length cm	Diameter cm	Pore volume ml	Φ Porosity %	K Permeability mD	S_{wi} %
I-A-1	6.5	3.8	31.1	42	2	10
I-A-2	6.5	3.8	31.7	43	1	10
I-A-3	6.5	3.8	32.2	44	1	10

Oil Samples

Two different crude oil samples were used in this study. The crude oil “RES 40” was used in the experiments carried out with the chalk cores and the other crude oil, “Reservoir crude oil” was the reservoir crude oil that was used in with the carbonate reservoir cores. The main properties of both crude oil are described below in Table 3. The wax precipitation point was observed at 35°C.

Table 3. Crude oil properties

Oil Sample	AN	BN	Density	Viscosity
	mg KOH/g oil	mg KOH/g oil	g/cm ³	cP
RES 40	0.50	0.30	0.806	2.6
Reservoir crude oil	0.37	0.27	0.825	4*

** Measured at reservoir temperature (65 °C).

Brines

All salts used to prepare the brines were reagent grade and purchased from Merck laboratories and Sigma Aldrich. Deionized water was used for the brine preparation, obtained from the Milli-Q device Integral-5 from Millipore with T.O.C <5 ppb and a resistivity of 18.2 M Ω cm.

The salts used for the catalyst experiments in chalk were sodium tetraborate decahydrate, and sodium triphosphate dodecahydrate, both were reagent grade and obtained from Sigma Aldrich laboratories.

The formation water composition was obtained from data provided by Total. The formation water (FWR) was prepared without sulfate, but allowing an equilibrium concentration of sulfate from dissolution of anhydrite, CaSO₄. The different “Smart Water” brines used were; (1) SW0Na4S, seawater depleted in sodium chloride and spiked four times with sulfate, (2) d₂₀SW, seawater diluted 20 times, and (3) d₁₀SW, seawater diluted 10 times. All brine compositions are given in the following Tables 4-6.

Table 4. Composition and properties of the brines used in the surface reactivity test

Ion	Units	SW	SW 0T	SW 1/2T
[Na ⁺]	mmol/L	450.1	460.0	427.0
[K ⁺]	mmol/L	10.1	10.0	22.0

[Ca ²⁺]	mmol/L	13.0	13.0	13.0
[Mg ²⁺]	mmol/L	44.5	45.0	45.0
[Cl ⁻]	mmol/L	525.1	58.3	538.0
[SO ₄ ²⁻]	mmol/L	24.0	-	12.0
[SCN ⁻]	mmol/L	-	-	12.0
TDS	mg /L	33360	33390	33390
pH	-	7.6	7.7	7.5
Density	g/cm ³	1.0227	1.0217	1.0222

Table 5. Composition and properties of the brines used in the catalyst test

Ion	Units	VB	SW0NaCl x1Borate	SW0NaCl x1Phosphate	SW0NaCl x1Sulfate
[Na ⁺]	mmol/L	966.0	2.0	74.0	26.0
[K ⁺]	mmol/L	5.0	10.0	10.0	10.0
[Ca ²⁺]	mmol/L	29.0	12.0	13.0	12.0
[Mg ²⁺]	mmol/L	8.0	44.0	45.0	44.0
[Cl ⁻]	mmol/L	1065.0	125.0	125.0	125.0
[SO ₄ ²⁻]	mmol/L	-	-	-	24.0
[PO ₄ ³⁻]	mmol/L	-	-	24.0	-
[B ₄ O ₅ (OH) ₄] ²⁻	mmol/L	-	24.0	-	-
TDS	mg /L	62830	11431	10536	10011
pH	-	7.3	8.7	-	8.0
Density	g/cm ³	1.0475	1.0079	-	1.0065

Table 6. Composition and properties of the brines used in the oil recovery tests

Ion	Units	FWR	SW0Na4S	d ₂₀ SW	d ₁₀ SW
[Na ⁺]	mmol/L	1516.0	194.0	22.5	45.0
[K ⁺]	mmol/L	89.0	10.0	0.5	1.0
[Ca ²⁺]	mmol/L	305.0	12.0	0.6	1.2
[Mg ²⁺]	mmol/L	90.0	44.0	2.2	4.4
[Cl ⁻]	mmol/L	2382.0	125.0	26.2	52.4
[SO ₄ ²⁻]	mmol/L	0	96.0	1.2	2.4
[SCN ⁻]	mmol/L	-	-	-	-
[HCO ₃ ⁻]		13.0	-	-	-
TDS	mg /L	138058	20240	1668	3336
pH	-	6.0	8.0	7.0	7.0
Density	g/cm ³	1.0941	1.0154	0.9991	1.0001

Surfactant C₁₂TAB (dodecyl trimethyl ammonium bromide)

In some experiments, after spontaneous imbibition with Smart Water, 1 wt% surfactant C₁₂TAB was added to the Smart Water brines. This surfactant is able to change wetting properties of carbonates without decreasing substantially the IFT (Strand 2005). The surfactant was added to observe if it was possible to improve the water wetness even further after using Smart Water.

RESULTS

Investigating different catalysts for wettability alteration in chalk by seawater

It has been documented by Austad and co-workers that sulfate is the catalyst for wettability alteration by seawater in carbonate cores (Strand et al. 2006a, Zhang et al. 2007). Recently however, according to Gupta et al. (Gupta et al. 2011), the oil production from limestone cores was enhanced using other catalysts than sulfate in seawater-based brines. Therefore, an attempt was made to test whether borate or phosphate were more efficient catalysts than sulfate in seawater-based brines, brine compositions are given in Table 5. Sulfate, phosphate or borate as catalysts had a concentration of 24 mmol/l in their respective brines.

Oil recovery tests by spontaneous imbibition were performed at 90°C using the chalk cores I-A-1 and I-A-2, Fig. 1. The pressure of the system was 10 bar, initial water saturation was $S_{wi} = 10\%$, the crude oil used was RES40 having an AN of 0.5 mgKOH/g and BN of 0.3 mgKOH/g, the oil viscosity was 2,6 cP, and the aging time was 2 weeks at 90°C.

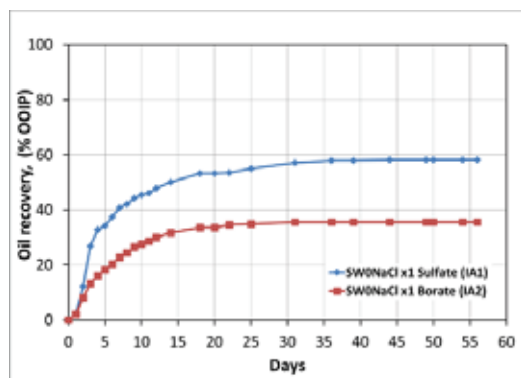


Figure 1. Oil recovery by spontaneous imbibition at 90 °C. The chalk cores I-A-1 and I-A-2 were imbibed with seawater containing 24 mM sulfate or borate as catalysts.

