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Evaluation of using Smart Water to enhance oil recovery from Norwegian Continental Shelf sandstone reservoirs.

by

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ABSTRACT

Recently, the scale of studies on smart water – one of EOR method - has increased. From decades, water flooding is one of the most used methods to increase oil recovery. However, more effective in sandstone reservoirs is injecting low salinity brine. Due to changing wettability, improved oil mobility in pores can be reached. The studies show, that the significant increase of oil recovery might be achieved.

Main objective of the thesis is to answer the question: Can "smart water" be used to enhance oil recovery from targeted fields? The thesis contains theoretical part and practical solution proposals for some of sandstone fields. In order to evaluate possibility of using smart water method on these fields, decision making scheme is presented. The initial wettability of the reservoir rocks will be estimated. Data from these fields will be presented and discussed in term of low-salinity waterflooding.

Field P-1 was determined as a good candidate for low-salinity waterflooding, due to its mixed-wet initial state. However to improve oil recovery, the alternation of wettability has to occur. Main obstacle, that may negatively affect "smart water" EOR method is high reservoir temperature.

Lack of needed data from field V-1 induces large uncertainty in evaluation process. The initial wettability of the field V-1 has been established as mixed-wet, but this conclusion requires some assumptions. More accurate data could allow to determine if the field may be used for "smart water" flooding.

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NOMENCLATURE

AN	acid number
BN	base number
CEC	cation exchange capacity
E	displacement efficiency
E_A	areal displacement efficiency
E_D	microscopic displacement efficiency
E_I	vertical displacement efficiency
E_V	macroscopic displacement efficiency
EDL	electrical double layer
EOR	enhanced oil recovery
FW	formation water
φ	total porosity
HS	high salinity
IFT	interfacial tension
IOR	improved oil recovery
θ	contact angle
k	permeability
k_{ro}	relative oil permeability
k_{rw}	relative water permeability
μ_o	dynamic oil viscosity
μ_w	dynamic water viscosity
LS	low salinity
MIE	multi-component ionic exchange
NCS	Norwegian Continental Shelf
OOIP	original oil in-place
PLT	production log tool
PNC	pulsed neutron capture log
PV	pore volume

RF	recovery factor
σ	interfacial tension
σ_{os}	interfacial tension between oil and solid
σ_{ws}	interfacial tension between water and solid
σ_{ow}	interfacial tension between oil and water
S_{iw}	immobile (interstitial) water saturation
S_{oi}	initial oil saturation
S_{or}	residual oil saturation
SWCT	single well chemical tracer
TDS	total dissolved salt
WAG	water alternating gas injection

1. INTRODUCTION

Waterflooding is known since late 1800's however it has become a widely used method to increase production from oil reservoirs in 50's of the XX century. After the natural energy of the field was depleted, the additional has to be provided by injected water. At first it was believed that only quantity of water was important to increasing recovery. However, later it was discovered that equally significant is composition of water. Then industry started using formation water as injecting fluid. In late 1950's the first observations of increased oil recovery, by decreasing of the injected water salinity, was made by Martin (Martin, 1959). Later Bernard (1962) flooded the reservoir outcrop with NaCl solution with different concentration. He noticed that reduction of the NaCl concentration lead to increased oil recovery (Bernard, 1967).

In last two decades, the investigation of the low-salinity waterflooding was performed by many academic and company research groups. During these years, laboratory test confirmed that low-salinity waterflooding alters the wettability of the rock to more water-wet and improves the microscopic sweep efficiency. It was performed also single-well tracer test, log-inject-log measurements and field-scale studies (Lager et al., 2008b; McGuire et al., 2005; Webb et al., 2004). Even nowadays, the main mechanism was not defined. Many propositions was pointed, however there are not confirmed as the primary one.

Low salinity brine injection is believed as the least expensive EOR method. Since no chemicals are injected with water it is also environmental friendly. Not to mention, that "smart water" flooding reduce probability of the souring and scaling or corrosion of the equipment (Collins, 2011). Another benefit is that low-salinity EOR method does not require any additional equipment that is used for conventional waterflooding.

It is important to continue research about "smart water" flooding. Knowing its mechanism will allow improving EOR water-based methods. It may be also the key to better understanding of the rock/brine/oil complex.

1.1. Thesis objective

In this thesis will be analysed two sandstone oil fields for their perspectives for using smart water method. The data was obtained from one of the companies that own licenses on the Norwegian Continental Shelf. The company wants to remain anonymous. In order to provide that, names of the field, formations and company will be coded. Information that is strictly confidential will not be used in this work.

The objectives of the thesis are:

- Through literature overview, underlay the most important parameters that have impact on low-salinity waterflooding effect.
- Compare two oil fields with data found in the available research findings according to low-salinity prospects.
- Evaluate the possibilities of using “smart water” injection on sandstones fields without performing expensive laboratory tests.
- Can “smart water” be used to enhance oil recovery from targeted fields?

2. THEORY

In this part of the thesis theory, which is essential to understand “smart water” flooding, will be presented.

In the beginning, one of the most common reservoir rock types will be described. There are two kinds of the porous medium in conventional reservoirs, which are sandstones and carbonates. However in thesis will be taken into consideration only sandstone reservoirs. Later, parameters, that characterise rock, like permeability and porosity, will be described. Then, clay minerals, which are common part of the sandstone, will be discussed. Due to their unique properties, they play a huge role in the “smart water” mechanism. Second mineral group that will be described are feldspar minerals that may change initial wetting state of the reservoir rock. Other minerals that occur in the rock will be only mentioned.

In next part, the oil recovery approaches will be introduced. There are three stages of them: primary, secondary and tertiary. The tertiary stage may be defined as enhanced oil recovery (EOR). All of the phases will be described more precisely. Furthermore, an effectiveness of the EOR methods will be defined.

In this paper there will be reviewed microscopic properties that stay behind explanation of the water/rock/brine interactions. That is, surface and interfacial tensions, rock wettability and relative permeability will be explained. Moreover, driving forces, that act on displace fluid in the reservoir will be also presented.

Before moving to explain “smart water” flooding, initial wetting state of reservoir has to be discussed. Mechanism of the rock wettability alteration in sandstones will be introduced too. There will be mentioned factors that may have influence in these mechanisms.

Finally, the main subject of that thesis will be introduced. Through the last decades, enhanced oil recovery by lowering salinity of injected water has been investigated. Due to many laboratory tests, cores flooding, the main mechanism of the “smart water” was examined. The most important research results were presented in this paper. In last paragraph, requirements needed to enhance oil recovery by low salinity flooding can be found.

2.1. Sandstone

Reservoir rock is the porous medium that contains hydrocarbon accumulation. Commonly, sedimentary rock (sandstone, carbonate) are reservoirs. But, rarely highly fractures igneous and metamorphic rock may play that role. However only sandstone reservoir will be taken into consideration as thesis title states.

Circa 60% of world's oil and gas reservoirs are sandstones. Needless to say, the shape of the reservoirs is determined by depositional environment. Among the reservoirs, the most common sandstones are formed in aqueous environments, e.g. alluvial, delta, fluvial or shallow marine. According to Zimmerle (1995), the average size of sandstone fields are: 25 m thick, 4 km wide and 50 km long.

Sandstone is a clastic sedimentary rock that consists of sand grains (particles between 63 µm and 2 mm). These grains are placed in fine-grained matrix and cemented. Sandstones are composed from quartz, feldspar rock fragments and clay. As every other type of rock, sandstones are also classified according to their composition and quantity of the various components (Bjorlykke, 2010). Among them can be mentioned: quartz sandstone, arkosic (feldspathic) sandstone, lithic sandstone, subarkosic and sublithic sandstones.

As was mentioned, sandstones are the prime reservoir rocks. Nevertheless not every rock may be appropriate for production of the accumulation. Factors that define the quality of the reservoir are porosity and permeability. Significant impact on the hydrocarbon production has also pore geometry and wettability. These parameters are individual for each reservoir; therefor they will be described more precisely in the following sections.

In rocks may be present fluids like water, oil or gas. The water saturation of the sandstones is minimum 10%, but usually it varies in the range of 15% and 40% (Zimmerle, 1995). Existing fluids has impact on the wettability, what will be described in section 0.

2.1.1. Porosity and permeability

As stated previously, some of the major factors, which have impact on hydrocarbons production, are porosity, permeability and pores geometry. All of them are related with porous space, consequently, with structure of the rock medium. Pores are the spaces not occupied by the grain, matrix or cement, usually containing gases, hydrocarbons (both liquid and gaseous) and brine. Meanwhile porosity is the ratio of pore volume to total volume.

Porosity may be defined as value relative to the whole pore space, or as the ratio of connected pores, that forming peculiar channels. That is respectively, total (φ) and effective porosity. Total porosity (φ) is the whole void space to total volume. It includes isolated spaces and spaces occupied by clay-bound water. Total porosity in sandstones ranges between 5% and 35% (Zimmerle, 1995). Effective porosity is the volume of the interconnected pore space to total volume. What is important, that creates possibility of the fluid flow among the pores that are connected. Moreover, the result of effective porosity is also the property called permeability.

An origin of the porosity divides it to primary and secondary. Primary porosity forms during deposition, when grains remain not compacted totally. Secondary porosity is the effect of the rock alteration, due to dissolution of minerals or amorphous material, fracturing and dolomitization.

Permeability (k) expresses the rock ability to transport a fluid in pore spaces. This parameter depends on the rock properties and stays unrelated to fluid characteristic. Permeability is highly connected to the effective porosity. Absolute permeability is measured when only single phase exists in pore space. When free space in rock is occupied by two or more phases, an effective permeability is established. That term means the ability to flow a specific fluid through the rock in presence of other immiscible phases.

A classification of the reservoirs according to porosity and permeability that characterizes the quality of the field is presented in table 1. According to that, reservoirs are subdivided into four classes: low quality, fair, good and excellent.

Table 1. The quality of the sandstone reservoir according to porosity and permeability of the rock (Zimmerle, 1995).

Quality	Porosity range	Permeability range
Low	Less than 5%	Less than 1 mD
Fair	5% - 15%	1 – 10 mD
Good	15% - 25%	10 – 100 mD
Excellent	Above 25%	Above 100 mD

It is worth mentioning that composition of the rock is the main factor that has an influence on its permeability and porosity in shallow depths. While proceeding burial, these properties are influenced by temperature, time and stresses in rock (Bjorlykke, 2010).

2.1.2. Clay minerals

Extremely important sandstone components, in context of “smart water” flooding, are clay minerals. The term “clay minerals” has two meanings. First one is related to grain size between 1 µm to 4 µm. However, this definition is not correct in thesis consideration. Second definition is referred to minerology and that is why it will be discussed (Bjorlykke, 2010).

Clay minerals are made from hydrous aluminium phyllosilicates. They may contain also magnesium, iron, and in smaller amounts potassium and sodium. The structure of the mineral is created from layers: ions and sheets. There are two types of sheets: tetrahedral and octahedral. Tetrahedron is made of oxygen-linked (O^{2-}) ions, which are mainly silicon cations (Si^{4+}), but sometimes aluminium cations may occur (Al^{3+}). Second type of sheets is octahedral, which is composed of aluminium cation (Al^{3+}) or magnesium cation (Mg^{2+}) in the centre and suitable number of oxygen (O^{2-}) or hydroxyl ions (OH^{-}) (Velde, 1995). Figure 2.1. illustrates simplifier sheets model that are described above. Sheets create structures, which are:

- 1:1 – one tetrahedral layer and one octahedral layer,
- 2:1 – two tetrahedral and one octahedral layer,
- 2:1:1 – two tetrahedral and two octahedral layers.

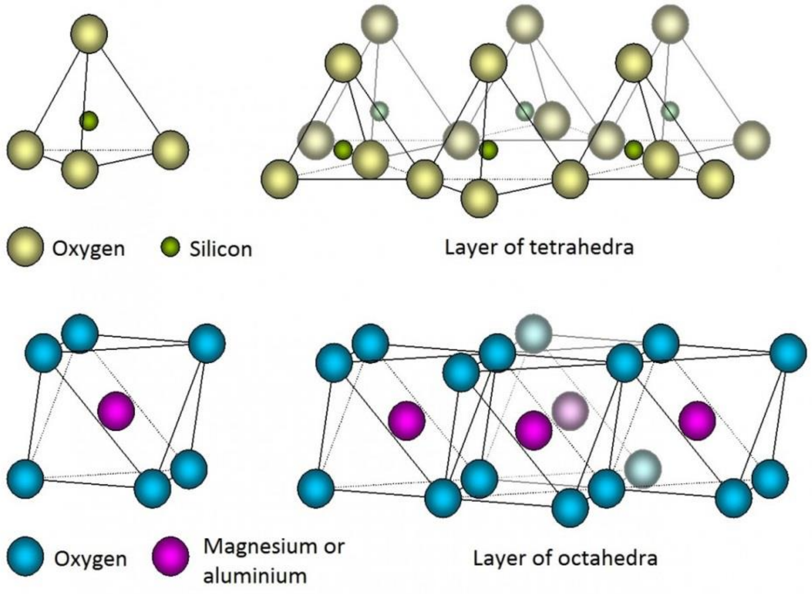


Figure 2.1. Clay structural units (Jordán, 2014).

Some of the clays are swelling. That is, water is incorporated to clay structure in interlayer space. This results in increased thickness of the combined structures. Due to that, clay can change their volume even 95% (Velde, 1995).

It is significant to mention, that clay minerals have large effective surface area, which is consisted of external and internal surfaces. Minerals from kaolin group have the smallest surface area, due to single-unit structure and the largest one have minerals from group 2:1 [Table 2.] (IDF, 1982).

Table 2. Cation exchange capacity and surface area (IDF, 1982).

Mineral	**CEC [mEq/100g]**	**Surface area BET [m^2/g]**
kaolinite	3-15	15-25
chlorite	10-40	140
illite	10-40	50-110
smectite	80-150	30-80

Important property of the clay is the interaction with ions in water solution, which is named cation exchange capacity (CEC). Clays external and internal surfaces are charged; therefore ions are attracted and adsorbed onto them. Generally, the clay minerals has negatively charged surface. The process, when the adsorbed ion is replaced by the other one, is named “cation exchange”. Selection of a cation, that may be able to exchange the other one, is driven by ions concentration in solution and affinity to the clay surface (Velde, 1995). Affinity of some cations is presented below:

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} << H^+$$

CEC is measured as the number of charged ions that can be adsorbed onto the clay surface. The unit of cation exchange capacity is mili-equivalents of charges per 100 g of dry clay (mEq/100g). The CEC of some minerals are presented in table 2.

Clay minerals are mainly weathering and soil formation product. In sandstones, they occur as a result of modification of feldspar, mica and rock fragments. As was shown in table 2., there are four main groups of clay minerals: kaolin, smectite, illite and chlorite.

Kaolinite is the mineral, that structure is composed of 1:1 units. It is non-swelling mineral. The thickness of one kaolinite structure is equal to 7 Å (angstrom; 1Å= 10^{-10} m) (Bjorlykke, 2010).

Illite is 2:1 mineral, that is also non-swelling, characterized by structure thickness of 10 Å. Ions adsorbed into interlaying surface are almost always potassium (K) (Bjorlykke, 2010).

Smectite has the same structure as illite (2:1); however it is a swelling mineral. Its properties, in contrast to illite, owe the low charge. The charge of the smectite is between 0.7 and 0.2, what allows hydrated or polar ions to be placed between layers. Adsorbed ions expand the structure, what results in thickness of the smectite minerals range from 12.5 Å to 15.2 Å (Bjorlykke, 2010; Velde, 1995).

Chlorite is composed of 2:1 structure (2 tetrahedral and one octahedral sheet) with an additional octahedral layer. It is non-swelling mineral. The thickness is 14 Å (Bjorlykke, 2010).

All presented above clay minerals are illustrated schematically on figure 2.2.

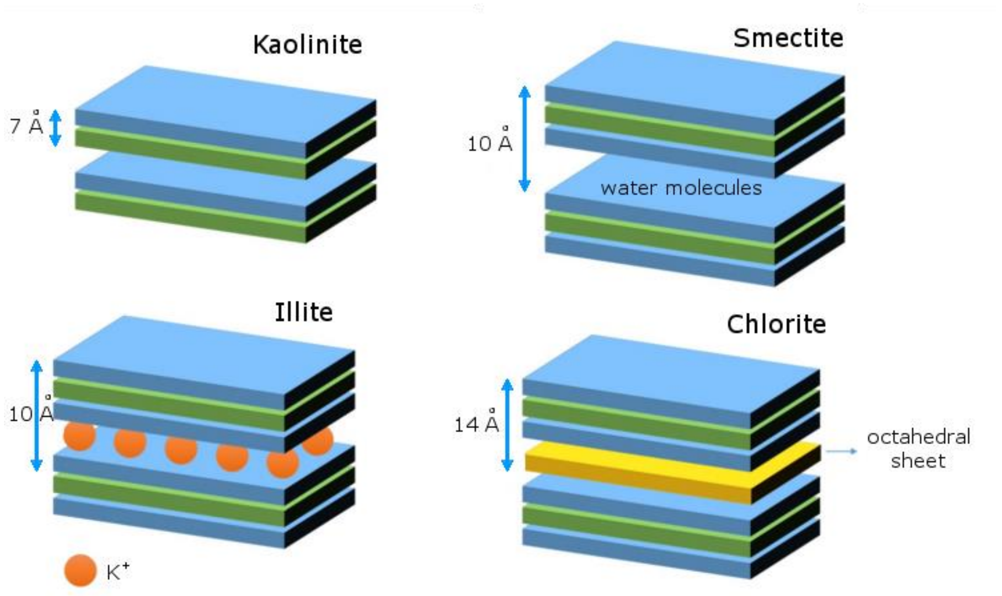


Figure 2.2. Structures of clay minerals (Jordán, 2014).

2.1.3. Feldspars

Feldspars are rock-forming minerals building almost 58% of the Earth's crust. They crystalize in igneous rocks from magma. Also metamorphic and sedimentary rocks are formed from feldspars (Dietrich, 2016; Haldar, 2013).