In Fig. 1 only sulfate or borate were used as catalysts. Phosphate as catalyst was unsuccessful due to immediate precipitation upon mixing with the seawater-based brine. Spontaneous imbibition with phosphate as catalyst was not possible to perform. No precipitation was observed with sulfate or borate as catalysts.

According to the results presented in Fig. 1, the system with borate as a catalyst reached the production plateau after 22 days of production, at 35 % OOIP. The system containing sulfate as catalyst reached the production plateau after 36 days of production, at 58% OOIP. The spontaneous imbibition results showed that sulfate was the better catalyst by improving the oil recovery by an extra 23 % OOIP compared to that by borate. It is worth noting that the production during the first ten days of the experiment was both faster and larger for the sulfate system, than for the borate system.

Investigating the Smart Water EOR potential for a reservoir carbonate field

Visual characterization of the core material

A visual inspection of the cores were performed, and the cores were graded depending on different factors that aimed to evaluate their degree of homogeneity, these factors included visible layers, vugs, fractures and apparent homogeneity. The evaluation of the cores is summarized in Table 7, where a final score has been given for each core. Cores with an overall score of 5, 6 and 7 have been graded as acceptable, good and excellent candidates, respectively, for the experiments evaluating Smart Water EOR potential

Table 7. Visual characterization of core plugs

Sample	Code	Layers	Fractures	Vugs	Homogeneity	Overall score	Comment
1	1	Medium	High	High	Low	2	
2	2	High	Medium	High	Low	2	
3	3	Low	None	Very-high	Low	2	
4	4	None	None	None	Very-High	7	Excellent candidate
5	5	Low	Low	High	Medium	4	
6	6	Medium	Medium	High	Low	2	
7	7	Medium	Low	Medium	Medium-Low	3	
8	9	Low	None	None	High	6	Good candidate
9	10-A	None	None	None	Low	2	
10	10-B	None	Low	None	Medium-High	5	Acceptable candidate
11	10-C	None	None	None	High	6	Good candidate
12	10-D	None	None	None	Very-High	7	Excellent candidate
13	10-E	None	None	None	Very-High	7	Excellent candidate
14	11	Highly	Low	Medium	Medium	4	
15	12	Medium	None	Low	Medium	4	
16	13	High	Medium	Medium	Low	2	
17	14-A	Low	None	Low	High	6	Good candidate
18	14-B	Low	None	Low	High	6	Good candidate
19	14-C	Medium	None	None	High	6	Good candidate
20	15-A	Medium	Low	High	Low	2	
21	15-B	Very Low	None	Medium	Medium	4	
22	15-C	Medium	None	High	Medium-Low	3	
23	15-D	Low	None	High	Low	2	
24	16	Low	None	None	High	6	Good candidate
25	17A	Very-Low	None	None	High	6	Good candidate
26	17B	Medium	None	None	High	6	Good candidate
27	18	Low	High	High	Low	2	
28	19	Low	None	Low	Medium-high	5	Acceptable candidate
29	20	High	High	None	Low	2	
30	24	Low	None	Low	Medium-High	5	Acceptable candidate
31	25-A	Medium	None	None	Medium-High	5	Acceptable candidate
32	25-B	Medium	None	None	Medium-High	5	Acceptable candidate
33	26	N/A	High	N/A	N/A		
34	27	Low	Medium	Medium	Medium	4	
35	28	Medium	None	Very High	Low	2	
36	29-A	None	High	Medium	Low	2	
37	29-B	Low	Medium	Low	Medium	4	
38	30	High	High	High	Very-low	1	
39	31	None	None	Low	Low	2	
40	33	Medium	High	High	Very-low	1	
41	34	None	Medium	High	Low	2	
42	35	Low	none	low	Medium	4	
43	36	Low	None	Very Low	Medium-High	5	Acceptable candidate
44	37-A	Low	None	Low	Medium	4	
45	37-B	Low	None	Low	Medium-High	5	Acceptable candidate
46	37-C	Medium	None	Low	Medium-High	5	Acceptable candidate

Sulfate content during core cleaning

All cores underwent a mild cleaning process prior to the actual experiments. The mild core cleaning process consisted of kerosene injection followed by heptane injection and lastly by distilled water injection. This procedure was followed to avoid drastically changing the original wettability of the reservoir cores, but instead trying to preserve it. During the kerosene flood, any crude oil left in the core dyed the first effluent samples of all cores, Fig. 2. All cores showed a dark-colored effluent when flooded with kerosene, which is a clear indication of crude oil presence in the core samples.



Figure 2. A sample of the kerosene effluent colored by the presence of crude oil in core 37C (left) and a clear heptane effluent after completing the kerosene injection in core 37C (right).

During the distilled water injection, a minimum of 3 PV of effluent was collected. Several effluent samples were collected, and any presence of dissolved sulfate was verified by addition of BaCl_2 . Dissolved sulfate was verified in all cores during the first cleaning process. As the distilled water injection continued, the effluent samples showed lower response upon BaCl_2 addition, indicating a gradual reduction of sulfate content in the effluent.

All cores were flooded a minimum of 3 PV with distilled water. However, in the first three experiments a maximum of 10 PVs were flooded because the objective was to reduce the dissolvable anhydrite concentration. As the presence of sulfate was persistent in all cores after several pore volumes (~10 PV), it was decided to inject, if possible, a maximum of 5 PV of distilled water not to significantly alter the properties of the core. The next figures, Figs. 3-6, show the evolution of sulfate concentration during distilled water injection, which was part of the cleaning process.

Sulfate content of core 10E

During the first mild cleaning of the core 10E, dissolved sulfate was confirmed by the batch test with BaCl_2 , however not quantified. In the second mild cleaning of the core, prior to the second restoration, the sulfate content during distilled water injection was monitored, Fig. 3. The initial concentration of sulfate was 6 mM, and it steadily declined for 3PV until becoming stable at around 1.8 mM up to 5 PV, after which another decline was observed for the next 3 PV, with a concentration finally ending up at 1 mM or sulfate after a total of 8 PV of distilled water injected.

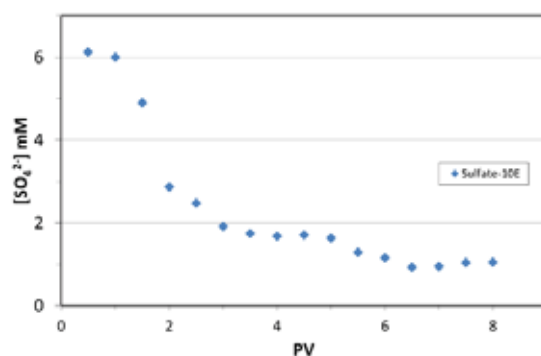


Figure 3. Sulfate concentration during 2nd mild cleaning prior to the 2nd core restoration, core 10E.

Sulfate content of core 14C

During the first mild cleaning of the core 14C, dissolved sulfate was confirmed by the batch test with BaCl₂, however not quantified. In the second mild cleaning of the core, prior to the second restoration, the sulfate content during distilled water injection was monitored, Fig. 4. In core 14-C the initial concentration of sulfate was 11 mM. After flooding 4 PV of distilled water the sulfate concentration reached 2 mM. At this point, the core was shut in overnight and when distilled water injection continued, a peak of 4mM in the concentration was seen, followed by a gradual drop in concentration until becoming stable at 1.2 mM at 8 PV injection.

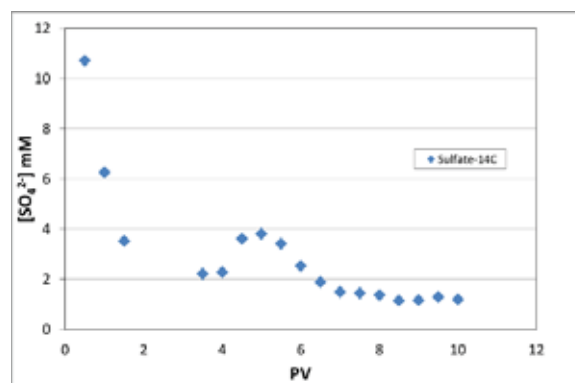


Figure 4. Sulfate concentration during 2nd mild cleaning prior to the 2nd core restoration, core 14C.

Sulfate content of core 37C

During the first mild cleaning of the core 37C, dissolved sulfate was confirmed by the batch test with BaCl₂, however not quantified. In the second mild cleaning of the core, prior to the second restoration, the sulfate content during distilled water injection was monitored, Fig. 5. For the core 37C the initial concentration of sulfate was 1.5 mM. After flooding 6 PV of distilled water the concentration reached 1 mM, and at this point the core was shut in overnight, and when distilled water injection continued, a peak of 2 mM in the sulfate concentration was

seen, followed by a gradual drop in concentration until reaching again 1 mM at 10 PV of distilled water injection.

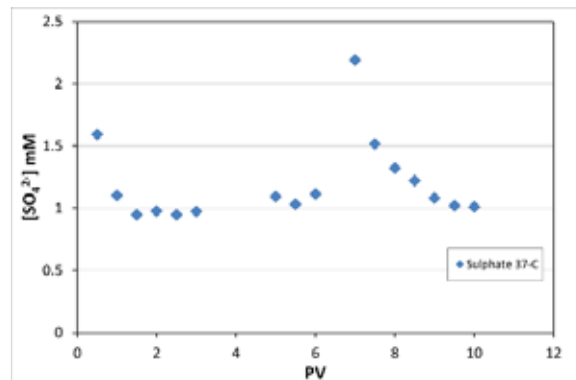


Figure 5. Sulfate concentration during 2nd mild cleaning prior to the 2nd core restoration, core 37C.

Sulfate content of cores 29A and 29B

For the core 29A in Fig. 6, the initial concentration of sulfate, during the 1st mild cleaning, was 2.2 mM. After flooding 5 PV of distilled water the sulfate concentration was lowered to 0.3 mM. The core 29B in Fig. 6 had an initial concentration of sulfate of 0.6 mM, and after flooding 5 PV of distilled water the concentration was lowered to 0.01 mM. Only core 29 B was afterwards used in an oil recovery test.

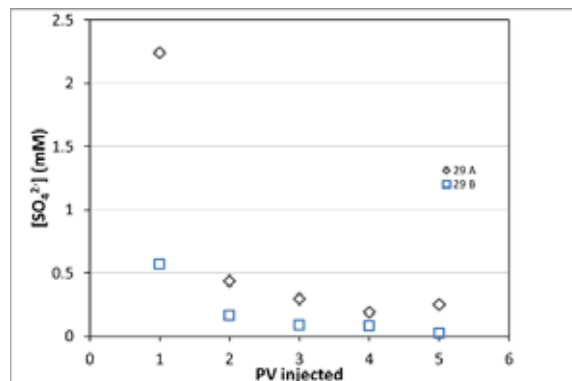


Figure 6. Sulfate concentration during 1st mild cleaning prior to the 1st restoration, cores 29A and 29B.

Towards the end of the cleaning stage with distilled water, a final water sample was collected and analyzed prior to the restoration for an oil recovery test, Table 8. The sulfate content of the final effluent sample is assumed to be close to the true value of sulfate content inside the core at the time of core restoration.

Table 8. Sulfate concentration prior to every core restoration.

Core Plug	SO ₄ ²⁻ [mmol/l]
10D-R1	< 0.10
10E-R1	> 6.00
10E-R2	1.04
14B-R1	0.00
14C-R1	>1.2
14C-R2	1.2
15A-R1	0.00
17A-R1	0.00
29B-R1	0.02
37A-R1	0.00
37C-R1	>1.0
37C-R2	1.0

Initial wetting and capillary forces

The cores were tested for capillary forces and initial wetting by performing a spontaneous imbibition test with a 100% heptane-saturated core imbibed with distilled water. After this, the cores were flooded with hot sea water (130 °C) (Austad et al. 2008) to try to improve the wetting. Subsequently, the spontaneous imbibition test with a 100% heptane-saturated core was repeated once again together with a spontaneous drainage test. The latter test was done by saturating the core with distilled water and using heptane as imbibing fluid. Both spontaneous imbibition and drainage tests were carried out at room temperature (25°C), Figs. 7-9.

The results showed, in general, no initial spontaneous imbibition in any of the cores. After flooding with seawater at 130 °C, no significant improvements in capillary forces were observed. The spontaneous drainage tests after flooding with seawater did not show any production. As shown in Fig. 7, core 10 D did not imbibe any fluid, neither distilled water nor heptane. Another example is the core 37 A, which after flooding with hot seawater produced only 2% of the heptane in place, Fig. 8. The core 14 B behaved similarly, it did not imbibe any water before the treatment with seawater, and after the treatment, water production was approximately 2% of OOIP, Fig. 9. The fact that oil production commenced after 3 days can indicate that gravity forces rather than improved capillary forces could account for the small production observed.