Feldspars are aluminosilicates of potassium, sodium, calcium and less often barium. They contain isomorphous additions of lithium, rubidium, caesium, strontium and iron. There exist three endmembers of these minerals that can describe most common feldspars. They are: potassium feldspar (K feldspar), albite and anorthite. K-feldspar minerals are potassium compounds. A chemical formula of theme is $KAlSi_3O_8$. Albite consists of molecule of sodium and chemical formula of it is $NaAlSi_3O_8$. It is the mineral with mixture of 90%-100% Na-feldspar and 0%-10% of the Ca-feldspar. Analogously, anorthite instead of Na or K molecules has calcium. Formula of anorthite is $CaAl_2Si_2O_8$ and it contains only 0% to 10% of Na-feldspar and 90%-100% of Ca-feldspar. (Dietrich, 2016; Haldar, 2013).

Isomorphic mixture of sodium-feldspars and calcium-feldspars forms plagioclases. Plagioclase can be formed in high and low temperature. However, the one formed in low temperature is more stable than plagioclase formed in high temperature. Water and weathering have significant influence on high-temperature plagioclases (Haldar, 2013).

Solid solution of K-feldspar and Na-feldspar is called the alkali feldspar. In low temperatures, mixture is not stable. Alkali feldspar group includes: orthoclase, sanidine (monoclinic minerals) and microcline and anorthoclase (triclinic feldspars). Sanidine is not stable on shallow depths and on the surface. Therefore it recrystallizes in orthoclase (Haldar, 2013).

Feldspars may have impact on low-salinity waterflooding method. In some environment, monovalent metals can exchange with H^+ and change the initial wetting condition of reservoir rock (Strand et al., 2014). The exact influence of the feldspars will be described in section “Initial wetting state”.

2.2. Oil Recovery

In order to qualify the reservoir as profitable for the production, economical amount of recoverable oil has to exist. Generally, the larger is the ratio of recoverable oil to initial oil in place, the more reasonable is production. That ratio is called oil recovery factor (RF). RF is a function of displacement mechanisms that depend on various parameters (these dependencies will be discussed in the further sections). The objective of reservoir engineers work is to increase the oil recovery factor by appropriate production of the field. With the intention to do that it is necessary to apply additional methods of production. Oil recovery performance usually is consisted of three stages, i.e. primary, secondary and tertiary. Names of these steps are referred to chronological succession. However, nowadays the order may be neglected [Chapter 2.2.3]. Next chapters will be dedicated to each of the production steps.

2.2.1. Primary Recovery

When the hydrocarbons production is started, a natural energy of the reservoir becomes a firstly used mechanism. As any additional methods are not used and this stage almost always is the first step of production it is called “primary recovery”. Production is handled without using any additional actions, like fluid injection (Ahmed & McKinney, 2005). The main performance is driving mechanism, which can be subdivided into six groups:

- rock and liquid expansion drive,
- gas cap drive,
- depletion drive,
- water drive,
- gravity drainage drive,
- combination drive.

Moreover, artificial lift belongs to primary recovery.

This stage runs until it is no longer economically justified. It is either when the pressure is too low and production is reduced, or when the production of water and gas becomes too high. Depending on drive mechanism and properties of reservoir the recovery factor (RF) ranges from 5% to 75%. However, usually the RF does not exceed 30% (Ahmed & McKinney, 2005).

2.2.2. Secondary Recovery

Proceeding production, the primary recovery eventually ends- the natural energy of reservoir is being depleted. To continue the exploitation, the need for extra energy arises. Then the secondary recovery is usually executed and provides this additional energy. The most common method in this period of production is fluid injection, i.e. water injection, gas injection or water alternating gas injection (WAG). However, the most widely used approach is water flooding. Because of such reason, secondary recovery method may be synonymously called the water flooding (Green & Willhite, 1998).

Mechanism used in secondary methods uses immiscibly fluid to displace oil or gas. This mechanism works consistently with relative permeability and volumetric sweepout which will be described in due course. Selection of injected fluid and distribution of injectors and producers is dictated by relative permeability of the phases. Widely, this theme will be described in chapter 0.

The limit of reasonable fluid injection application is dictated by economic issues. It can be said, that the main reason of deciding to use fluid injection to increase the recovery factor, is big enough difference between injection cost and higher production rate profit and this difference depends on actual market state. However, after primary and secondary processes, the recovery factor may reach from 35% to 50% of OOIP (Green & Willhite, 1998).

2.2.3. Tertiary Recovery / EOR

The last, after secondary, stage of production is “tertiary recovery”. However, that concept is not entirely appropriate. Many fields are exploited using advanced techniques from the very beginning. In other situation, instead of secondary method, the tertiary ones are applied. As a result of possible misunderstanding the phrase “tertiary recovery”, new expression named “enhanced oil recovery” (EOR) was made for that group of methods, (Green & Willhite, 1998). In contrast to secondary oil recovery methods, tertiary ones lead to altering the oil and/or rock properties, what improves the mobility of oil.

There are five categories of EOR methods: chemical, thermal, mobility-control, miscible, and other [figure 2.3.]. Depending on the characteristic of the field profitability of methods should be taken into account. That is, not every method used is reasonable. Despite similarities between reservoirs, usage of the same method may have different effects.

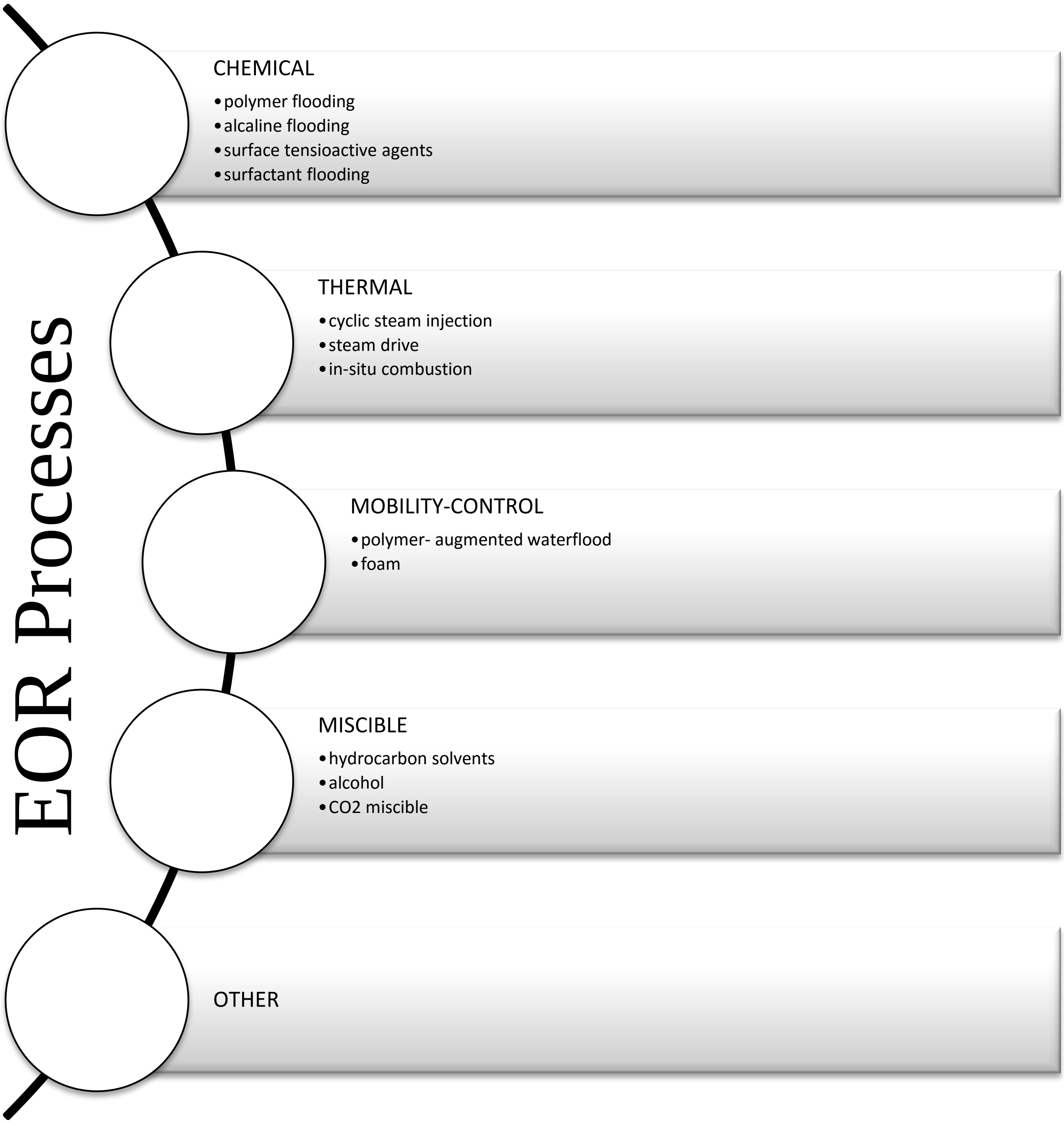


Figure 2.3. Enhanced oil recovery (Carcoana, 1992; Green & Willhite, 1998).

Applicability of each method is dictated by specified criteria. The most important of these are:

- economic issues
- reservoir fluid properties
  - oil viscosity
  - oil gravity
  - oil composition
- geological data
  - heterogeneity
  - anisotropy
- reservoir characteristics
  - oil saturation
  - formation type
  - net thickness
  - average permeability
  - depth
  - temperature

Thermal method is used to enhance the production of heavy oil with great oil saturation. In this process, oil is used as a fuel to power the generators (steam flooding method) or is combusted in order to reduce oil viscosity (in-situ combustion). Miscible processes can be carried out on thin reservoir with low-viscous oil. Thickness in this case decreases gravity effect. Chemical processes cannot be applied in reservoirs, where temperature is above 200°F (93°C). Most of the chemicals break down under the influence of high temperature.

Besides above factors there do exist many different that affect selection of the EOR method. For example, great heterogeneity, which can be characterized by faults or fractions, can cause a situation where fluid injection may be not universal, which has an impact on poor oil recovery and results in ineffective EOR process.

2.2.4. Sweep efficiency

EOR methods are used to increase oil production as possible. Effectiveness of these is defined as sweep (displacement, E) efficiency. It describes the ratio of oil recovery by EOR method and oil in place at the beginning of the performance, measured at the same pressure and temperature. In other words, it shows how effective EOR will be at a certain time. This is related to microscopic (E_D) and macroscopic (E_V) displacement (Green & Willhite, 1998; Terry, 2001). The relation between these factors is given by the equation:

$$E = E_D \cdot E_V \tag{1}$$

Microscopic sweep expresses displacement of oil in the pore scale. That is, moving the oil from places, where it contacts with displacing fluid (e.g. water). Equation 2. presents the relation between microscopic displacement efficiency and the residual oil saturation quantity (S_{or}). E_D depends on surface/interfacial tension, wettability, capillary pressure and relative permeability (Terry, 2001).

$$E_D = \frac{S_{oi} - S_{or}}{S_{oi}} \tag{2}$$

Macroscopic displacement (volumetric sweep) efficiency is described as reservoir volume fraction occupied by the displacing fluid. This can be presented as product of areal (E_A) and vertical (E_I) sweep efficiencies [equation 3.]. The first one refers to fraction of area that is flooded, while the other represents the fraction of the vertical pay zone swept by injected fluid (Green & Willhite, 1998; Terry, 2001).

$$E_V = E_A \cdot E_I \tag{3}$$

Volumetric sweep is related to properties of displacing fluid, oil, rock (i.e. heterogeneity, anisotropy) and geometry of the well pattern (Green & Willhite, 1998). One of the factors that can ensure good macroscopic displacement is density of the fluids. The similarity in densities of injected fluid and oil can be an advantage. If there is a difference between these densities, the fluids will be gravitational separated. This indicates reduction of reservoir volume that has contact with injected fluid.

Another important factor is mobility ratio, which depends on relative permeability of fluids and their viscosities. Mobility ratio is presented by equation 4. This quantity specifies the stability of displacement. When $M<1.0$, the process is stable, what means that oil moves easier than water. In another situation ($M>1.0$), the process is unstable and water mobility is greater than oil’s.

$$M = \frac{\left(\frac{k_{rw}}{\mu_w}\right)_{S_{or}}}{\left(\frac{k_{ro}}{\mu_o}\right)_{S_{iw}}} = \frac{k_{rw} \cdot \mu_o}{k_{ro} \cdot \mu_w} \tag{4}$$

Where:

k_{rw}	relative water permeability,
k_{ro}	relative oil permeability,
μ_w	dynamic water viscosity,
μ_o	dynamic oil viscosity,
S_{or}	residual oil saturation,
S_{iw}	immobile (interstitial) water saturation.

2.3. Microscopic properties

As was mentioned in chapter 2.2.4, properties affecting on microscopic sweep efficiency are surface/interfacial tension, capillary pressure, wettability and relative permeability. It is highly important, for EOR theme, to understand these factors. All of these will be described and explained in the following sections.

2.3.1. Surface/interfacial tension

Every single physical body has molecular forces, which attract each molecule together. The surface tension exists, because the molecules at the surface have different individual molecular interaction, than whole fluid. That tension can also present a magnitude of fluids immiscibility. In order to mix the air with liquid or two liquids it is necessary to provide mechanical energy or additional component to lower the interfacial tension.

Interfacial tension (σ) can be expressed as the Gibbs energy per unit area or tensile force per unit length [figure 2.4.]. The phrase “interfacial tension” refers to the surface between two liquids or a liquid and a solid. If the surface is between vapour (e.g. air) and liquid, term “surface tension” is used. Interfacial tension is function of pressure, temperature and composition of each fluid (Green & Willhite, 1998; Terry, 2001).

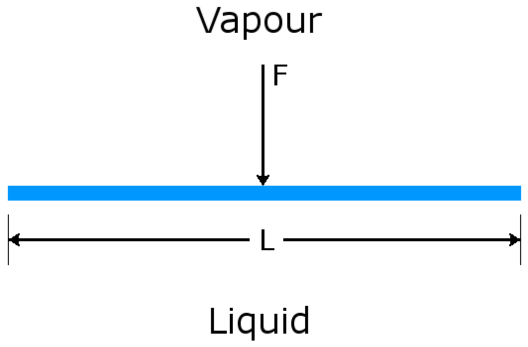


Figure 2.4. Free liquid surface; force per length (Green & Willhite, 1998).

2.3.2. Wettability

Phenomenon of the interfacial tension induces the property of the porous medium, which is wettability. Wettability is the preference of solid to contact a fluid. Wettability occurs, when more than one fluid is present. In such system of solid and two fluids, one of the fluids is a wetting phase and the other one is a nonwetting phase. Wetting phase means fluid which is more attracted to the solid than another one. For example, in porous system with water and gas, water is wetting phase and gas is nonwetting phase. The wettability is function of composition of the fluid.

In consideration were taken facts, that all sediments are strongly water-wet and that there were aqueous environments, where reservoir rocks were deposited. As a result of later migration, oil was transported to reservoir. Oil film that was created on the rock surface altered the wettability (Anderson, 1986).

In oil/brine/rock system, it is possible to describe effect of the wettability. There are three main types of the system: water-wet, oil-wet and mixed. However, it is difficult to define the property of the rock. Due to complexity of the rock structure and numerous minerals, the wettability may be different in rock structure. In water-wet structure [figure 2.5. a], the oil is in the centre of the pore, while water adheres to rock. Inversely is in oil-wet system [figure 2.5. c]. Mixed-wet case is when oil adheres in some places and in other is repulsed [figure 2.5. b] (Abdallah et al., 2007).

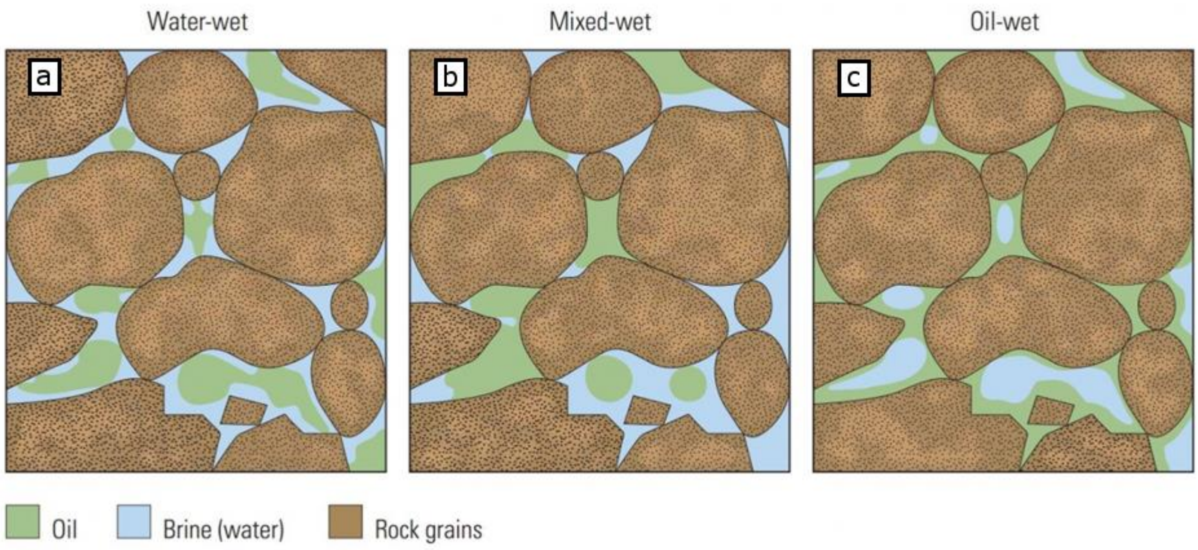


Figure 2.5. Wetting types in pores (Abdallah et al., 2007).

Figure 2.6. illustrates the wettability of the rock respectively to the water drop. The contact angle between the solid and water can be used to determine the value of the wettability. In first case (left), the surface is water-wet, and the contact angle is ranged from 0° to 90°. If the contact angle is bigger than 90°, solid is oil-wet (Green & Willhite, 1998). The classification of wettability depended by the contact angle is present in table 3.