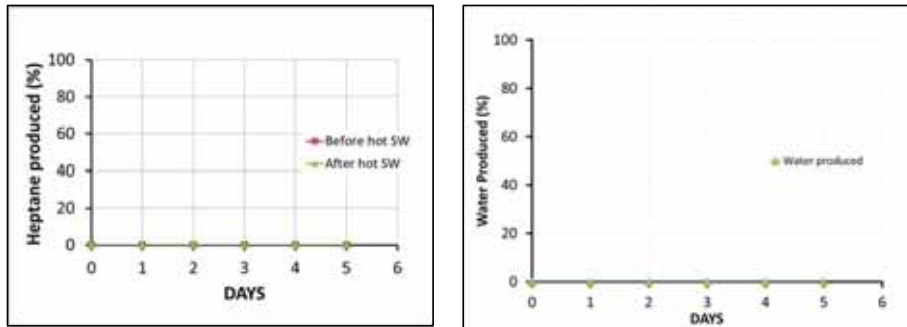


Figure 7. Core 10D. Left: Spontaneous imbibition test at ambient temperature before and after hot seawater flooding. Right: Spontaneous drainage test at ambient temperature after hot seawater flooding.

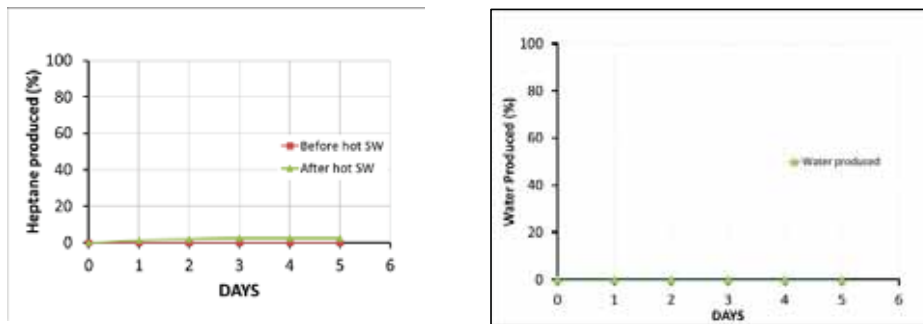


Figure 8. Core 37A. Left: Spontaneous imbibition test at ambient temperature before and after hot seawater flooding. Right: Spontaneous drainage test at ambient temperature after hot seawater flooding.

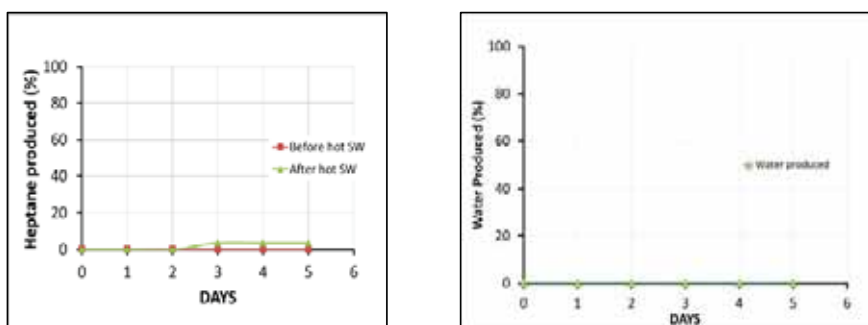


Figure 9. Core 14B. Left: Spontaneous imbibition test at ambient temperature before and after hot seawater flooding. Right: Spontaneous drainage test at ambient temperature after hot seawater flooding.

Surface reactivity tests - does sulfate have an affinity for the core surface?

After the spontaneous imbibition tests involving heptane, a surface reactivity test was performed. It was expected to observe low concentrations of sulfate after the initial flooding with seawater without sulfate (SWOT), however in some cases, when the sulfate concentrations were analysed, they were too high to quantify a chromatographic separation of the non-adsorbing tracer, thiocyanate, and the sulfate ions. Two examples are described below.

In the core 10 D right after flooding seawater at 130°C a new tracer test was carried out and the levels were slightly higher, probably due to the contribution of sulfate present during the hot seawater flooding. It was not possible to correctly quantify the area between the concentration curves Fig. 10. Note that the sulfate concentration is due to both dissolution of a mineral containing sulfate and contribution from the brine containing sulfate. If the sulfate has an affinity to the rock surface it may adsorb during the hot seawater flood, and later desorb during the surface reactivity test procedure, giving incorrect sulfate concentrations, as in the second reactivity test observed in Fig. 10.

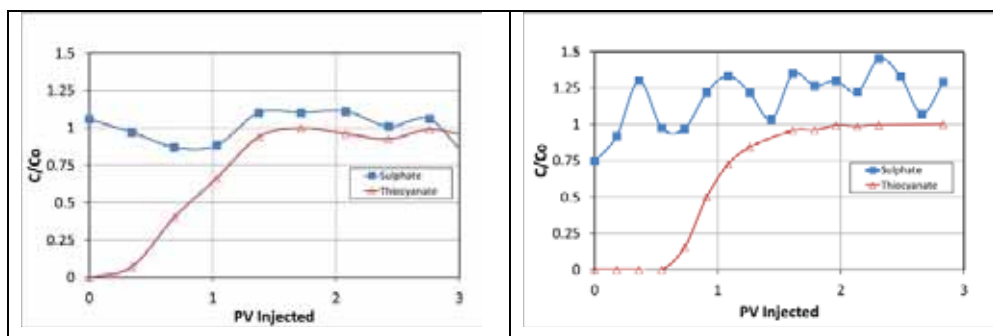


Figure 10. Surface reactivity test for core 10D performed at ambient temperature. Left: before hot seawater flooding. Right: after hot seawater flooding.

However, as the thiocyanate ion does not interact with the limestone surface, it is possible to use the shape of the tracer curve to get information about the pore distribution inside the core. A tracer curve profile, such as that in Fig. 10 (right), shows that at approximately 2 PV injected the core has been flooded quite homogeneously, and that there is an even distribution of pores across the core.

In the tests carried out in the core 14 B, Fig. 11, it was possible to observe a minimal chromatographic separation between the sulfate and the thiocyanate curves, but the initial sulfate concentration was around 1.5 mmol/l. After the flooding with seawater at 130°C a new tracer test was carried out and the sulfate concentration was once again around 1.5 mmol/l. There was no net change in the area between the curves after the hot seawater flood.

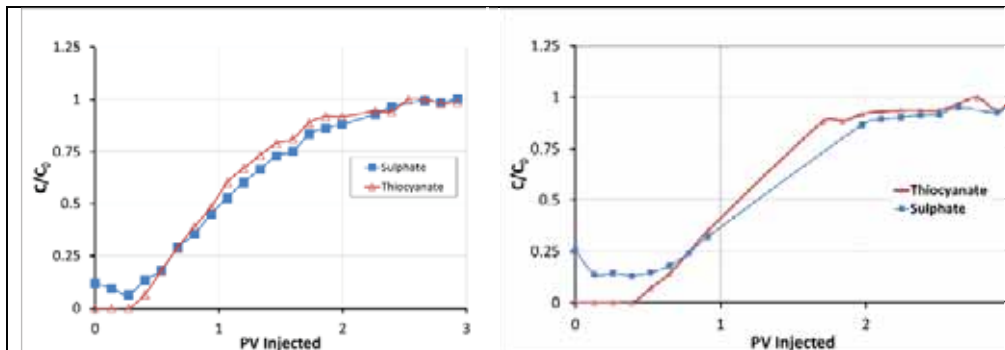


Figure 11. Surface reactivity test for core 14B performed at ambient temperature. Left: before hot seawater flooding. Right: after hot seawater flooding.

During the first test in Fig. 11, 2.5 PV were required to displace completely the resident brine (SWOT), with the brine containing the tracer (SW½T). In the second surface reactivity test the full displacement seemed to be achieved after 2.5 PV injected as well.

An overall lower initial concentration of sulfate in the effluent allowed the observation of a minimal separation of the tracer and the sulfate curves in both cases; both before and after hot seawater flooding. However, there was no significant difference in the separation area between the sulfate and thiocyanate curves.

A lower content of sulfate in core 37A had a positive impact on the resolution of the results in Fig. 12. However, regardless of the initial sulfate concentration in this test (1.5 mmol/l), there was no noticeable change in the area of separation and no significant change in the wetting was observed before and after hot seawater flooding. These results confirm the spontaneous imbibition results showing that hot seawater flooding was not able to improve wetting conditions in the tested core plugs.

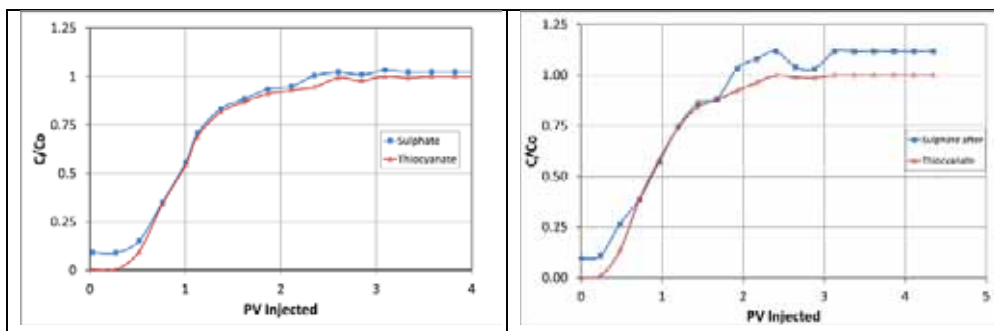


Figure 12. Surface reactivity test for core 37A performed at ambient temperature. Left: before hot seawater flooding. Right: after hot seawater flooding.

Core mineralogy and pore structure

Elemental chemical analysis

A full area scan of the top surface of a small piece of each core sample was performed in order to obtain an average chemical composition of the sample. For all the samples tested, it was

found that the main mineralogy was limestone, however some cores were characterized as dolomitic-limestone (Group 10). The complete list of core material tested and the analyses results are presented both in Table 9 and in Fig. 13.

Table 9. Elemental analysis made with EDAX

Core plug	Ca (At %)	Mg (At %)	S (At %)	Si (At %)	Al (At %)	Type
1	96.27	2.09	0.57	0.62	0.45	Limestone
2	96.05	0.95	0.52	1.18	1.30	Limestone
4	95.92	1.95	0.89	0.69	0.55	Limestone
10 D	56.00	35.43	2.24	5.19	1.14	Dolomitic-limestone
10 E	51.65	41.08	1.51	1.79	3.97	Dolomitic-limestone
11	97.78	1.19	0.36	0.34	0.33	Limestone
13	97.03	1.73	0.52	0.25	0.47	Limestone
14B	91.43	2.03	0.00	5.67	0.87	Limestone
14 C	90.48	1.50	1.24	1.32	5.46	Limestone
15 D	95.80	1.15	0.40	1.47	1.18	Limestone
16	95.80	1.15	0.40	1.47	1.18	Limestone
17 A	96.99	1.05	0.35	0.58	1.03	Limestone
25	94.17	0.54	0.51	0.98	3.80	Limestone
26	94.37	1.67	0.67	0.91	2.38	Limestone
29 B	86.41	0.69	1.34	5.02	6.54	Limestone
31	96.86	0.00	0.12	1.27	1.75	Limestone
34	94.17	0.54	0.51	0.98	3.80	Limestone
37C	90.73	3.21	1.57	2.03	2.46	Limestone

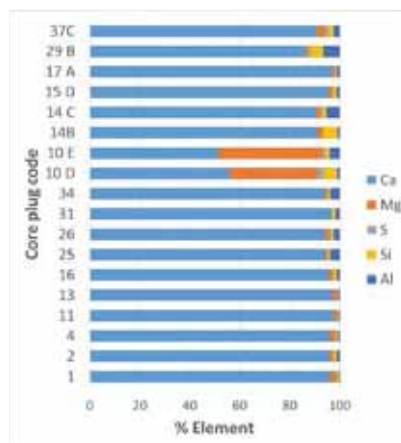


Figure 13. Elemental distribution derived from the mineralogical analysis by EDAX.

SEM and pore structure

The pore structure of several rock samples was examined using a Scanning Electron Microscope. In the dolomitic limestone samples analyzed, regular grain sizes were observed in different areas, but most of the scanned areas presented homogeneous shapes of the crystals with predominant grains larger than 10 μm .

In the limestone cores a higher degree of heterogeneity of grain sizes was observed. There were areas with mixed grain sizes, others with regular sizes and others with larger crystals. Example images are presented below in Figs. 14-17.