Table 3. Wettability classes for water/ oil system (Zolotuchin & Ursin, 2000).

Wetting angle	**Wettability type**
0 – 30	strongly water-wet
30 – 90	preferentially water-wet
90	neutral
90 – 150	preferentially oil-wet
150 – 180	strongly oil-wet

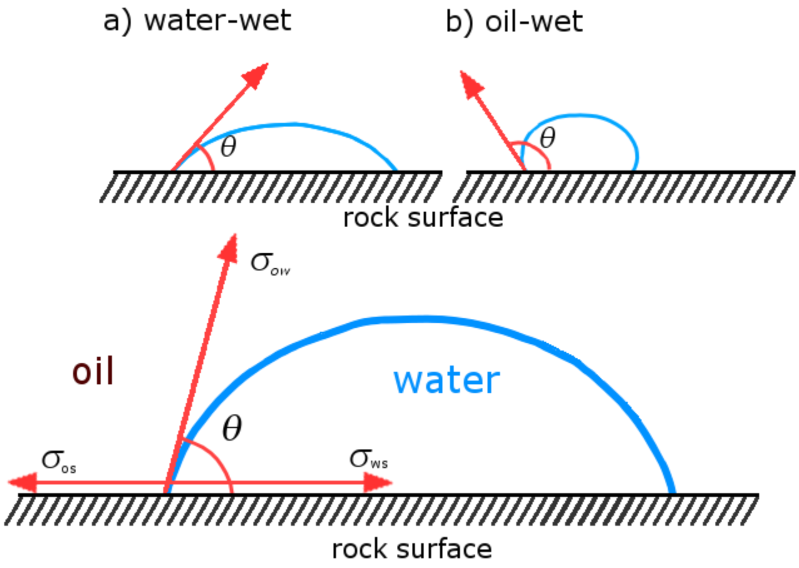


Figure 2.6. Contact angle between rock and water drop surrounded by oil.

The equilibrium between forces that exists between two immiscible fluids and solid surface can be determined by the Young-Laplace equation [equation 5.].

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} * \cos\theta \tag{5}$$

where:

σ_{os} interfacial tension between oil and solid,
σ_{ws} interfacial tension between water and solid,
σ_{ow} interfacial tension between oil and water,
θ contact angle.

In reservoir, the wetting phase occupies the narrowest regions of the pore space. The non-wetting fluid fills the biggest parts. From largest pores non-wetting phase flows more easily. The same relative permeability is higher for that fluid, than for non-wetting one (Bavière, 1991). Relative permeability is described in next section.

2.3.3. Relative permeability

In some recent chapters there was mentioned the property called relative permeability. It is of course related to permeability itself and expresses relationship between absolute and effective one. Following this phrase, “relative permeability” (k_r) is the ratio of the effective permeability of a particular phase at some saturation to absolute permeability at full saturation. It is function of wettability and phase saturation, rock and fluids properties, reservoir conditions and absolute permeability (Zolotuchin & Ursin, 2000).

Figure 2.7. presents relative permeability. In first area only oil is produced. When saturation of water will be greater than residual water saturation, oil and water flow. In third area, when oil relative permeability approach 0, mobility of oil will be terminated (Bjorlykke, 2010).

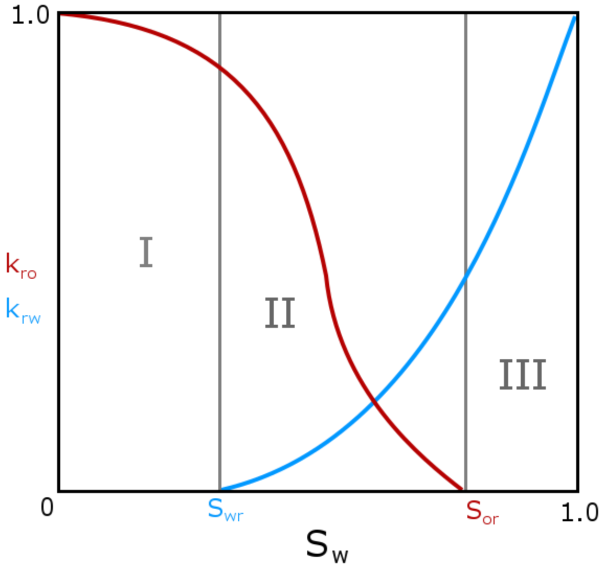


Figure 2.7. Typical water-oil relative permeability curves for a porous medium (Terry, 2001).

2.4. Displacing forces

2.4.1. Capillary forces

A pressure difference between interfaces is called capillary pressure. The capillary pressure is a function of interfacial tension between two fluids, contact angle and radius of the capillary [equation 6.].

$$P_c = P_o - P_w = \frac{2\sigma_{ow}\cos\theta}{r} \tag{6}$$

Where:

P_c	capillary pressure,
P_o	pressure in oil phase, measured adjacent to the interface,
P_w	pressure in water phase, measured adjacent to the interface,
σ_{ow}	interfacial tension between oil and water,
θ	contact angle.

Figure 2.8. presents the definition of capillary forces in capillary tube described by equation 6. Depending on which phase is wetting, the capillary pressure has positive or negative sign. The non-wetting phase has always larger pressure. In example showed on figure 2.8. non-wetting fluid is oil, so capillary pressure [from equation 6.] has positive value.

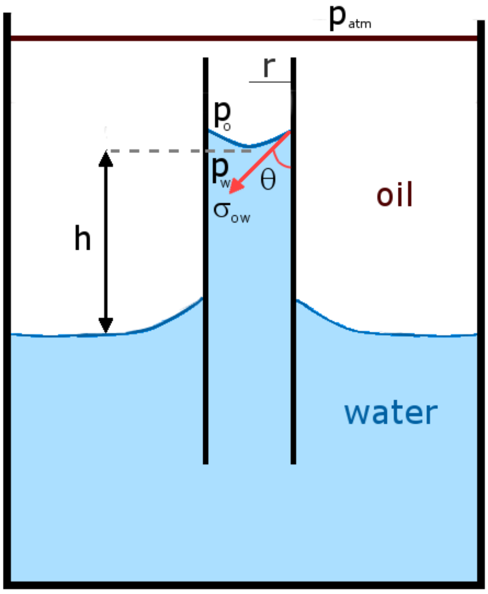


Figure 2.8. Capillary pressure in a capillary tube.

Capillary forces in reservoir are larger than gravity forces, described below. Because of that reason, the main forces acting on fluid transport are capillary one (Bavière, 1991).

2.4.2. Gravity forces

Gravity forces occur when difference in densities between two fluids is large. Phases segregate according to density [equation 7.], where the densest fluid is on the bottom of the column and the least dense is on the top. Gravity forces are important in some EOR processes (i.e. steam displacement, in-situ combustion, CO2 flooding, solvent flooding) (Green & Willhite, 1998), but it is important to remember the statement, that capillary forces in reservoirs are bigger.

$$\Delta P_g = \Delta \rho g H \tag{7}$$

Where:

ΔP_g	pressure difference over the phase's surface due to gravity,
$\Delta \rho$	difference in density between fluids,
g	gravitational acceleration constant; $g = 9{,}81\ m/s^2$,
H	height of the column.

2.4.3. Viscous forces

In the porous rock the great impact on medium displacement has also viscosity of fluids. Moreover, it is a major parameter when discussing about EOR methods. As there were gravity and capillary forces, there are also one more, strictly connected to viscosity and named under it as viscous forces. They are represented by the pressure drop, emerging as a result of the fluid flow through the porous medium. In order for the flow, it is essential that capillary forces have to be larger than viscous.

To describe the viscous forces, the assumption, that porous medium is bundle of parallel capillary tubes, has to be determined. The pressure drop in single tube for laminar flow is calculated by the Poiseuille's equation [equation 8.] (Green & Willhite, 1998).

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

Where:

ΔP	pressure difference across capillary tube,
μ	viscosity,
L	length of capillary tube,
v_{avg}	average flow velocity in capillary tube,
r	radius of capillary tube,
g_c	conversion factor.

2.5. Initial wetting state

The low-salinity effect may be observed when the reservoir rock is around mixed-wet state. If initially reservoir is too water-wet the low-salinity injection will not give any results.

The wetting condition of the reservoir rock is hard to determine. There is effect of the interaction between rock, brine and crude oil system. Wettability is influenced by several parameters. They are: mineral surface, oil components, formation water chemistry, initial water saturation, pH of the brine and temperature. All the factors will be discussed below.

Mineral surface

The impact on enhanced oil recovery by low salinity fluid depends on type of clay minerals, especially their cation exchange capacity. Sandstones are believed to be more water-wet comparing to carbonates. Sandstones have negatively charged surface that can interact with the polar components of crude oil and alter the wettability of the rock (Anderson, 1986). In this situation great impact have clay minerals, due to their large cation exchange capacity. The amount and type of clay minerals are taken into consideration during establishing the initial wetting state of the reservoir. According to growing CEC, the importance of clay minerals can be ordered in following way: kaolinite < illite < montmorillonite (Austad et al., 2010). There was proved that low salinity effect is not related to occurrence of kaolinite in the rock. This is confirmed by experiments conducted by Cissokho et al. (2010). There was obtained oil recovery after implementation of the low-salinity water on core that contains sufficient amount of clay, excluding kaolinite (Cissokho et al., 2010).

Zhang & Morrow (2006) carried out the smart water flooding on two cores with different types of clay. Results show no respond on low-salinity treatment in core with high content of chlorite. They speculated that chlorite has limited contact with crude oil due to its protruding asperities (Zhang & Morrow, 2006).

Impact on wettability has also occurrence of feldspars in reservoir rock. Depending on the salinity of formation water, plagioclases have different impact on initial wetting state. More precise description of this phenomenon will be described below, in section “pH variation”.

Oil components

Originally, sandstones were strongly water wet. They were filled only with water. When in reservoir was accumulate also oil the equilibrium between rock/brine/oil complex had to be established. After some time, wettability of the reservoir became more mixed-wet. As was mentioned before, the crude oil may change the wettability of the sandstone due to adsorption of polar components. They are mostly present in heavier fractions like resins and asphaltenes. Polar components are determined by acid number (AN) and base number (BN). In oil/ brine/ rock complex the rock surface has ability to adsorb both acidic and basic components of oil.

The adsorption of polar components has to be performed through the water film. It was proven, that solubility of surface-active organic compounds in water is sufficient to adsorb onto rock surface after crossing the water layer (Kaminsky & Radke, 1998).

Formation water chemistry and saturation

Water content reduces the adsorption of polar components onto rock. Bulk water can prevent the adsorption if the water film is stable. That is to say, formation water has to be present in reservoir rock. It has been shown, that increasing water saturation leads to more water-wet conditions (Jadhunandan & Morrow, 1995).

Multivalent ions may act like bridges between polar components and rock surface. That may alter the wettability of the rock to more oil-wet. Different types of ion bonding may have also impact on limitation of the wettability alteration. There are: oil–divalent cation–oil and mineral–divalent cation–mineral interactions. However, much higher concentration of monovalent cations may be preferentially attracted by negative surface. Above all, presence of the divalent cations in formation water contributes to more water-wet conditions (Austad et al., 2010). Active ions like Ca^{2+} and Mg^{2+} compete with organic polar components and holding back their adsorption. With increasing initial water saturation amount of the divalent cations in pore space increase too. It is worth to mention, that usually formation water that has large salinity will contain more cations, also divalent ones.

Temperature

High temperature has negative impact for low-salinity waterflooding. Increasing temperature will increase solubility of the polar components and reduce the adsorption of theme.

Aghaeifar et al. (2015) studied impact of high salinity of formation water and high temperature on smart water effect. Two core flooding experiments at 110 °C were conducted on similar core material. First core was saturated with formation water that salinity was 200 000 ppm. Then succeeding water flooding of FW, SW (33 000 ppm) and LS water (660 ppm) was performed. In result of that experiment, no LS effect was observed. Because of high concentration of Ca^{2+} cations and their dehydration caused by high reservoir temperature, reservoir rock became too water-wet. Water used to flooding for second experiment was FW with salinity 23 000 ppm, SW and LS water with the same salinity as previous. No effect was observed after switching FW to SW. After implementation LS water, oil recovery increased to 6% of OOIP. Also pH value increased about 1,5 pH, what leads to change in wettability of the rock (Aghaeifar et al., 2015).

In conclusion, due to dehydration of Ca^{2+} cations in high temperature, the adsorption of calcium cations will increase. That will cause reduction of adsorption of polar components. In the end it will lead to strong water-wet initial conditions (Aghaeifar et al., 2015). However, this effect will be reduced, if the formation water has moderate salinity.

pH variation

Salinity and pH of the formation water will influence on surface charge and the same wettability. At pH exceeded 2 to 3.7 clay minerals becomes negatively charged. Calcite has negative charged, when the pH is increased above 8 to 9,5 units.

Burgos et al. (2002) conducted adsorption studies of quinoline (base) onto kaolinite and montmorillonite. Process was depending on the pH of the solution. The maximum of adsorption for both clay minerals was at 4 pH unit. At pH around 8, adsorption became very low. What is more, at pH lower than 4, concentration of H^+ became so high, that it replaced the polar components [figure 2.9.] (Burgos et al., 2002). However, it is worth to mention that, with increasing pH adsorption of acids decrease. Maximum of acidic compounds adsorption is close to 5 pH unit (Austad et al., 2010). It is expected that very high concentration of hydrogen ions will lead to lowering adsorption of acidic materials.

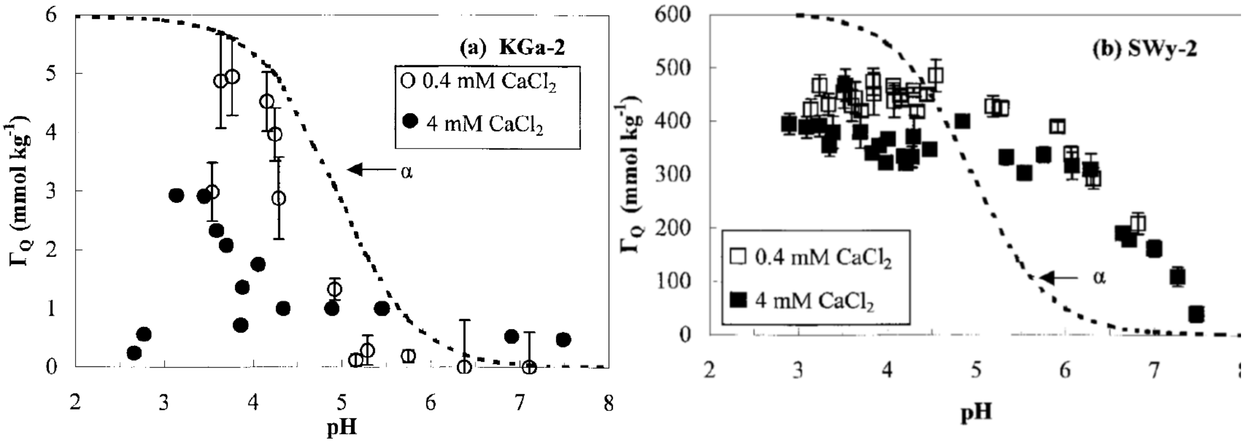


Figure 2.9. Adsorption of quinoline onto a) kaolinite and b) montmorillonite. The dotted line represents the fraction of ionized quinoline (Burgos et al., 2002).

At high pH, adsorption of polar organic compounds is reduced. Acids and bases transforms to alkaline forms: R3N: and $RCOO^-$. They have lower attraction toward the clay mineral (Aghaeifar et al., 2015). However, usually pH of the reservoir is ranged between 5-6,5, which promotes adsorption of the surface-active organic compounds.

The typical pH of formation water range 6-7 units. However, the sour gases may be present in the reservoir and lower the initial pH. Acidic gases like CO_2 and H_2S, that occur in the reservoir, act like buffering agents. That is, the presence of sour gases causes reduction of pH gradient (Aksulu et al., 2012). Previously was indicated that too low pH of the reservoir will lead to sharp reduction of the crude oil polar materials adsorption.

However plagioclases present in the reservoir may increase or decrease the pH of the formation water depends on their composition. Some plagioclases that contain monovalent ions may exchange it with protons (H^+). Strand et al. (2014) present behaviour of plagioclase (based on albite- $NaAlSi_3O_8$) in an environment of different formation waters. When formation water has moderate salinity, insufficient amount of Na^+ ions will lead to increase of OH^- concentration (the environment will be alkaline). Equation 9. presents reaction that illustrates this case.

$$NaAlSi_3O_8 + H_2O \rightleftarrows HAlSi_3O_8 + Na^+ + OH^- \tag{9}$$

Chemical equilibrium will be moved to the right. As was mentioned before, the high pH in the reservoir inhibits adsorption of crude oil polar components and rock is water-wet.

A different situation is when formation water has very high salinity. High concentration of monovalent ion will lead to moving the chemical equilibrium of equation 10. towards right. Therefore, environment in the reservoir will be acidic. With lowering the pH, adsorption of both acidic and basic organic compounds will increase.

$$HAlSi_3O_8 + Na^+ \rightleftarrows NaAlSi_3O_8 + H^+ \tag{10}$$

In this case, the wettability of the rock will be mixed-wet (Strand et al., 2014).

2.6. Wettability alteration in sandstones

It was proved that main cause of oil recovery increase by implementation of the smart water is wettability alteration to more water-wet. That will increase the capillary forces and improve the microscopic sweep efficiency. Therefore, the most important is to analyse processes and parameters involved in wettability alteration.

Four mechanisms of altering wettability by polar crude oil components can be distinguished. These are: polar interactions, surface precipitation, acid/base interactions, ion binding. More than one mechanism at the same time takes place in oil/brine/rock interaction (Buckley et al., 1998).

Polar interaction usually occurs when a water film between oil and solid is absent. It is adsorption of asphaltenic fraction of the crude oil onto the mineral (i.e. clay) surfaces. Parameters that have influence on that process are: type of clay, the exchangeable cations, nitrogen content of the crude oil and the solubility of polar components (Buckley et al., 1998).

Surface precipitation is the adsorption of high molecular polar components come from crude oil. It depends on the solvent properties of the crude oil. If the oil is the modest solvent of asphaltene, the wetting alteration is improved. Indicators of the oil's solvent characteristic are oil density, gravity and refractive index. Oils considered as poorer solvents have high API gravity and low refractive index (Buckley et al., 1998).

Acid/base interaction controls oil/water and solid/water interface charge. In water solution, solid and oil interfaces become charged. Both surfaces may act as acids by giving up a proton, or as bases by gaining a proton (Cuiec, 1975). Charge of the surface depends on the dissociation reaction of acid/base components, which is determined by pH. If oil/water and solid/water interfaces has the same charge, repulsion forces will stabilize a water film. Stable water film induces strong water-wet rock. If interfaces between solid/water and oil/water have opposite sites, water film will be collapsed and rock surface will be altered by adsorbed acid/base components. Acid/base interaction mainly depends on brine composition (Buckley et al., 1998).

Ion-binding is the relation between charged surface and divalent or multivalent ions. When in a system occurs Ca^{2+} cations, they act as bridges between negative site of the rock surface and negative charged polar components. It can be dependent on temperature. It is main mechanism of oil/brine/rock interaction, when acidic crude oil is presented (Buckley et al., 1998).

In order to evaluate the potential for a crude oil to alter wetting properties of the rock gravity, acid number and base number has to be known. Buckley et al. (1998) illustrated the mechanism type dependency on acid/base number and oil gravity. The great wetting alteration had oil with low acid and base number, but with the highest API gravity. In this case main mechanism was surface precipitation. When oil was characterised by high acid number and low base number, the prime mechanism was ion-binding. It was also noticed, that with increasing BN, the altering wettability is enhanced.

2.7. “Smart water” flooding

Water flooding was considered as secondary recovery method. The mechanisms acted on increasing oil production are:

1) increasing the reservoir pressure,
2) displacing the oil by viscous forces.

In early days as a source of water was used nearby streams and rivers. However fresh water may react with some of the clay minerals and causes their swelling. It may lead to reduction of permeability, and to a failure of the waterflooding (Schumacher, 1978). Later, produced water along with oil was used to reinject it into reservoir. On offshore, seawater is used to improve oil recovery.

In order to increase oil recovery there were invented other methods, which are based on the original water flooding. To water-assisted techniques belong EOR methods, e.g. polymer flooding, surfactants flooding, microbial EOR and “smart water” flooding.

“Smart water” flooding is injection of modified water. These modifications, which makes water “smart” and leads to greater oil recovery, are lower salinity of water to value smaller than in formation water and reduce concentration of active ions (Ca^{2+}, Mg^{2+}). In next chapter proposed mechanisms and conditions for smart water flooding will be described.

2.7.1. Proposed mechanisms

The mechanism of low salinity waterflooding is not clearly defined. A lot of research teams are working on “smart water” flooding. They distinguished some processes that occur between oil/brine/rock complexes and may explain the low salinity phenomenon. It may be assumed, that most significant processes lead to altering the wettability of the rock surface. In this chapter some of the mechanisms will be introduced.

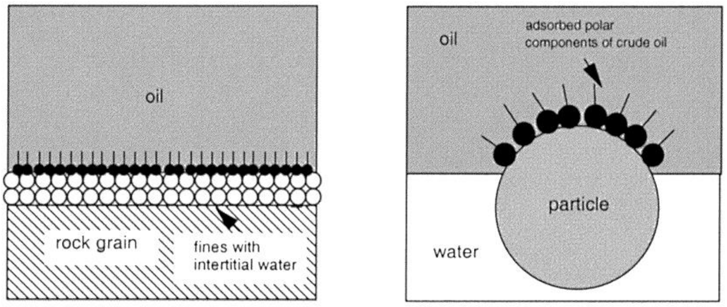
Fines migration

Tang and Morrow (Tang & Morrow, 1999) observed that during low salinity core waterflooding, the increased pressure drop across the core was presented. It was related to appearance of the fine in effluence. Fines are defined as small particles of the rock, mostly kaolinite.

Adsorbed polar components onto surface of sandstone is mainly related to clay minerals, thereby oil is adhered by fine particles. There are two main fines behaviour possibilities during waterflooding. First poses that fines adhere the crude oil, that remains as drops and stay as the trapped oil fraction. Second one is related to fine migration. The mixed-wet clay particles are mobilized by the flowing oil and locate at the oil-water interface. Mixed-wet fines migration from pores wall lower the residual oil [figure 2.10.].

Balance between mechanical forces and colloidal forces determine the attachment of fines to rock surface. Mechanical forces include capillary and viscous forces. Colloidal forces are a resultant of the van der Waals attractive forces and electrostatic repulsion (Israelachvili, 1991). During low salinity waterflooding, the double layer is expanded and fines are stripped away, thereby the increase of oil recovery is observed.

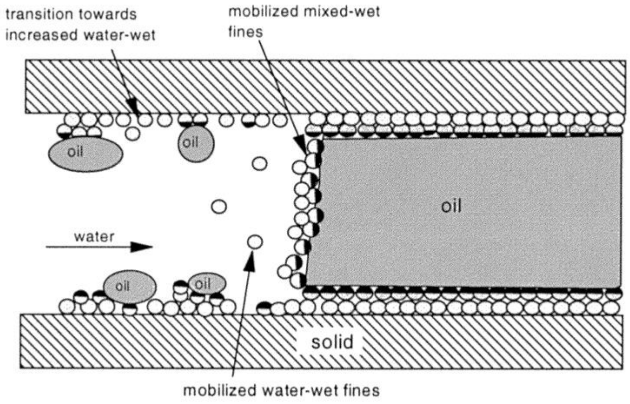
However some core flooding experiments showed that low salinity effect occurs also without fine production (Lager et al., 2008a; RezaeiDoust et al., 2011).



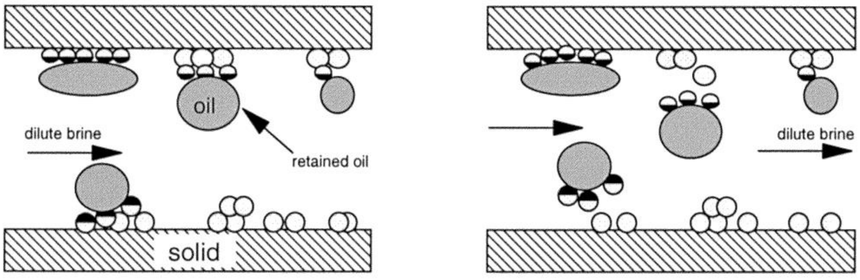
adsorption onto potentially mobile fines at low initial water saturation

mobilized particle at oil-water interface

a. Adsorption of Polar Components from Crude Oil to Form Mixed-wet Fines



b. Partial Stripping of Mixed-wet Fines from Pore Walls during Waterflooding



retained oil before injection of dilute brine

partial mobilization of residual oil through detachment of fines

c. Mobilization of Trapped Oil

Figure 2.10. Role of potentially mobile fines in crude oil-brine-rock interactions and increase in oil recovery with decrease in salinity (Tang & Morrow, 1999).

Increase in pH

Observations in many core flood tests showed that after injection of low salinity water the pH has increased. The pH of the effluent brine range from 6-7 to 9. This elevation is caused by two processes: ion exchange and dissolution of carbonates (Tang & Morrow, 1999). Austad explained the local pH changes at the water-clay interface in following way. After injection of low salinity water, the Ca^{2+} ion concentration in water is reduced. Then the substitution of calcium cations by H^+ is carried out [equation 11.]. It leads to increase of pH, what induces desorption of acid/base components of crude oil (Austad et al., 2010). Other studies proved that pH may be elevated up to 3 pH units. The strongest effect was observed, when high-concentrated NaCl brine was injected. The lowest increase of pH was noted for the "smart water" with calcium cations (RezaeiDoust et al., 2011). Ca^{2+} cations react with OH^-, what leads to reduction of the low salinity water efficiency [equation 12.]. Equilibrium of reaction showed on equation 11. will move to the left, due to high concentration of Ca^{2+}.

$$Ca^{2+}Clay + H_2O \rightleftarrows H^+Clay + Ca^{2+} + OH^- \tag{11}$$

$$Ca^{2+} + OH^- \rightleftarrows [CaOH]^- \tag{12}$$

Dissolution of the calcite materials may result enhanced oil recovery. Usually in sandstone calcite can occur as a cementing material (Ramez et al., 2011). This process is illustrated by equation 13. However, the dissolution of carbonates is a slow process and ion exchange plays a major role in elevation of the liquid phase pH (Lager et al., 2008a).

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3{}^- + OH^- \tag{13}$$

According to McGuire low salinity flooding is acting similar to alkaline- flooding in high pH (McGuire et al., 2005). Alkaline flooding leads to lowering the interfacial tension between the fluids. Furthermore due to increasing pH, the water wetness is enhanced. Similarity between alkaline flooding and smart water flooding is that they affect the crude oil. In high-pH environment charges of oil components are changed. The polar material of crude oil reacts with ions present in water. The product of this reaction is soap, that play role of surfactant. This leads to lower IFT and alters the wettability. Surfactants cause the oil-in-water emulsification. Occurrence of divalent cations (Ca^{2+}, Mg^{2+}) in injection water has negative effect on increasing oil recovery. These cations react with surfactants, caused their precipitation. Nonetheless in low salinity fluid concentration of divalent cations is low. Due to this effect of surfactant is preserved (McGuire et al., 2005). Nonetheless, lowering of IFT was not observed.

Multi-component ionic exchange (MIE)

Lager presented the new possible mechanism that stays behind the low salinity effect. Multi-component ionic exchange can be defined as a cation exchange between mineral surface and the injected low salinity fluid. There were introduced two evidences to prove the advisability of the MIE mechanism. The first one is that in formation water the divalent cations have to be present, what is described earlier in section 2.5.1. The second proof is the depletion in the divalent cations concentration, especially Mg^{2+} and less Ca^{2+}, showed in effluent of the brine during low salinity core flooding. The reduction in Mg^{2+} is result of the strong divalent cations adsorption on the rock surface (Lager et al., 2008a; Lager et al., 2008b).

There are existing eight mechanisms related to adsorption of crude oil components on the clay surfaces. Only four of them appear during low salinity waterflooding. They are: cation exchange, ligand bonding, cation bridging and water bridging. The mechanisms schemes are showed on figure 2.11.

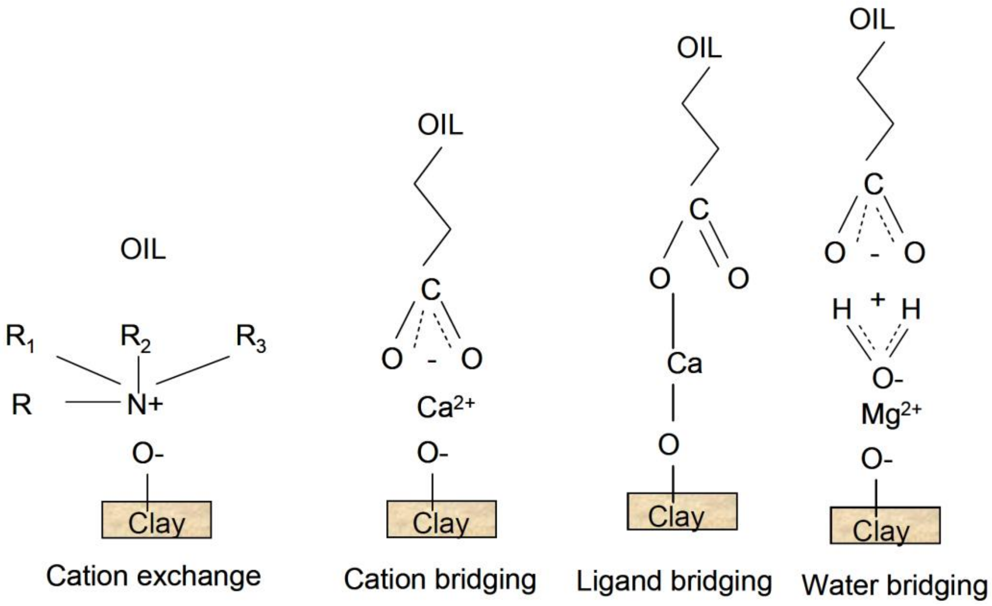


Figure 2.11. Clay/Oil attraction by divalent cations (Lager et al., 2008b).

Polar compounds from oil (resin, asphaltene) are bonded with clay surface either by direct adsorption or through multivalent cations that creates the organo-metallic complexes. MIE mechanism occurs after injection of low salinity water. The organic-metallic complexes and organic polar compounds are replaced by the simple cations (e.g. monovalent cation as Na^+). That leads to alter wettability (from mixed-wet to more water-wet) and increase in oil recovery (Lager et al., 2008a).

It was performed field test in an Alaskan reservoir that bears out MIE mechanism. In result of this test the concentration of Mg^{2+} in produced water dramatically decrease. Similar observation was done on Ca^{2+}, but the reduction was slighter. Simultaneously, concept that pH rising and fine migration are the major mechanism during low salinity waterflooding was rejected (Lager et al., 2008b).

Austad et al. (2010) contest validity of the MIE mechanism. They suggested that reduction in concentration of divalent cations in effluent may be caused by precipitation of $Mg(OH)_2$ and $Ca(OH)_2$. He showed that with growing pH of the fluid the solubility of the $Mg(OH)_2$ and $Ca(OH)_2$ decreasing. Figure 2.12. shows the change in Mg^{2+} concentration in produced water during low salinity water flooding test performed by BP (Lager et al., 2008b). Austad et al. explained the curve (Austad et al., 2010). First, the concentration of magnesium cations is constant. Due to desorption of that ions from clay surface, the concentration sharply increase. Simultaneously, the pH of fluid phase is elevated (according to equation 11.). The alkaline environment contributes to dilution of the Mg^{2+} solubility and $Mg(OH)_2$ precipitations occurs. Finally, the equilibrium in the system has been established and concentration of magnesium cations is back to stable state. To conclude, reduction of the Mg^{2+} may be caused by solid precipitation and decreasing of brine pH, what results in oil compound desorption.

Furthermore, low salinity effect can be achieved using the brine containing any divalent cations (Austad et al., 2010).

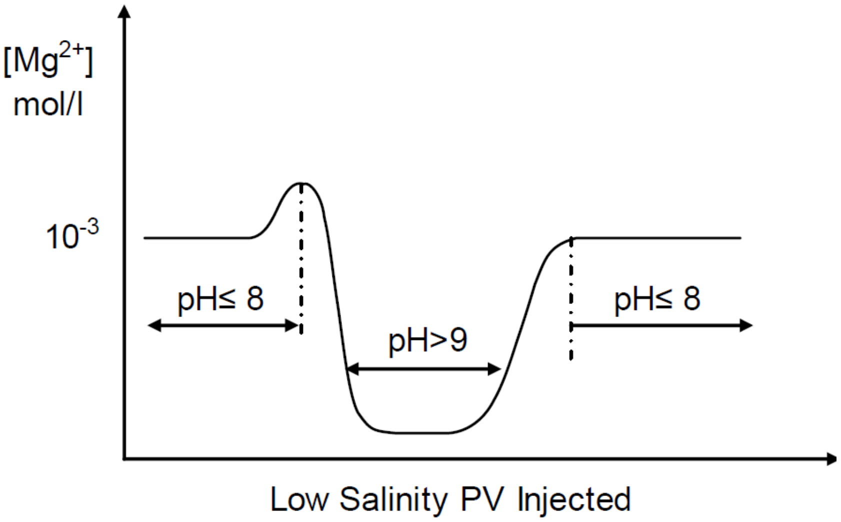


Figure 2.12. Schematic change in Mg^{2+} concentration in the produced water during a low salinity flood. The concentration of Mg^{2+} is suggested to be quite similar for the initial FW and low saline brine (Austad et al., 2010).

Double-layer expansion

Impact of double-layer expansion on IOR was proposed by Ligthelm (Ligthelm et al., 2009). The clay minerals and crude oil usually have the negative electrical charge, what results in strong repulsive forces. However, the multivalent cations presented in formation water act as bridges between minerals surface and crude oil. In high concentration of multivalent cations (Mg^{2+}, Ca^{2+}) polar oil compounds will adsorb on the clay surface. That will lead to local oil-wetness.

The electrical double-layer (EDL) is the structure of ions in a solvent (i.e. formation water) that are next to charged surface (i.e. clay surface) (Lee et al., 2010). EDL is electrically neutral. Scheme of the EDL is presented on the figure 2.13. The wettability of the rock is determined by the stability of water film. Stable water film depends on EDL thickness and results in water-wet rock.

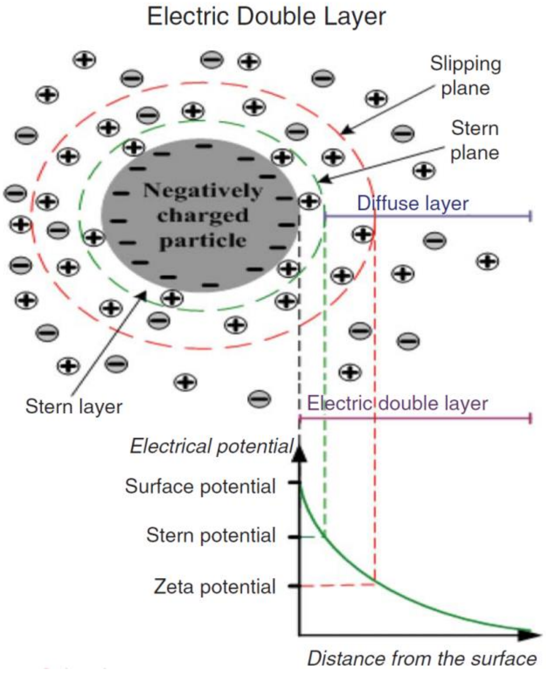


Figure 2.13. Scheme of the EDL (Nasralla et al., 2012).