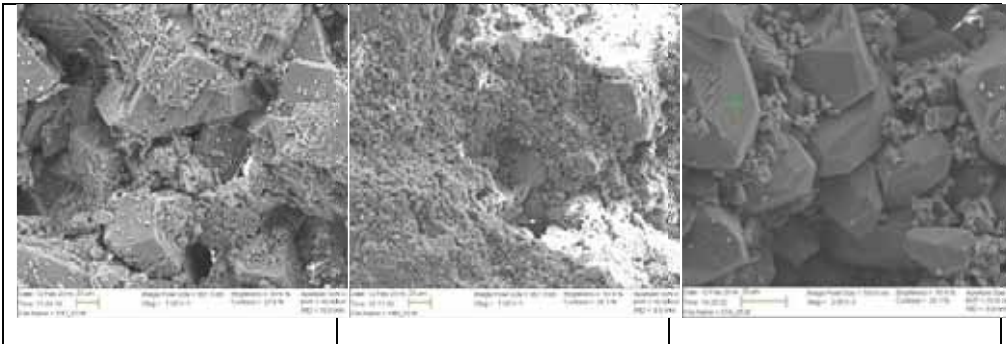


Figure 14. SEM images showing grains and pore conformations in; core 10D dolomitic-limestone (left), core 14B limestone (center), and in core 37A limestone (right).

Presence of anhydrite was confirmed in the SEM picture in Fig. 15.

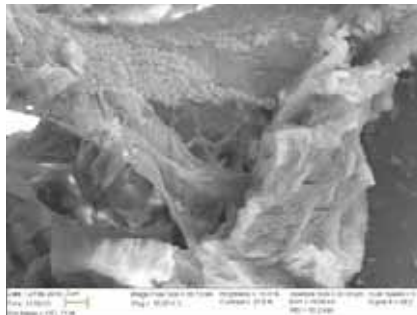


Figure 15. Mineral structure containing anhydrite in core 10D dolomitic - limestone.

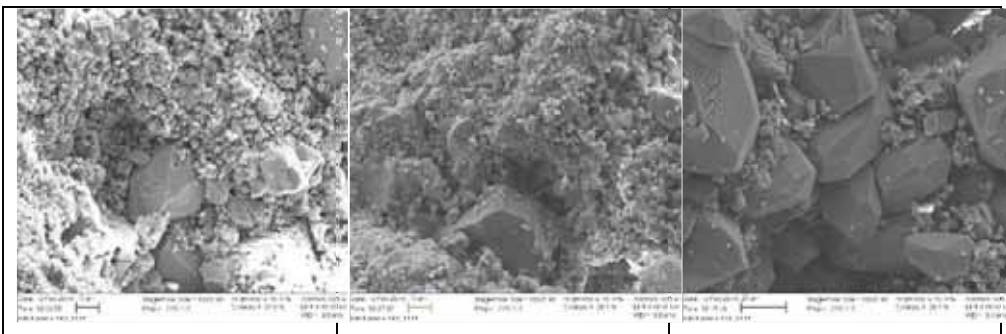


Figure 16. Mixed grain sizes in the limestone cores 14B (left and center), and 37 A (right).

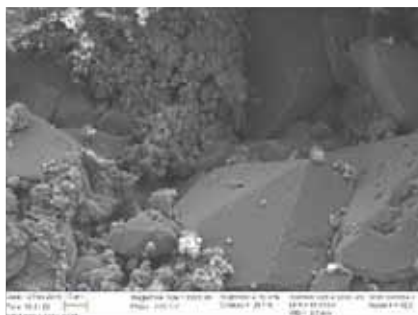


Figure 17. Mixed grain sizes in limestone core 37 A.

Oil recovery tests

After matching all the data collected from the screening tests, customized Smart Water compositions for the different group of cores were designed; the mineralogy and presence of dissolvable sulfate were important factors to evaluate in the process.

Dolomitic limestone

In some in-house experiments made in the past with dolomitic cores that were included in the work of Romanuka (Romanuka 2012), Smart Water compositions of 20 times and 10 times diluted seawater were used.

Core 10E, a dolomitic limestone, was used to test if diluted seawater could promote wettability alteration in this rock type and improve recovery beyond that of FW. Oil recovery tests by spontaneous imbibition at test temperature 65 °C was performed using successively FWR-d₂₀SW-d₂₀SW1%C₁₂TAB, Fig. 18a and FWR-d₁₀SW-d₁₀SW1%C₁₂TAB, Fig. 18b, as imbibing fluids. The EOR effect using d₂₀SW as imbibing fluid in the first restoration was positive, Fig. 18a. Oil recovery by FWR was about 6% OOIP, but when Smart Water was introduced, in this case d₂₀SW, an incremental recovery of 10% OOIP was observed. When oil recovery plateau was reached, 1 wt% of the cationic surfactant C₁₂TAB was added to the Smart Water, and an additional 8% OOIP was produced, showing that there was room for further improving the wettability after using Smart Water.

Core 10E was restored, and another oil recovery test by spontaneous imbibition at 65 °C was performed, this time with d₁₀SW as Smart Water composition, Fig. 18b. Oil recovery by FWR was similar to that of the first restoration, 4% OOIP, however the 10 times diluted seawater, d₁₀SW only gave a 2.5% OOIP increment in oil recovery. Whether this difference in response is due to the Smart Water composition, to the previous exposure to the surfactant, or due to a difference in initial wetting upon restoration, is uncertain. It is well known that reusing a carbonate core can be difficult, because a reproducible wetting is hard to achieve.

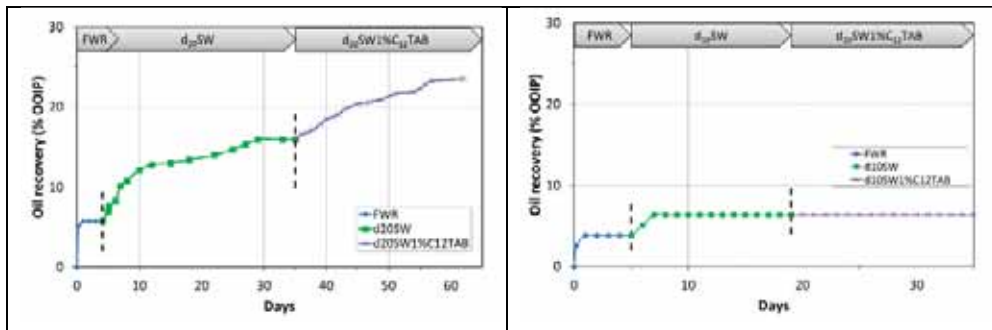


Figure 18. Oil recovery by spontaneous imbibition in core 10E at 65°C. a) First restoration (left), b) second restoration (right).