Zeta potential is related to thickness of the electrical double-layer and surface charge at the oil/brine and rock/brine interfaces and is defined as the potential at the shear plane of the electrical double-layer (Nasralla et al., 2011).

Low salinity brine contains less divalent cation that reduces the screening potential between cations. It leads to increase of a ζ-potential and expansion of the electrical double layer. Continuing of low salinity flooding, the repulsive forces between the oil phase and clay surface will exceed the binding forces that form the organo-metallic complexes. The oil will be desorbed from the clay surface and enhanced oil recovery will be achieved.

However, if the salinity will be reduced further, the repulsive forces inside clay minerals will increase above the bonding force. That may cause deflocculation and formation damage. Probably, cores flooding with fine migration registered were carried out causing the formation damage (Ligthelm et al., 2009).

Expansion of double-layer is affected by the ionic strength of the water and cation type. Compared to Na^+ divalent cations like Ca^{2+} or Mg^{2+} more influence on the ζ- potential reduction (Farooq et al., 2011). Furthermore, Buckley et al. carry out the experiments with different concentration NaCl in injected water. It turned out that lower concentration of the Na^+ cations effects in stronger negative charge of brine/oil interface, expansion of double-layer and finally greater oil recovery (Buckley et al., 1989). According to Nasralla et al. higher concentration of Na^+ conduct higher oil recovery compared to brine with lower concentration of Ca^{2+} or Mg^{2+}. However, NaCl injection may not cause the great expansion of double-layer. Formation water contains also divalent cations that cushion effectiveness of low salinity flooding. But after injection few PV of NaCl, the effect could be greater due to dilution of the formation brine (Nasralla et al., 2011).

It was noticed, that low salinity treatment did not always work in tertiary mode. That shows that double-layer expansion is not working during the tertiary recovery. It can be caused by lack of the oil film continuity. Other reason may be not strong enough repulsive forces to displace oil after high-salinity treatment (Nasralla et al., 2012).

Desorption of crude oil polar components

In 2010 Austad proposed a new chemical mechanism based on adsorption and desorption of polar components (Austad et al., 2010). By desorption of polar components, the wettability alteration at the clay surface was obtained. Precisely, a two-step mechanism causes change of wettability. Firstly, when low salinity water displacing the high salinity brine, the H^+ cations replacing the Ca^{2+}, that are adsorbed at negative sites of the clay. This reaction creates the alkaline environment adjacent to the clay surface. Secondly, the proton transfer reaction between adsorbed basic and acidic components takes place.

First reaction is presented on equation 11., it was described in this chapter before. However it is important to mention, that reaction proceeds slowly and it is exothermic (Aghaeifar et al., 2015).

$$Ca^{2+}Clay + H_2O \rightleftarrows H^+Clay + Ca^{2+} + OH^- + heat \tag{11}$$

Below are presented two equations (14.; 15.) illustrating the proton-transfer reaction on basic and acidic polar components of crude oil. These reactions are known as very fast (Aghaeifar et al., 2015). The protonated form of the non-dissociated carboxylic acid (RCOOH), represents the acidic polar components in crude oil. The ammonium ion (RNH^+) represents basic polar components. Most of them are present in the resin and asphaltene fractions. The values of pK_a (acid dissociation constant) of the naphthenic acids and pyridines (base) are almost the same (4.9 and 4.7 respectively). This means that both of them will act similarly in various pH (Austad et al., 2010).

$$R_3NH^+Clay + OH^- \rightleftarrows Clay + R_3N\!: + \ H_2O \tag{14}$$

$$RCOOHClay + OH^- \rightleftarrows Clay + RCOO^- + \ H_2O \tag{15}$$

Studies on quinoline (base) adsorption onto kaolinite and montmorillonite shows that the maximum adsorption occurs at pH around 4. Moreover, that process is 100 times greater onto montmorillonite than onto kaolinite (Burgos et al., 2002). The adsorption onto clay minerals increases according to the succession: kaolinite < illite < montmorillonite (Austad et al., 2010). Acidic compounds adsorb maximally at pH close to 5 (Madsen & Ida, 1998). Adsorption increases with decreasing pH, increasing ionic strength and presence of Ca^{2+} ions which may form bridges between clay surface and polar components. Calcium ions have also affinity to the clay surface, what is enhanced if the concentration in the formation water is increasing. Low salinity water is reducing the concentration of the Ca^{2+} and desorption of cations can be observed. Hydrogen ions can be adsorbed due to its strong affinity towards the clay and causing elevation of the pH. This is the main cause leading to desorption of the polar organic components [figure 2.14.].

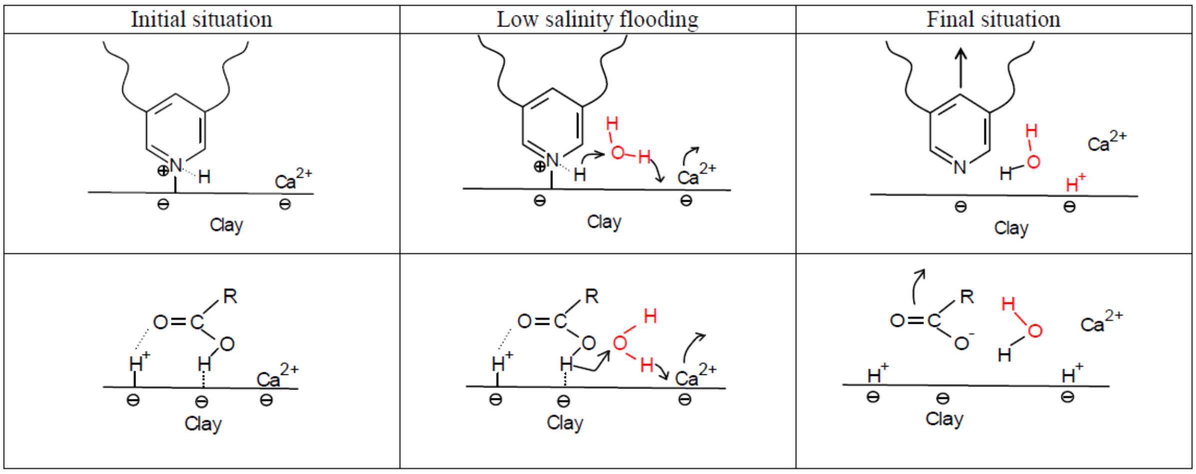


Figure 2.14. Proposed mechanism for low salinity EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5 (Austad et al., 2010).

In order to observe the effect of low salinity, initially reservoir has to be mixed-wet (Reinholdtsen et al., 2011). “Smart water” treatment is causing alteration of the reservoir wettability to more water-wet conditions. It was proved that high water-wet condition can induce no low salinity effect response. The alteration increases the capillary forces and improves the microscopic sweep efficiency. It is enhanced by spontaneous imbibition of low salinity water in pores that was bypassed before (Aghaeifar et al., 2015). Figure 2.15. represents the behaviour of low salinity and high salinity water.

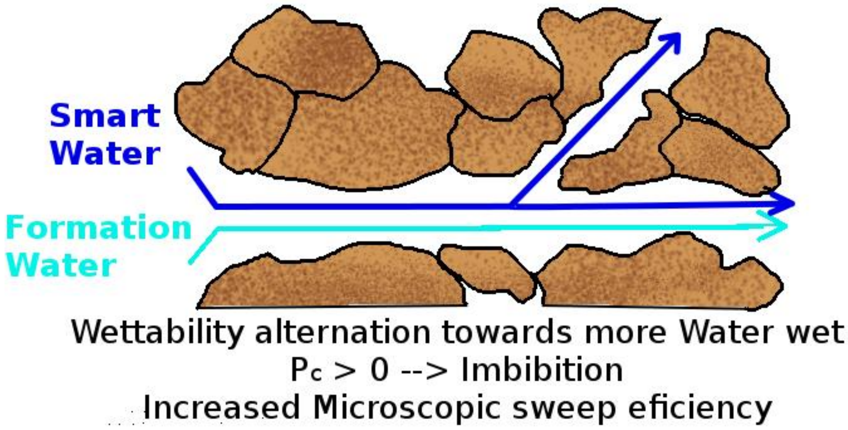


Figure 2.15. Smart water imbibition (redrawn from Puntervold (2015)).

The temperature has significant influence on the effectiveness of the “smart water” flooding. With increased temperature, the pH gradient decreases. High temperature (T_{res}>100°C) will decrease the pH gradient, caused by exothermic character of the equation 11. In this situation, a chemical equilibrium will be shifted to the left, and concentration of OH^- will be low. High-temperature may cause precipitation of anhydrite that could inhibit Ca^{2+} desorption. During core flooding tests Aghaeifar at al. (2015) found that the concentration of SO_4^{2-} and Ca^{2+} are similar in effluent. They explained that phenomenon as effect of dissolution of the anhydrite. They performed waterflooding test four times, each in different temperatures: 40°C, 90°C, 130°C and 40°C. The results show reduced pH gradient in two first tests and increase in the last one. They explained it, that during two first tests the anhydrite dissolution inhibit Ca^{2+} desorption and at the same time lower pH gradient resulting in reducing LS effect (equation 11. is moved to the left). In two next tests, the LS effect could be observed because of fact, that waterflooding in 40°C and 90°C have completely dissolved anhydrite. However with increasing temperature, the effect of LS waterflooding is decreased. In conclusion, high temperature combined with high Ca^{2+} concentration in formation water may result in too water-wet conditions in the reservoir and as a consequence no-enhanced oil recovery. Similar effect has presence of the anhydrite, that during low salinity is being dissolved and concentration of calcium cations is rising. (Aghaeifar et al., 2015).

2.7.2. Conditions for low salinity effect

To conclude proposed mechanisms of low salinity water flooding, the conditions were listed in previous chapters. In many experimental works it was found out what affects the LS effect. Researchers are not fully agreed with mechanisms, but they had similar results in their work and the list of parameters and circumstances could be identified. Such list is presented below.

1. **Porous medium:** Reservoir rock has to contain clay minerals. Core flooding on the clay-free rock shows no low salinity EOR effect (Tang & Morrow, 1999). Clays minerals had different CEC, and this is the factor, that allows ions to be adsorbed onto surface. As was mentioned before, the type of clay mineral plays the role. The adsorption is bigger onto montmorillonite, than illite and the lowest rate has kaolinite. Also sandstones containing dolomite show enhanced oil recovery after low salinity water flooding (Pu et al., 2008). Contribution of plagioclase has also impact on LS effect. Depending on the formation water salinity, plagioclases may have beneficial or opposite influence (it was described in section 2.5. "Initial wetting state").
2. **Oil:** Crude oil has to contain polar components- acids and bases. There are presented in higher fractions of oil, like resins and asphaltenes. It was observed no effect in LS experiments, when refined oil was used (Tang & Morrow, 1999).
3. **Formation brine:** High salinity formation water has to be present in pore space. Especially high concentration of divalent cations has impact. Active cations, like Ca^{2+} during LS water flooding could be desorbed and acid/base proton transfer reactions may take place (Ligthelm et al., 2009).
4. **Injected water:** At the beginning it was believed, that injected fluid has to have low ionic strength to obtain enhanced oil recovery. The salinity of the water used to tests is between 1000-2000 ppm, but effect was observed also at salinity up to 5000 ppm (Webb et al., 2004). However, more important is low concentration of the divalent cations like Ca^{2+} and Mg^{2+} (Jerauld et al., 2006; Tang & Morrow, 1999).
5. **Initial wetting state:** It was proved, that rock has to be mixed-wet. If the reservoir is strongly water-wet then no effect will be obtained during "smart water" flooding. The wettability is strongly depended on the pH of formation brine. With decreasing pH,

the adsorption of the crude oil polar components and Ca^{2+} cation increases. That makes rock more oil-wet.

6. **Temperature:** Most of the experiments were performed in temperature below 100°C. However, this parameter may have impact on LS effect. Aksulu et al. (2012) performed the LS core flooding in different temperatures: 40°C, 90°C, and 130°C. It was observed that large pH gradient, ranging 3 points, was achieved at 40°C. At 130°C pH gradient was a little above 1. Moreover, at 130°C desorption of active cations (e.g. Ca^{2+}) takes more time than in low temperature. The low salinity effect was obtained at 40°C and 90°C, but not at 130°C. The influence of temperature on LS effect should be investigated more precisely (Aksulu et al., 2012).

3. FIELDS OVERVIEW

In this chapter "smart water" flooding theory was implemented to field cases. The first case describes the log-inject-log test implemented on sandstone reservoir. Next, the Alaska's fields are described and tested using single well chemical tracer method. Outcomes were promising. Following that Snorre field, that is located on the North Sea, is discussed. In the end, one of the Russian oil field, Pervomaiskoye, is presented. On the Snorre field was performed SWCT test and some core flooding experiments. The results were negative in respect to low-salinity flooding. The Pervomaiskoye reservoir was investigated using laboratory core flooding tests, field experiments and finally 3D modelling and simulation.

The aim for presenting these field cases is full understanding of the "smart water" method. Thanks to these tests, comparison of laboratory experiments and field tests may be performed.

3.1. Log-Inject-Log test review

In order to verify whether the low-salinity water injection will enhance oil recovery in the near-well zone the log-inject-log test was performed. The description, results and analysis was published by Webb et al. (2004).

3.1.1. Reservoir description

The test was carried out on the fine-grained sandstone reservoir interbedded with shales. Content of quartz ranges from 70% to 95%, while the remainder is kaolinite, plagioclase, illite and smectite. The reservoir is characterized by average porosity equal to 20% and horizontal permeability range between 200 mD and 700 mD. Gross thickness of the interval is 150 m, while net to gross varies from 65 to 70%.

Oil viscosity ranges from 0,4 cP to 50 cP and gravity from 33 °API to 12 °API. Water saturation in the reservoir is 23%. Formation water has very high salinity equal to 250 000 ppm.

3.1.2. Test procedure

Logging will be performed by PNC method. Pulsed neutron capture log measures the time of fading away a thermal neutron pulse. Chlorine has great cross section intercept of short-lived neutrons. Through measuring neutron-lifetime, concentration of the chlorine in the brine may be calculated. The same way, assuming constant porosity, water saturation can be obtained (Holstein & Lake, 2006). The production log tool was equipped with spinner, gradiometer, pressure and temperature monitors.

With the aim of choosing the right injector following criteria were applied: vertical, dry oil producer, good reservoir quality and undamaged near-well region, formation homogeneity, never implemented fracturing and acidization.

There were used three different salinities of the injected brine: 220 000 ppm (high-salinity), 120 000 ppm (intermediate salinity) and 3 000 ppm (low salinity). Brines were injected below fracturing pressure. The injection rate was sufficiently low to avoid viscous stripping of the oil that could cause lowering the S_{orw}. Logging tool run every hour at the rate of 10 feet/minute and was repeated three more times.

Abbreviated description of the procedure is presented below [figure 3.1.]:

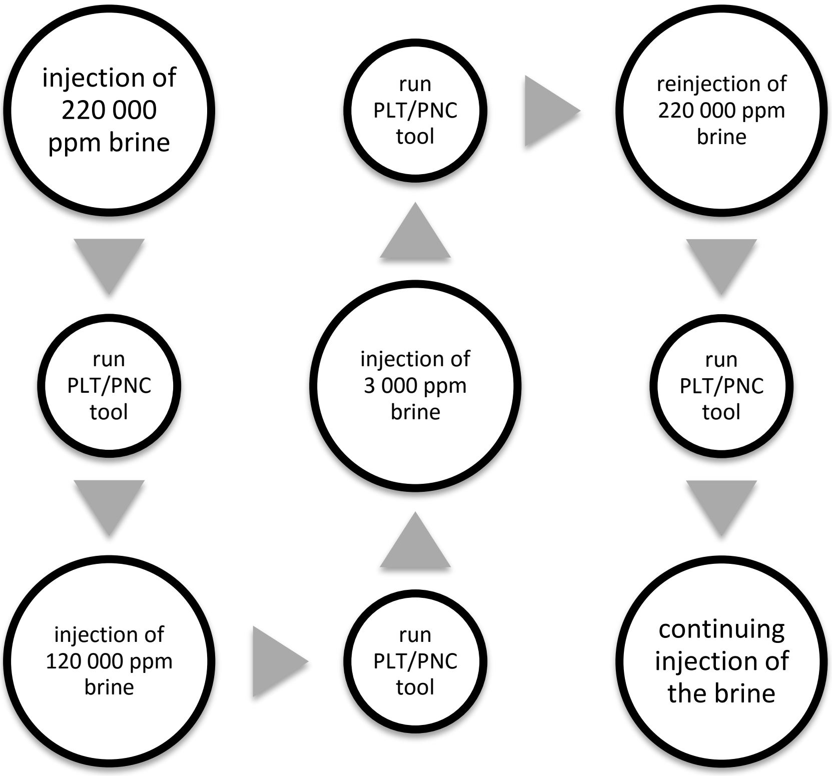


Figure 3.1. Log inject log test procedure (PLT- production log tool; PNC- pulsed neutron capture log).

First, the PNC log was run to get a standard reading. Then, water with different salinity has been injected during logging. When initial formation fluids are replaced by the injected one, the reading is not changing. The S_{orw} was achieved. The difference in the PNC logs between two successive brines was used to calculate remaining oil saturation (Holstein & Lake, 2006).

3.1.3. Results and conclusions

There is significant oil quantity produced using low-salinity water injection compared to high-salinity brine. Depending on the interval, the remaining oil saturation ranged from 30% to 50%. In relation to the high-salinity waterflooding, the low-salinity reduces the oil saturation of about 10-20%, in some area- even 50%. This test shows that laboratory core flooding has application to the near-well area of the field.

3.2. Alaska's North Slope

Single well chemical tracer tests (SWCTT) were performed to evaluate the low salinity effect in field area of Alaska's North Slope. It was described by McGuire et al. (2005). Results of their findings are shown below.

3.2.1. Reservoirs description

The first two tests were performed on the Borealis Pool. Reservoir rock is the Kuparuk C Sand of the Prudhoe Bay Unit (McGuire et al., 2005). It consists of mid- to lower marine shore sediments. Tested interval is from 2758,44 m to 2764,54 m depth. The average porosity is equal to 16% and the reservoir temperature is 66 °C (*Alaska Oil and Gas Conservation Commission*).

Further, test was completed on the Prudhoe Bay Field, Ivishak sandstone. Reservoir rock age is Triassic (McGuire et al., 2005). Deposition environment is complex of fan, alluvial fans and deltas (*Alaska Oil and Gas Conservation Commission*). First place that was tested is Eileen Area was. The perforation zone is about 33 m and reservoir temperature is 103 °C. Second tested well was placed in the Western Operating Area. Well is penetrates 8 m of net vertical interval under deviation 67°. Average porosity of that sandstone is 22% (McGuire et al., 2005).

Last test was performed in the Endicott Field, Duck Island Unit. The reservoir rock was fluvial Kekiktuk sand, that average porosity is 24% (McGuire et al., 2005). The age of the sediments is Missisippian (Lower Carboniferous). Perforated interval is 18,3 m thick and reservoir temperature is 100 °C.

3.2.2. Test procedure

Single well chemical tracer (SWCT) test is a method used to determine the reservoir fluid saturation, especially residual oil saturation. The SWCT test can measure oil/water fractional flow, when phases are mobile. It can be also used to measure the effectiveness of EOR methods (Holstein & Lake, 2006).

The SWCT method procedure consists of injecting the brine mixed with chemical tracers and then producing back the chemicals. First, the fluid with 1% volume of an ester (e.g. ethyl acetate) is injected. Then, the brine is pumped, until the ester reaches the investigated area (3 m to 4,5 m). Injected water is also labelled by material balance tracer (usually iso-propanol or normal-propanol). The next step is to shut in the well for several days, depends on the reservoir temperature and the reactivity of the ester. Throughout this time, part of the ester reacts with water and forms an ethyl alcohol. Usually, conversion of the ester (primary tracer) to ethanol (secondary tracer) ranges from 10% to 50%. After that, well is producing until no tracers are presented. During that, the secondary and primary tracers are separated. The ethanol is produced with brine and ester production is delayed because of the presence of the residual oil (ethyl acetate is more soluble in oil than in water). Produced fluids are sampled at regular intervals and analysed by gas chromatography (Holstein & Lake, 2006). The schematic SWCT test performance is shown on the figure 3.2.

In order to calculate the residual oil saturation, the separation ratio of primary and secondary tracers is used. If the separation ratio is high, the high S_{or} is obtained. When separation ratio is low, the S_{or} is also lower.

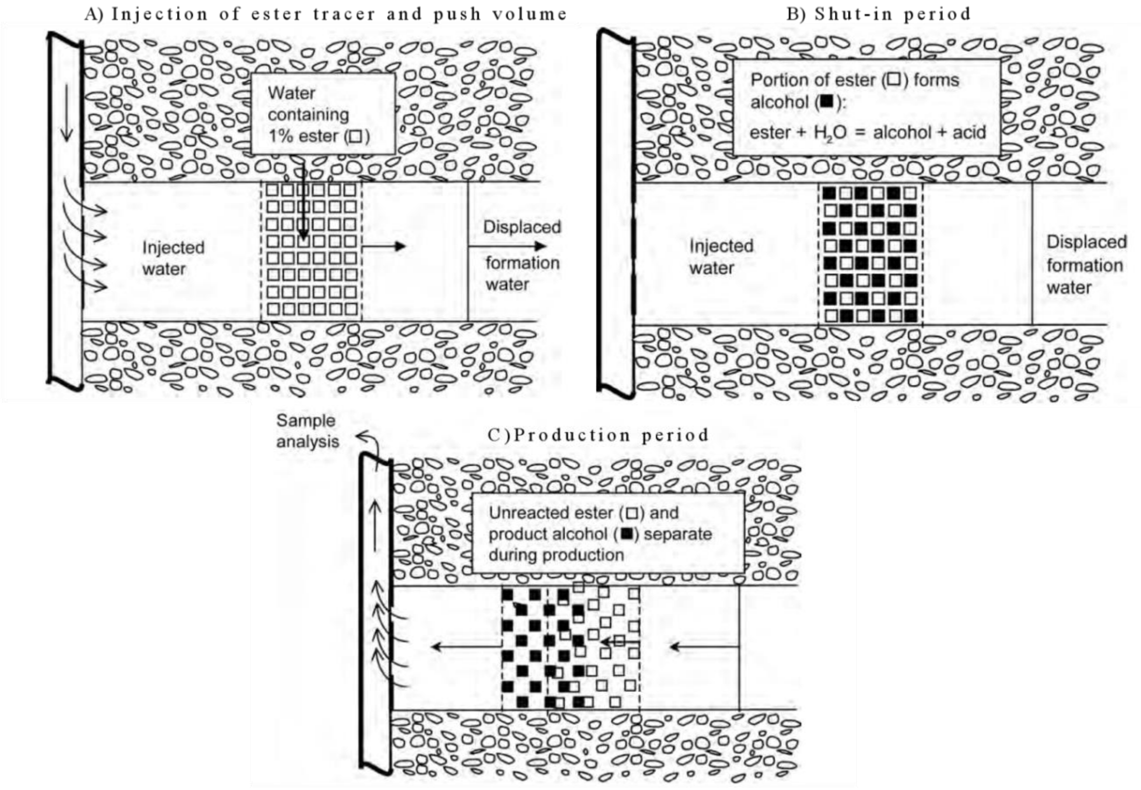


Figure 3.2. Steps of the SWCT test (Holstein & Lake, 2006).

First test was performed to measure S_{orw} to high-salinity water (23 000 ppm). It was conducted according to the following steps:

I. Preparation of the reservoir- reduction of the oil saturation to residual.
II. Injection of the high-salinity brine with ethyl acetate, normal propanol, iso-propanol.
III. Injection of the high-salinity brine with trace of iso-propanol.
IV. Shut-in the well for several days.
V. Production and water sampling.
VI. Results interpretation- calculation of the S_{orw}.

The same scheme was applied to the second test, but started in point II. Injected water was low-salinity (2 500 ppm). Tests were performed on 4 different sandstone reservoirs.

3.2.3. Results and conclusions

The results are collected and presented in table 4.

Table 4. SWCT test results on Alaska's North Slope fields.

Test description		**Test size [bbls]**	**Depth of investigation [m]**	**Measured S_{or}**
sandstone	test			
L-122 Kuparuk	Test 1. (HS)	600	3,66	21% ± 2%
	Test 2. (LS)	600	3,96	13% ± 2%
L-01 Ivishak	Test 1. (HS)	1	2,44	19% ± 2%
	Test 2. (LS)	1	2,44	15% ± 2%
3-39A Kekiktuk	Test 1. (HS)	1 800	4,27	43% ± 3%
	Test 2. (LS)	1 600	4,27	34% ± 3%
N-01A Ivishak	Test 1. (22 000 ppm HS brine)	1	4,57	21% ± 2%
	Test 2. (7 000 ppm brine)	1	4,57	21% ± 2%
	Test 3. (2 200 ppm LS brine)	1	4,57	17% ± 2%

The result shows the increase of oil recovery after LS water flooding in every reservoir. The largest residual oil saturation reduction was on Kekiktuk sand interval and was about 9% PV. The enhanced oil displacement is considered to be almost whole effect of low salinity fluid injection. The same conclusions are made to the remaining intervals. The residual oil saturation reduction represents 18%, 16%, 19% and 8% increase in oil recovery compared to high-salinity brine respectively to Kuparuk, L-01 Ivishak, Kekiktuk and N-01A Ivishak sand intervals. These tests confirm that “smart water” flooding is effective in near-well scale.

McGuire et al. (2005) suggested that application LS flooding may be economically problematic. The large initial investments are required, and benefits are shown after several years. In addition, the verification of this method at pattern level was never done.

3.3. Snorre field

To evaluate the impact of the low-salinity brine flooding, the laboratory test and SWCT test at the Snorre field were carried out. The effect of these works was described by Skrettingland et al. (2011). Laboratory experiments were retaken by other research group and results were described by Reinholdtsen et al. (2011). Performed experiments are described below.

3.3.1. Reservoirs description

Snorre is an oil field in the North Sea. The reservoir lies on 2000-2700 m depth. The maximum gross thickness is even 1000 m and net to gross is approximately 0,45. The initial reservoir pressure was 383 bara, while the reservoir temperature is 90 °C.

It consists of sandstones from Statfjord and Lunde formation that are age of the Lower Jurassic and Late Triassic respectively. The quality of the field is described by average porosity, that is 23% and permeability, that range from 100 mD to 4 000 mD. The clay content is between 5% and 35%. The initial wettability is defined as neutral-wet, and the average water saturation is 32% (*Norwegian Petroleum Directorate*; Skrettingland et al., 2011).

3.3.2. Core flooding and SWCT tests performed by Skrettingland et al. (2011)

3.3.2.1. Test procedure

For laboratory test, cores from three formations were used (Upper and Lower Statfjord and Lunde). Cores were properly prepared and cleaned. After that they were flooded by formation brine and the permeability, initial oil saturation was measured. There were performed nine low-pressure and five reservoir-pressure core flooding. First, the seawater had been injected until no longer was oil produced, then low-salinity seawater was used and finally the low-salinity NaCl brine was pumped. The concentration of salts ranged from 3 500 to 375 ppm. In some cases the alkaline injection was implemented as a final stage.

Next the SWCT test was executed on the Upper Statfjord formation. The SWCT procedure was described earlier in section 3.2.2. The tracers used in this test were: ethyl acetate, n-propanol and iso-propanol, while secondary tracer was ethanol. Three tests were performed: after injection seawater, low-salinity brine and again seawater.

3.3.2.2. Results and conclusions

Laboratory tests showed that seawater flooding and following low-salinity phase did not increase the oil recovery significantly. All the experiments showed very low to none impact on oil production. For Upper Statfjord, increased oil recovery by low-salinity water injection was equal to 2%, while the applied alkaline method was not effective at all. The Lower Statfjord formation showed slightly more response to seawater than to low-salinity brine. There were no reactions to alkaline flooding. For Lunde formation none of the experiments effected in enhanced oil recovery.

The SWCT test results show correlation with laboratory’s conclusions. The reduction in residual oil saturation was investigated and its value is 2% of PV.

Skrettingland at al. (2011) suggested that minor improve in oil recovery is caused by the initial wetting state. They explained, that initial wetting condition is close to state after seawater flooding. Therefore, the reduction in oil saturation is fully realized (with minor influence on S_{or}) and no LS effect was occurred.

3.3.3. Core flooding performed by Reinholdtsen et al. (2011)

3.3.3.1. Test procedure

For experiments two cores from Lunde Formation were used. They are characterized by high content of clays (average: 15%) and plagioclases (average: 33,7 %). Average porosity and permeability is 26,6% and 629 mD. Waterflooding was performed using 5 types of brine: formation brine (35 138 ppm), seawater (33 400 ppm), diluted formation brine (7 028 ppm), 500 ppm NaCl water and 26 800 ppm $CaCl_2$ brine. The crude oil had AN equal to 0,07 mgKOH/g and BN= 1,23 mgKOH/g and was saturated with CO_2. Initial water saturation was established at 20%.

3.3.3.2. Results and conclusions

For first core, the increase in oil recovery occurred when FW was switched to SW (3% of OOIP), and no effect was obtained after switching for LS water. Second core flooding shows slight increment of oil recovery after changing FW to SW (1% of OOIP); however low-salinity water and 26 800 ppm $CaCl_2$ solution injections did not show any results.

Results were similar to these obtained by Skrettingland et al. (2011). The low salinity was taken by seawater. Even injection of $CaCl_2$ brine did not get any effects due to high pH. Ca^{2+} cations at low pH can take the place of the basic materials adsorbed onto clay and alter wettability to more water-wet. According to Reinholdtsen et al. (2011) the initial water-wet conditions was the reason of the lack of low-salinity effect. This is the result of high pH in the reservoir. At pH above 7, that was reached in discussed experiments, the adsorption of the basic organic materials onto clay are small. The active protonated basic and acidic materials are decrising with increasing pH. A factor resulting in high pH is presence of plagioclase in the reservoir rock. H^+ ions from water replace the cations, that apper in plagioclase structure (e.g. Na^+, K^+, Ca^{2+}) and water with pH ranged between 7,5 and 9,5 is received (Friedman et al., 1992; Reinholdtsen et al., 2011)

3.4. Pervomaiskoye Field

For Pervomaiskoye Field core flooding, field experiments and simulation of low-salinity water injection were performed. Results were described in article written by Akhmetgareev & Khisamov (2015).

3.4.1. Reservoir description

The Pervomaiskoye Field is a Russian field located in central part of the country. Field is divided to five blocks. The central block consists of five layers (four oil bearing layers and one water saturated). Gross thickness of the layers varies between 20 and 40 m and net thickness is 8-18 m. External block is composed of only one or two oil layers and one water-saturated. The gross thickness of these formations ranges from 10 to 30 m, while net thickness is 1-8 m. Two upper layers are called Kynovsky horizon, and three lower layers are Pashiyski horizon. Reservoir rock is considered as Devonian.

The average porosity and permeability measured from core samples are: for first core- 20,4 % and 432 mD; for second core- 17,1% and 291 mD. Temperature of reservoir is 30°C.The reservoir rock is made by sandstone (65%) and siltstone (35%). It is composed of the quartz c. 95%, clay 0,1 % to 0.8 % and other minerals.

The field was discovered in 1958, for the first seven years oil was produced using primary oil recovery. Water used to injection in part of the wells was taken from the Kama River, which is considered as low-salinity water (fresh water). It is estimated, that 30% of used water was LS. The number of producers is 189, while injectors are 127. At the moment oil recovery factor reaches 0,482.

3.4.2. Test procedure

For core flooding experiments water from Kama River was used (848 ppm) and high-salinity water (252 728 ppm), which is actually formation brine. Core taken from Kynovsky horizon was used for test. The oil that was used is light oil from the reservoir. Test was performed according to the standard procedures in room temperature.

In 2005 field experiment started. Seven injectors began pumping the low-salinity water. These wells had injected the HS water for the first 20-25 years (depend on the well). Oil recovery from corresponding producers was analysed.

After that 3-D model of displacement in a five-spot pattern was performed. For simulation the black-oil model was used. The simulation was based on the two supposed mechanisms of low-salinity effect, which are fine mobilization and migration, alteration of the wettability. Three cases were under consideration: five-layer cake, three-layer cake and two-layer cake.

3.4.3. Results and conclusions

Results from laboratory test show that fine migration was observed only in first core (clay content 0,8%). Simulated data demonstrates increase in oil recovery about 12% and 19% respectively for first and second plug. Akhmetgareev et al. (2015) explained that in first core the main mechanism was formation damage, migration of clay particles and blocking pore throats. This resulted in twofold decrease in water relative permeability. Mechanism, that took place during second experiment is wettability alteration. It leaded to decrease in oil saturation two-times.

The field test showed significant increment in oil recovery after injection LS brine. Figure 3.3. ilustrates dependence of the oil recovery factors and injected pore volume of water (PVI). Values show, that oil recovery was enhanced about 5-9%.

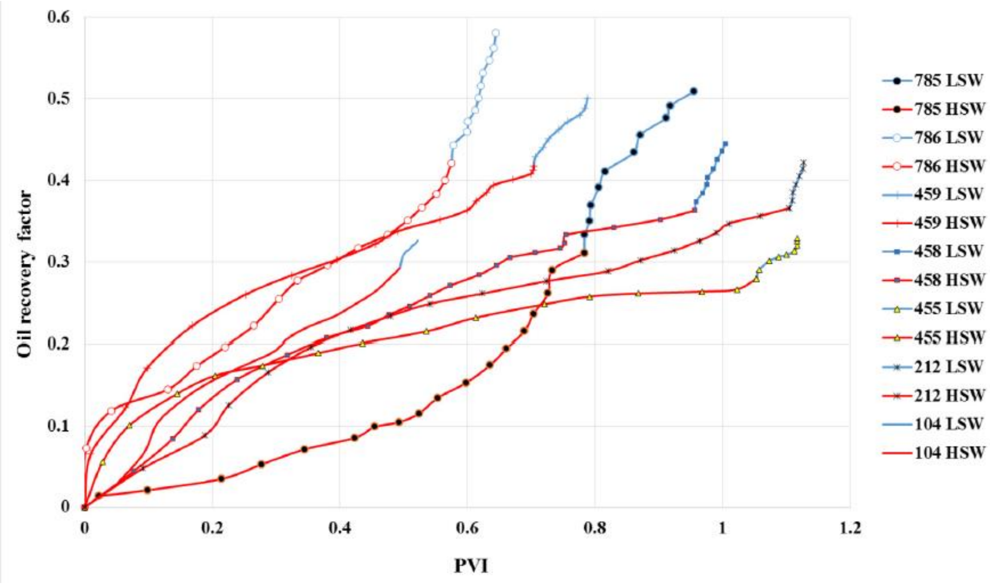


Figure 3.3. Oil recovery factor for 7 LSW pilots versus pore volume injected with LSW (blue curves) following HS (red curves) (Akhmetgareev & Khisamov, 2015).