In a similar core with the same dolomitic-limestone mineralogy, core 10 D, a typical Smart Water composition used for limestone cores was tested to see if wettability alteration and increased oil recovery could be achieved. Oil recovery by spontaneous imbibition at 65 °C using SW0Na4S as Smart Water was performed, and the recovery results are presented in Fig. 19. Oil recovery by FWR was similar to those of the previous two experiments in Fig. 18, 7 % OOIP. However, when SW0Na4S was used as imbibing fluid, there was no extra oil produced, and this brine with its specific composition was not able to cause wettability alteration in this dolomitic limestone material.

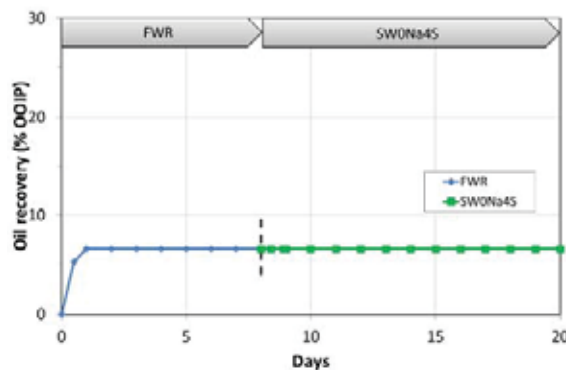


Figure 19. Oil recovery by spontaneous imbibition at 65°C in core 10D, first restoration.

Limestone

In the material identified as limestone a different approach was made based on the mineralogy. The best Smart Water composition known for limestone is seawater depleted in sodium chloride spiked with four times sulfate (SW0Na4S). Oil recovery tests by spontaneous imbibition at 65 °C was performed in a number of limestone cores and the results are presented in Figs 20-22. All results in Figs. 20-22 are from the first restoration of each core.

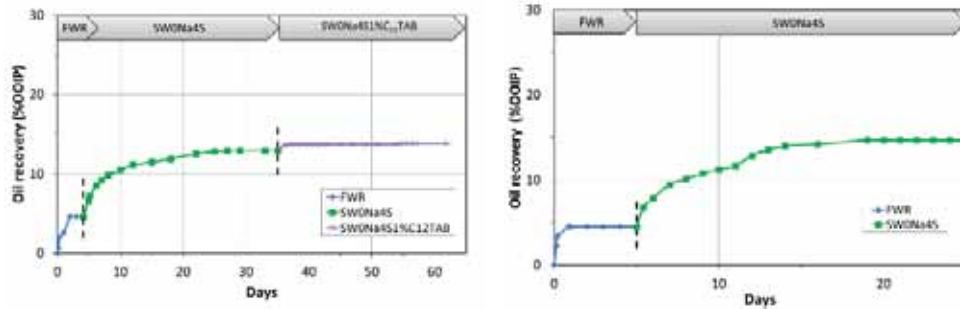


Figure 20. Oil recovery tests by spontaneous imbibition of first restoration limestone cores at 65 °C. a) core 14C (left) and b) core 29 B (right).

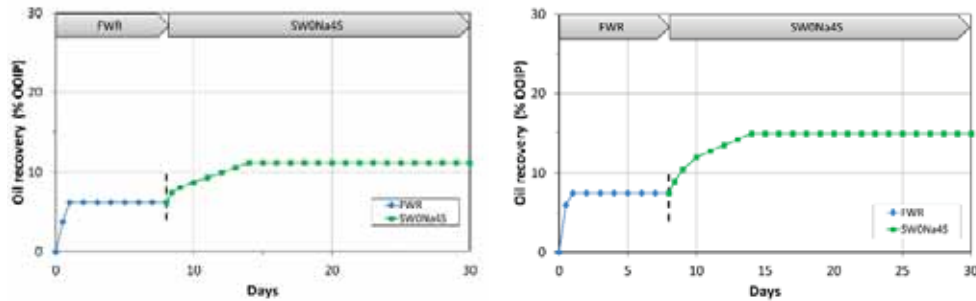


Figure 21. Oil recovery tests by spontaneous imbibition of first restoration limestone cores at 65 °C. a) core 15A (left) and b) core 17A (right).

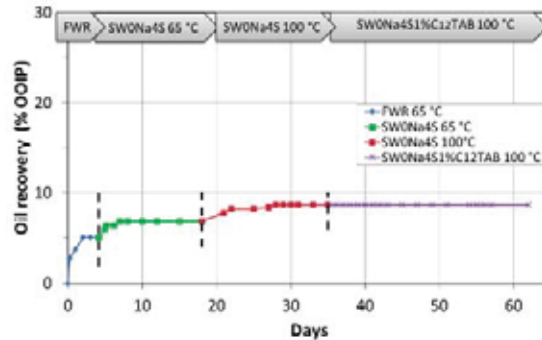


Figure 22. Spontaneous imbibition tests in limestone core 37C, first restoration at 65 °C.

All cores responded positively to the Smart Water brine SW0Na4S. However, there was a spread in the incremental recovery between 1.8 to 10.4 % OOIP. By regarding core 37C in Fig. 22 as a possible outlier, then incremental recovery was between 5-10 % OOIP. The variability in oil recovery response between the cores could be attributed to the heterogeneity present in the core samples, if compared one to another. There was a clear indication that the oil recovery response was higher in the first restoration of the core and decreased in the second restoration, Fig. 23. This trend was also observed for the dolomitic limestone material in Fig. 18, but in this case the imbibing fluids were not the same.

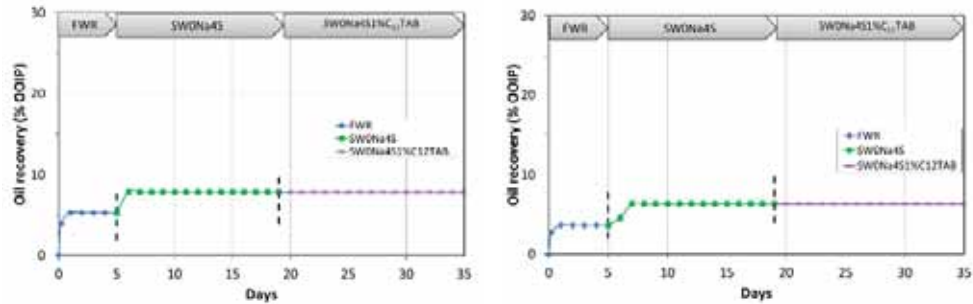


Figure 23. Spontaneous imbibition tests in limestone core 14C (left) and 37C (right), second restoration at 65 °C.