Figure 3.4. illustrates the oil recovery factor obtained by 3D modelling. The increase in oil recovery was observed after injection of LS brine. The best results were in three-layer cake case. For three-layer cake, after injection of 0,19 PVI, the oil recovery factor incremented by 10,8%. Five-layer cake result in 6,1% of increased oil recovery factor, after injection of 0,53 PVI. For two-layer cake after injection of 0,23 PVI 4,5% of additional oil recovery factor was obtained. Also maximum increment of oil recovery was modelled. The effect is showed below:

- three-layer cake: 17,3 % more of RF, reached after 0,41 PVI
- five-layer cake: 6,8 % more of RF, reached after 0,67 PVI
- two-layer cake: 14,1 % more of RF, reached after 0,56 PVI

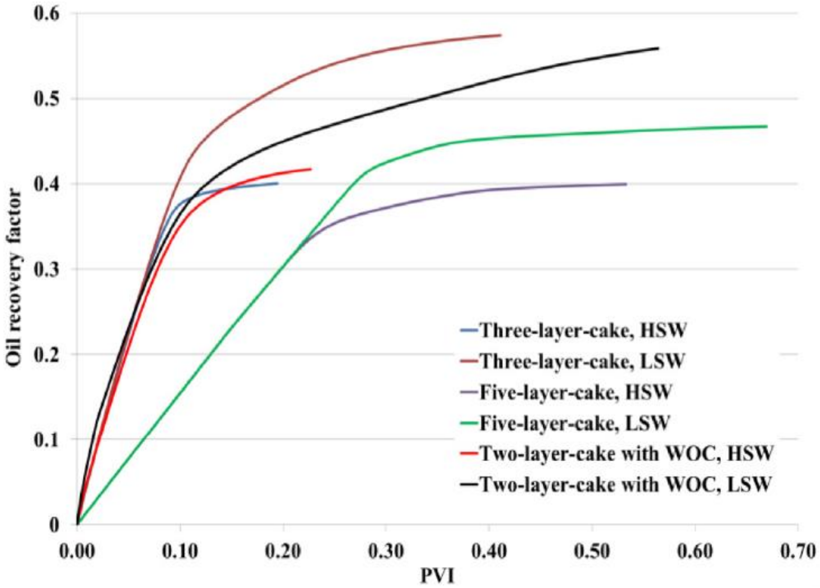


Figure 3.4. Results of 3D modelling; oil recovery factor vs. PVI (Akhmetgareev & Khisamov, 2015).

Above results show, that LS waterflooding may have positive impact on the Pervomaiskoye Field. Low salinity water was injected before, but the effect was buffered by simultaneously injection of formation water (high-salinity brine) and injection of LS brine in the aquifer.

4. EVALUATION OF EOR POTENTIAL BY SMART WATER

To show examples of EOR potential evaluation for smart water method, there will be presented two fields in following section. One of the fields is located on the Norwegian Sea, while the second on the North Sea. Therefore next section is a short introduction to Norwegian Continental Shelf. The most important characteristics of each field will be described, including depositional environments, porosity, permeability, mineralogical composition, and formation water and oil properties. The reservoir data was delivered by company that owns the licenses. The restriction they put was to not publish some significant data and name of the company.

Main objective of the thesis is to evaluate whether presented fields are good candidate for “smart water” flooding. In order to do that it is necessary to estimate initial wetting condition of the reservoir rock. To make it easier, decision making scheme was created by author. It is illustrated on figure 4.1. and it is in line with theory presented above (larger version of the flowchart is given in appendix A). It can be treated as a summary of all factors that have influence on the wettability of the rock. Flowchart has been adopted to particular case, which is application of “smart water” flooding. Comments that can be found on this scheme inform how individual factors affect the wettability of the rock and if field may be considerate to apply this method.

Initial wetting state will be evaluated. If the rock surface will be estimate as mixed-wet, the possibility of the wettability alteration will be discussed.

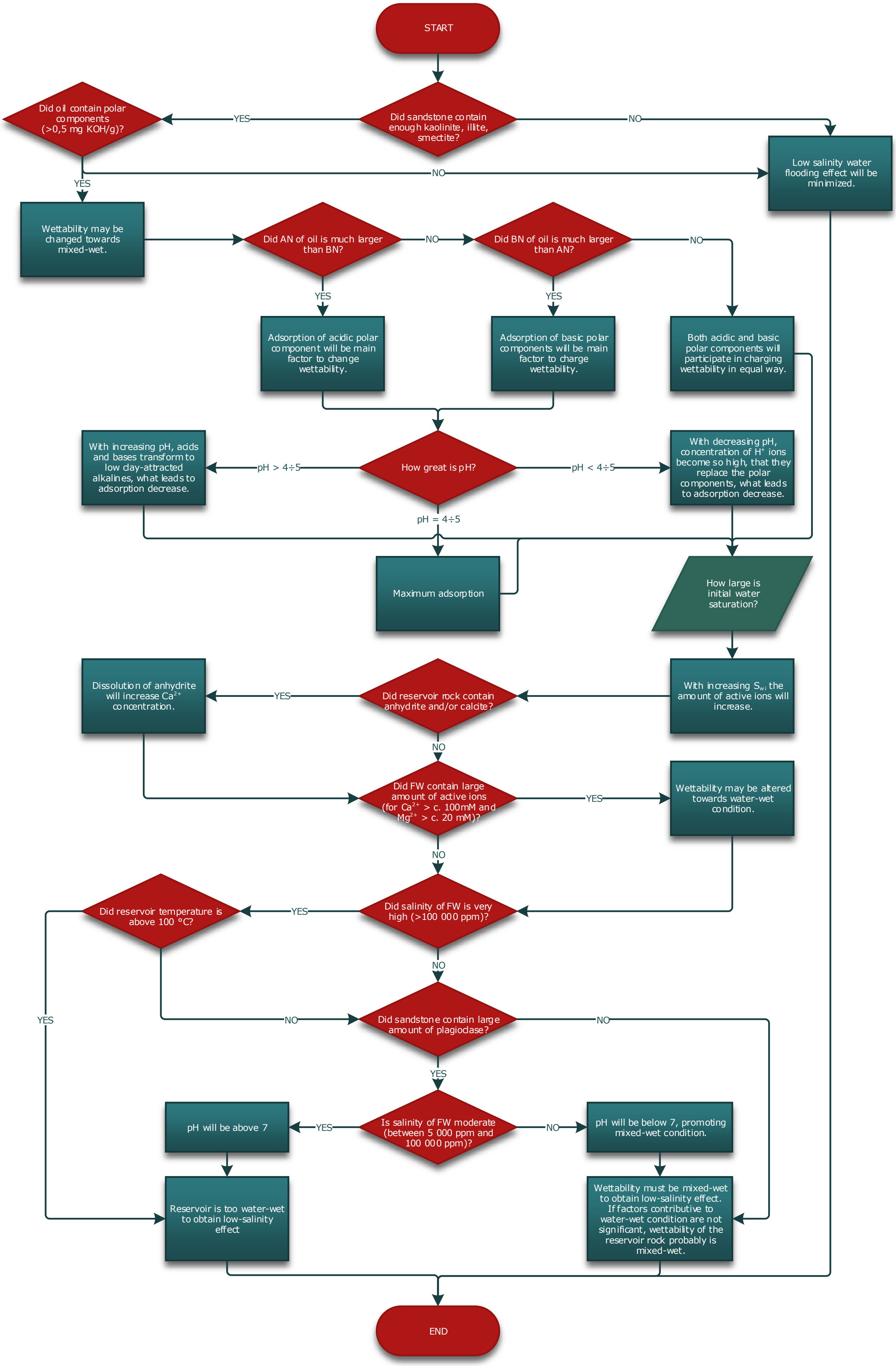


Figure 4.1. Decision making scheme of application the "smart water" method.

4.1. Norwegian continental shelf

Discussed field is placed on the Norwegian continental shelf (NCS), which is subdivided into the three provinces: North Sea, Mid-Norwegian continental shelf and western Barents Sea [figure 4.2.]. There are some similarities in the stratigraphy and geological evaluation, but also certain differences between these provinces. The NCS extends over 2,2 million km^2. It is estimated, that three-fourth of the resources has been discovered and approximately third of that has been already produced (Bjorlykke, 2010).

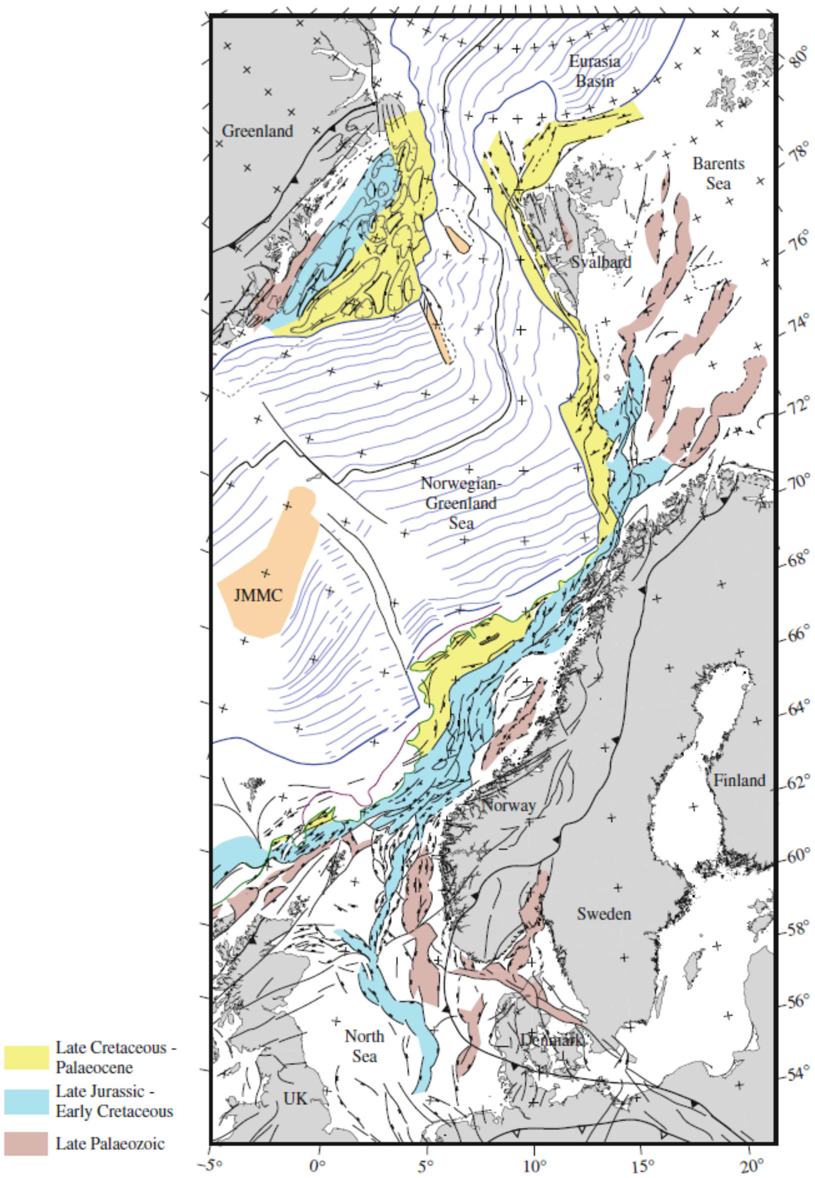


Figure 4.2. Main structural elements of the Norwegian Continental Shelf and adjacent areas (Faleide et al., 2008).

The North Sea is intracratonic basin that was formed within continental crust. There are two petroleum provinces that are part of the North Sea area. First one is the Central Graben; the second one is the Northern North Sea. They represent different petroleum systems. Main source rocks of that region are: Upper Jurassic shales and clays and Middle Jurassic coal. Most of reservoirs are Upper Cretaceous, Upper Jurassic and Upper Palaeozoic. The most important discovery on this area was Ekofisk- chalk reservoir, found out in 1969. It became the largest oil field in Europe. In the northern part of the North Sea there are large oil fields in Brent Group (Middle Jurassic) and Statfjord Formation (Lower Jurassic) sandstones. Some of them are Statfjord, Gulfaks, and Snorre. Other fields can be founded in the Upper Jurassic, Palaeocene and Eocene sandstones (Bjorlykke, 2010).

The Mid-Norwegian shelf includes three segments: Møre, Vøring and Lofoten- Vesterålen. Source rock was formed in the Late and Early Jurassic. The main reservoir rock is Early and Middle Jurassic age sandstones and shales and Upper Cretaceous sandstone. The problem in many of the reservoirs in this area is that they are deep, so oil may escape because of overpressure. High pressure may cause the fracturing and leakage through cap. The most important fields in that area are: Kristen, which represents HPHT reservoir, Draugen and Ormen Lange, which is a gas field (Bjorlykke, 2010).

The Barents Sea lies on the northwest of the Eurasian continental shelf. The Middle and Late Triassic shales are known as the source rocks, however there are probably source rock in Lower Cretaceous and Permian shales, in addition to Lower Permian evaporates and Lower Jurassic coals. The reservoir rock may be Jurassic, Triassic and Cretaceous age sandstones and Carboniferous to Permian age carbonates. This region is dominated by gas and gas condensate reservoirs. The most important discoveries were: Snøhvit, Goliath and Nucula fields. Barents Sea hydrocarbons had certain obstacles to establish an accumulation. Some of the problems may be: uplift and erosion, which cause gas escape and oil leakage; the trap gaping or stopped maturation of oil due to cooling the source rock (Bjorlykke, 2010).

4.2. Field P-1

4.2.1. Reservoir description

A development is consisted of three different deposits, named P-1; P-2; P-3. They are containing gas, condensate and separated oil zone. The reservoirs are divided into several fault segments.

Field P-1 is located in the northern part of the Norwegian Sea. The water depth in this area is 350-450 metres.

P-1 and P-2 are primary reservoirs aged Middle Jurassic. Formations that build the reservoir P-2 are F-1, F-3, and F-6. Field P-1 is made mainly of F-1 formation and consists of oil, which will be major consideration in following sections.

The F-1 formation is typically ~50m thick and consists of sandstone that is deposited in a shallow tidal marine environment. The reservoir contains clean, stacked, medium grained sandstones with good to excellent reservoir properties (average porosity 18.8%, arithmetic mean permeability 2100mD).

The F-3 formation is typically ~30m thick and consists of siltstones and sandstones deposited in an open shallow marine shelf. The reservoir has poor to moderate reservoir properties (average porosity 13.1%, arithmetic mean permeability 12.5mD).

The F-6 formation is typically ~100m thick and consists of an alternating sandstones, siltstones and shales interpreted to be deposited in a tidal marine environment. Overall, the reservoir has moderate reservoir quality (average porosity 14.9%, arithmetic mean permeability 42mD).

4.2.2. Depositional environment

The F-1 base is characterised by a renewed period of transgression, with a marked increase in water depth and depositional energy and the initiation of a tidal dominated transgressive coastline. There were proposed three possible models for the depositional environment, but only one was adopted for the P-1 field. That is tide dominated estuarine deposition model [figure 4.3.].

Estuary is a drowned valley that becomes flooded with seawater during a transgression. Sediments are transported to the estuary from river and marine sources. In every estuary there are three zones. First – outer zone – is dominated by marine processes, and the sediments are moved from the sea to the land. Second – central zone – marine energy offsets the fluvial energy which causes formation of the fine-grained sediments. Last one – inner zone – where sediments are transported from river to the sea. Estuaries could be grouped into wave dominated and tide dominated. Tide dominated estuaries are formed where tidal energy exceeds wave energy. That depositional environment is characterised by well sorted, commonly conglomerated mud, sand or less (Dalrymple et al., 1992).

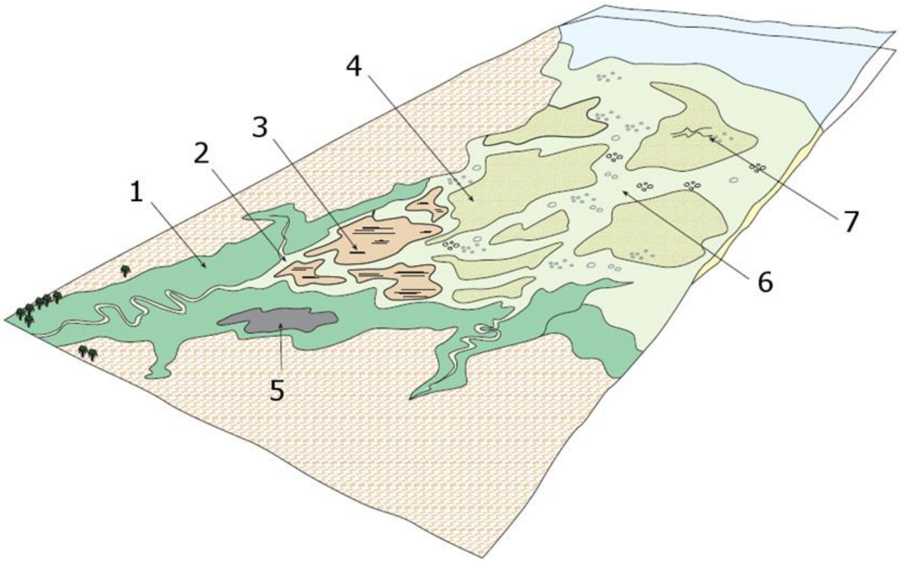


Figure 4.3. The tide dominated estuarine depositional model for the F-1 Formation; 1- salt marsh and marginal to non-marine facies, coals and lagoonal facies developed in this setting; 2- tidal channel; 3- upper flow regime sand flats; 4- Large scale tidal bars with finer grained facies on the flanks; 5- lagoon/marsh/lake/potential coal formation; 6,7- Inter-sandwave tidal channels.

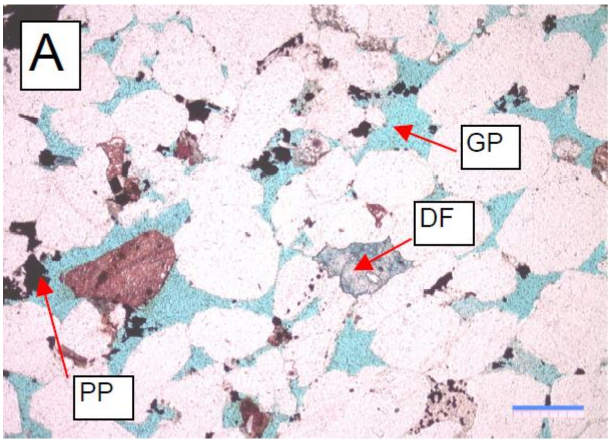
4.2.3. Rock characteristic

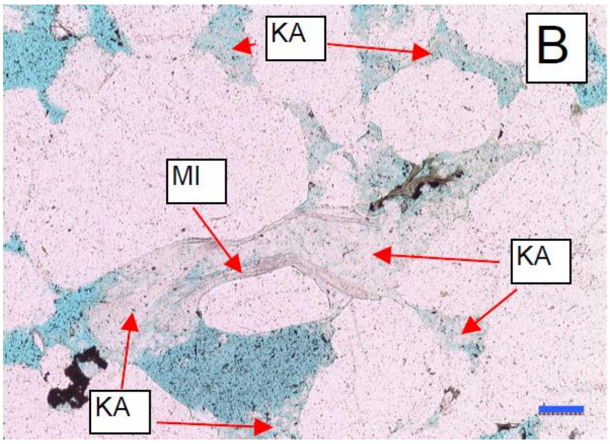
The F-1 Formation sandstones are slightly compacted, poorly to well sorted, mainly medium grained, lithic to sublithic arenites in which detrital clay abundance is generally minor. The main detrital grain type is quartz. Feldspars are minor type and there have been partly leached. The minerology of the F-1 formation is presented in table 5.