Given the low EOR response by Smart Water in core 37C in Fig. 22, this core was chosen to test the effect of an increment in temperature. The oil recovery by FWR was 5 % OOIP after 3 days of imbibition. By switching to a Smart Water SW0Na4S an incremental oil production of around 2% OOIP was observed after an extra 3 days of imbibition. At this point the temperature was raised to 100 °C and an extra 2 % OOIP was produced due to thermal expansion. Finally, there was no additional production when introducing the cationic surfactant C₁₂TAB to the Smart Water brine 100°C.

An important observation was that the surfactant C₁₂TAB when mixed with the brine SW0Na4S did not change the wetting significantly, as observed in Figs. 22 and 23. This observation could be due to a screening effect caused by the amount of sulfate on the cationic surfactant. It is not known whether the large amount of sulfate influences the ability of the surfactant to work as a wettability modifier. The sulfate concentration in this case was 80 times higher than that in 20 times diluted seawater, where an effect was observed.

Finally, a typical Smart Water brine composition used for dolomitic-limestones cores, d₂₀SW, was tested in the limestone cores 14 B and 37 A, but no EOR effects with this brine was observed, Fig. 24. It should be noted that these experiments were performed on second restoration cores, due to the limited amount of preserved cores, which could give lower recoveries compared to those in a first restoration, Figs. 20 and 22. Nevertheless, there was no extra oil produced with the diluted seawater brine in these cores, Fig. 24, no wettability alteration had taken place.

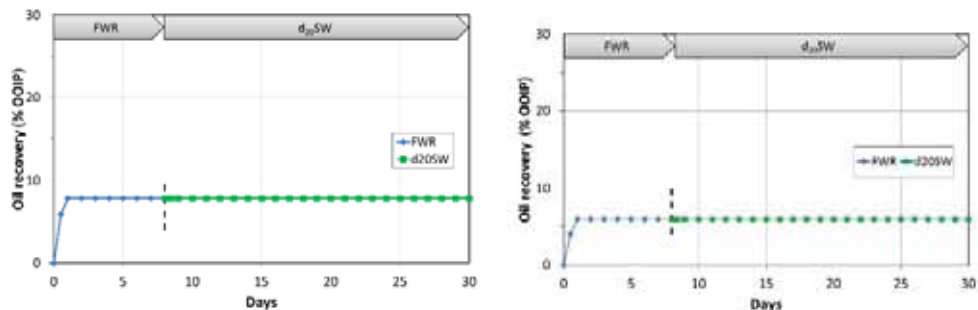


Figure 24. Spontaneous imbibition tests in limestone core 14B (left) and 37A (right), second restoration at 65 °C.

SUMMARY OF RESULTS

In general, Smart Water EOR effects were observed at the unfavourably low test temperature of 65 °C, but with somewhat varying results. The Smart Water compositions were targeted to match the mineralogy of the cores; limestone or dolomitic limestone. In some experiments, the Smart Water brine compositions and the core mineralogies were interchanged on purpose to observe the response. These interchanged core experiments are typed in **bold** in Table 10.

The most successful oil recovery experiments were those performed on first restoration cores, results illustrated in Fig. 25.

Enhanced oil recovery results with Smart Water varied from 1.8-10.1 %OOIP, however 5/6 cores gave a response between 5-10 %OOIP extra oil.

Much poorer results were observed in the second restoration for both dolomitic-limestone and limestone cores. Both first and second restoration results are illustrated in Fig. 26.

There was no extra oil recovered by using unfavourable injection brines in both core materials. All oil recovery results are listed in Table 10.

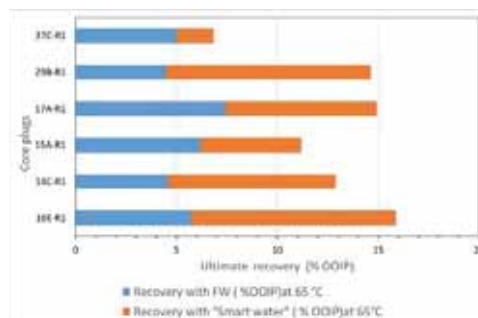


Figure 25. Oil recovery tests performed on only first restoration cores, including both dolomitic limestone and limestone cores.

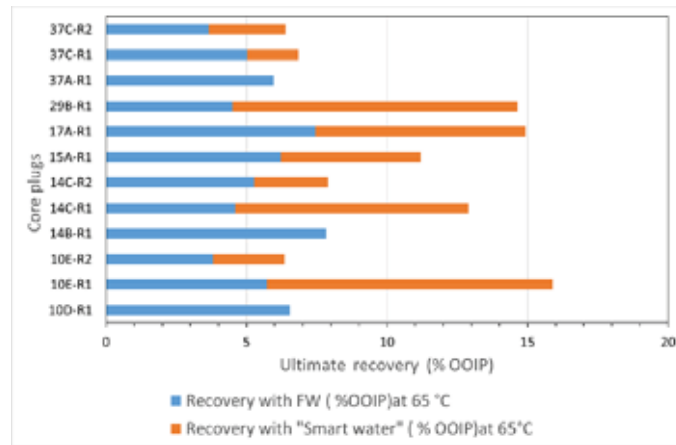


Figure 26. Oil recovery tests by spontaneous imbibition performed on both first and second restoration cores.

Table 10. Summary of all oil recovery tests performed

Core Plug	Mineralogy (EDAX)	Smart water at 65 °C	Recovery with FW (%OOIP) at 65 °C	Incremental recovery with "Smart water" (% OOIP) at 65°C	Ultimate recovery (% OOIP)
10D-R1	Dolomitic limestone	SW0Na4S	6.55	0.00	6.55
10E-R1	Dolomitic limestone	d ₂₀ SW	5.72	10.17	15.89
10E-R2	Dolomitic limestone	d ₁₀ SW	3.81	2.54	6.35
14B-R1	Limestone	d₂₀SW	7.84	0.00	7.84
14C-R1	Limestone	SW0Na4S	4.60	8.29	12.89
14C-R2	Limestone	SW0Na4S	5.27	2.63	7.90
15A-R1	Limestone	SW0Na4S	6.22	4.98	11.20
17A-R1	Limestone	SW0Na4S	7.46	7.46	14.92
29B-R1	Limestone	SW0Na4S	4.50	10.14	14.64
37A-R1	Limestone	d₂₀SW	5.96	0.00	5.96
37C-R1	Limestone	SW0Na4S	5.02	1.83	6.85
37C-R2	Limestone	SW0Na4S	3.65	2.74	6.39

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