Table 5. Average minerals content in the F-1 formation.

Minerology of the F-1 formation [%]											
illite/smectite	**illite/mica**	**kaolinite**	**chlorite**	**quartz**	**k- feldspar**	**plagioclase**	**calcite**	**dolomite**	**siderite**	**pyrite**	**total**
0,33	7,63	7,23	2,85	71,94	3,44	0,37	0,23	1,69	3,50	0,80	**100,00**

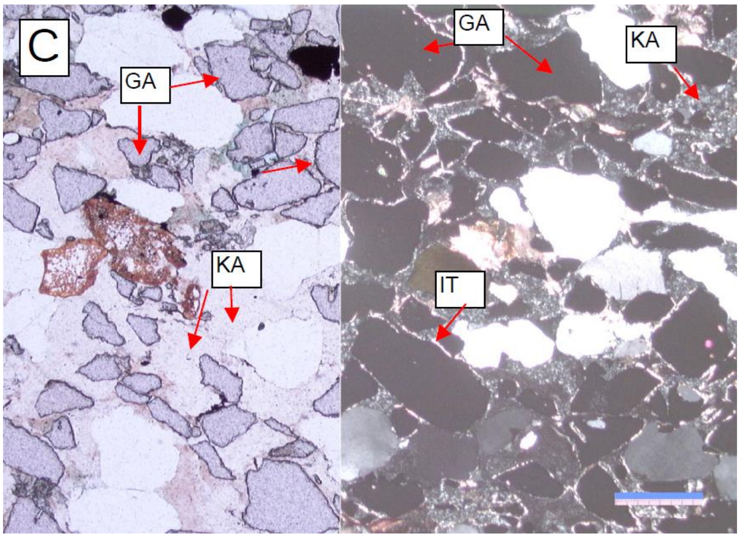
Diagenetic modification is moderate. However, kaolinite is locally abundant and has a detrimental effect on permeability. Chlorite is rare to absent. Pore networks are dominated by primary intergranular macropores supplemented by subordinate grain dissolution pores. The pores are typically well connected, hence permeability are high. The main three upper reservoir layers have well to excellent reservoir properties with porosity between 18 - 20 % and permeability above 1 Darcy [Table 6.]. Figure 4.4. illustrates typical photomicrographs of the formation.





A. The sample contains common intergranular pores and some larger, probably secondary pores (GP). Some porosity has been lost because of cementation by ferroan dolomite (stained blue, DF), pyrite (opaque, PP), and kaolinite (KA). 3515.8m. Scale bar: 400 microns.

B. The plate shows a sericite grain (MI) that has been splayed and replaced by kaolinite (KA). Microporous kaolinite fills other intergranular spaces nearby. 3524.25m. Scale bar: 100 microns.



C. Garnet (high relief on left, black on left, GA) is abundant and is rimmed by illite (moderate birefringence colours on right, IT). Kaolinite (KA) fills most of the intergranular space and no macropores are visible. 3551.34m. Scale bar: 400 microns. PPL on left, XPL on right.

Figure 4.4. Summary of photomicrographs from the F-1 formation.

Table 6. presents the summary of the reservoir initial condition. It includes average porosity and permeability, reservoir temperature, pressure and depth. It was also established the initial water saturation. The initial wetting state of the rock is slightly water-wet.

Table 6. Reservoir properties of P-1 field.

Field P-1	
Reservoir Depth [mTVD]	3300-3700
Reservoir Pressure- P [bara]	360-386
Reservoir Temperature- T [°C]	135-145
Average porosity- φ [%]	18,8
Average permeability- k [mD]	2100
Water saturation- Swi [%]	0,25

4.2.4. Fluids properties

Crude oil

Reservoir crude oil has gravity equal to 33,6 °API and the viscosity 0,316 cP. The total acid number (AN) is 0,044 mg KOH/g. Base number can be adopted according to literature overview. In high temperature reservoirs base number is significantly higher than AN. Decarboxylation in high temperature of carboxylic acids leads to destruction of the acid materials, what result in low AN (RezaeiDoust et al., 2011). It may be assume that base number is over 1 mg KOH/g. The summary of the oil properties are demonstrated in Table 7.

Table 7. Crude oil properties- field P-1.

Crude oil properties			
AN [mg KOH/g]	**BN [mg KOH/g]**	**Gravity [°API]**	**Viscosity [cP]**
0,044	>1	33,6	0,316

Formation water

Composition of formation water is presented in tables 8. and 9. For calculation, density of the brine was assumed to be 1 g/cm^3.

Table 8. Formation brine composition (salt content) - field P-1.

	CONCENTRATION	
	[g/l]	**[mole/l]**
NaCl	43,562	0,745
$CaCl_2*2H_2O$	9,352	0,064
$MgCl_2*6H_2O$	1,882	0,009
KCl	22,309	0,299
$NaHCO_3$	0,599	0,007
$SrCl_2*6H_2O$	0,606	0,002

Table 9. Formation brine composition (ionic) - field P-1.

CONCENTRATION		
ion	**[mole/l]**	**[ppm]**
Na$^+$	0,753	17 300
Cl$^-$	1,195	42 363
Ca^{2+}	0,064	2 549
Mg^{2+}	0,009	225
K$^+$	0,299	11 699
Sr^{2+}	0,002	199
HCO^{3-}	0,007	435
	TDS:	74770

4.2.5. Evaluation of the initial wetting condition

Reservoir rock of P-1field consists mainly of quartz and clay minerals. Over 18% of the rock is clay minerals. This is sufficient amount to alter the wettability to less water- wet. Figure 4.5. shows distribution of the clay minerals. Approximately 84% of the clay minerals contained in the reservoir rock have significant impact on adsorption of the polar components. There are illite and mica, illite/smectite and kaolinite. As was mentioned before chlorite has large surface area, but the CEC is similar to kaolinite. However, Zhang and Morrow noticed (2005) that chlorite-rich sandstone does not taking part in adsorption of polar organic components (Zhang & Morrow, 2006).

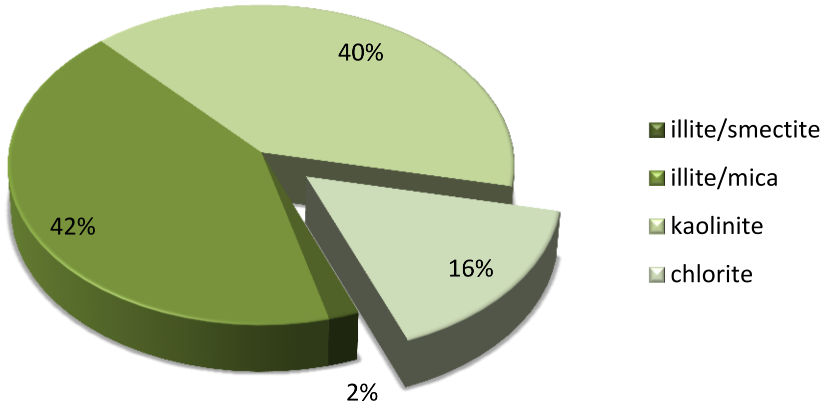


Figure 4.5. Type of the clay minerals- field P-1.

From P-1 reservoir there is also information about origin of the clay minerals. Over one third of the clays are authigenic [figure 4.6.]. Probably illite is the main authigenic clay. The process of formation this kind of illite is called illitization and occurs in high-temperature environment (like in P-1 field, where temperature is c.140°C). Illite forms from authigenic kaolinite and by dissolution of k-feldspar [equation 16.] (Ehrenberg & Nadeau, 1989). Therefore percentage of k-feldspar is low (average 3,4%).

$$K - feldspar + kaolinite \rightarrow illite + 2quartz + water \qquad (16)$$

It can be assumed, that adsorption of polar components is increased due to high participation of illite and illite/smectite. The initial wettability of the rock turns towards mixed-wet.

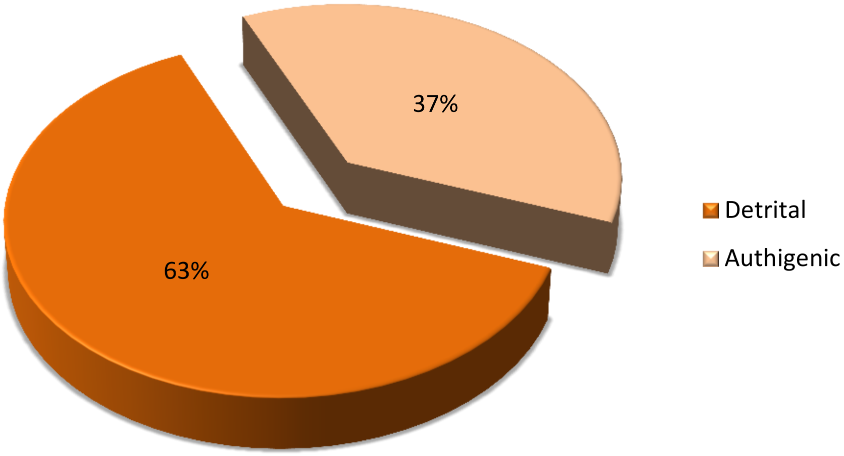


Figure 4.6. Origin of the clay minerals - P-1filed.

Crude oil data obtained from P-1 fields contain only AN, which is equal to 0,044 mgKOH/g. However, in high-temperature sandstone reservoirs, BN tends to be higher than AN (Austad et al., 2010). It was assumed that base number will be significantly higher than 1 mgKOH/g. Nonetheless, it can be only proved by results of the experiment. In this situation we cannot rate the magnitude of polar components adsorption, however it can be said that main material adsorbed on mineral surface are organic bases.

Formation water of P-1 field is medium- high salinity brine (74 770 ppm). Fluid has high concentration of Na^+ (17 300 ppm) and K^+ (11 699 ppm) ions, with presence of the Ca^{2+} (2 549 ppm) and Mg^{2+} (255 ppm). Reservoir has a high temperature equal to 140 °C.

Sajjad (2015) in his Master Thesis performed core flooding at similar condition to P-1 field. The temperature of the reservoir was 136 °C and salinity of the formation water equal to 60 461 ppm. Core flooding results show that in tertiary mode the smart water flooding gave 9% of OOIP additional oil recovery (Sajjad, 2015). According to this experiment it is believed that despite the high-reservoir temperature, salinity of the formation water and in particular concentration of divalent cations is too low to alter wettability towards strong water-wet conditions.

Initial water saturation is 25%. It is a median of typical value for sandstone reservoir. That is, it will not have large negative impact on displacement efficiency of waterflooding treatment. Also, the amount of active cations like Ca^{2+} and Mg^{2+} is not elevated. Adsorption onto mineral surface of the polar organic components can be effective.

In P-1 fields pH is unknown, however it may be assumed, that it is equal to common value of this parameter, which is 6-7 pH. Oil contains 2% of CO_2, which can slightly lower the pH of the reservoir. In this condition adsorption of polar components, which are strongly depend on pH of the environment, can take place. As was mention earlier, maximum adsorption of basic materials occur in pH=4÷5. In reservoir P-1 pH was estimated as slightly higher, what leads to reduced adsorption. Nonetheless it will happen. Adsorption of polar components causes wettability alteration to mixed-wet.

Conclusion

The initial wetting state of the reservoir rock from field data is slightly water-wet. Taking everything into account previous considerations confirm that statement. Presence of sufficient quantity of the clay minerals and their type allow modifying the initial wettability towards mixed-wet. Likewise, the amount of polar organic components may have the same consequence. On the other hand, high temperature and presence of divalent cations may have opposite effect and remain reservoir water-wet. However, not so high salinity of the formation water and moderate concentration of divalent cations markedly reduce this effect.

4.2.6. Other notable factors

Important factor that has to be taken into account is heterogeneity of the field. Previously presented Pervomaiskoye field has great heterogeneity of the rock. There was performed simulation of “smart-water” flooding. Results shown that the largest increase in oil recovery may be obtain in three-layer cake, then two-layer cake and the lowest RF was in five-layer cake (Akhmetgareev & Khisamov, 2015). Reservoir P-1 has also large heterogeneity. Horizontal permeability varies from 7470 mD to 330 mD. This is connected with distribution of micropores that are product of illitization process. Confirmation of this argument is showed in table 10. It may be noticed that occurrence of illite, that replaced grains increase contribution of micropores, what have impact on decreasing permeability of the reservoir. That is because micropores are isolated from flow. The large surface area of illite and fibrous pore-bridging morphology will lead to cut off the flow from micropores (Ehrenberg, 1990). In this situation smart-water flooding will not have any impact of that part of the pore space. On the other hand, not every micropore may be blocked by illite and low-salinity water injection will change wettability of the rock. The same, capillary pressure will be reduced. Injected water will be able to invade micropores and displace oil. That will lead to incremental oil recovery.

Table 10. Core analyses from field P-1.

					Authigenic		**Illitic Clay**	
Core depth (m)	Porosity (%)	Hor. Perm. [mD]	Macropores [%]	Micropores [%]	Clays [%]	Other cements [%]	Grain Coating/ Pore Lining [%]	Grain Replacing [%]
3540,50	15,6	1580	8,33	7,27	3,33	3,35	0,00	0,33
3543,50	20,1	2280	17,00	3,1	1,66	4,69	0,00	0,00
3545,50	15,8	372	12,66	3,14	3,99	4,35	0,00	0,00
3548,50	20	445	8,99	11,01	15,65	4,01	0,00	0,33
3554,25	17	7470	14,99	2,01	0,99	1,7	0,33	0,00
3557,00	18,2	351	11,66	6,54	7,32	2,99	0,00	0,33
3562,75	19	330	9,99	9,01	13,98	1,33	0,00	2,00

Sandstone from reservoir P-1 contain small amount of plagioclase that probably will not have large influence on low-salinity waterflooding. However, appearance circa 1,7% of dolomite may have some impact. The maximum value of the dolomite in some places exceeds 13,4 %. It was showed that "smart water" injection, where sandstone contain dolomite has positive response (Pu et al., 2010).

4.2.7. Possibility of wettability alteration by low-salinity water injection

Mechanism proposed by Austad (2010) is two-steps desorption mechanism. First step is replacing active cations by H^+. This is slow, exothermic reaction [equation 11.]. In result of this reaction, the pH will increase.

$$Ca^{2+}Clay + H_2O \rightleftarrows H^+Clay + Ca^{2+} + OH^- + heat \tag{11}$$

Second step of this mechanism is desorption of organic polar components showed in equations 14. and 15. These reactions are very fast and strongly depend on the environment pH.

$$R_3NH^+Clay + OH^- \rightleftarrows Clay + R_3N\!: + H_2O \tag{14}$$

$$RCOOHClay + OH^- \rightleftarrows Clay + RCOO^- + H_2O \tag{15}$$

High temperature of reservoir P-1 (140°C) will lead to smaller desorption of Ca^{2+}. Consequently, pH gradient, caused by low-salinity flooding, will decrease. Desorption of organic materials will be reduced giving lower oil recovery.

Enhance oil recovery will be lower than in reservoir with the same rock/oil/brine characteristic and lower temperature. However, concentration of active ions in formation brine is relatively poor; therefor reduction in pH gradient will not be very large.

Conclusion

By injection of "smart water" of low salinity, alteration of reservoir rock wettability towards more water-wet can takes place. It can lead to desorption of polar organic components and improving of microscopic sweep efficiency. Incremental oil recovery can be achieved.

4.3. Field V-1

There is much less data available from field V-1 than from described before field P-1. Unfortunately it is impossible to get additional data. In such case it is necessary to focus on the most important information that may be collected.

Field V-1 is an oil field in the central region of the North Sea. The developments consist of three horizontal wells. The water depth in area is equal 120 m. The reservoir rock is turbidite sandstone, Palaeocene age.

4.3.1. Depositional environment

The field consists of one formation, named H-1. The H-1 Formation was deposited on a shallow-marine shelf under high-energy conditions. In the east part, formation was deposited as submarine fans. Sand was derived from shallow shelf from the west (*Norwegian Petroleum Directorate*).

Shallow marine environments are region of significant amount of accumulation. It may stretch to hundreds of kilometres. Most of the clastic material is eroded from the continents. Clastic materials are spread out on shelves by tides, storms, waves and currents. In that way, sediments are sorted by grain size and deposit areas. Shallow marine sands are mainly made from quartz grains. In shallow marine are presented also marine organisms, as shells, skeletons, that may occur in sandstone deposits (Bjorlykke, 2010; Levin, 2009).

Turbidites are sediments that were transported seaward on the deep sea by high- dens currents. Turbidites commonly form the submarine fans. Water in turbidity current is much denser than nearby water. The density of the turbidity current water is elevated by suspended sediments. Dense water flows downwards the slope, current slows and the sediments gradually clogging onto the sea bed. The coarser grains will fall onto the bottom first, then finer grains and the finest sediments. Thereby graded sequence of sediments is created (Levin, 2009).

4.3.2. Rock property

The reservoir is located at 2150 m below sea level. Initial condition of the reservoir is presented in table 11. The net thickness of the formation is 56 m.

Table 11. Reservoir properties of V-1 field.

Field V-1	
Reservoir Depth [mTVD]	2150
Reservoir Pressure- P [bara]	206
Reservoir Temperature- T [°C]	86

The sand had very good reservoir properties and was oil bearing. The formation is composed of poorly sorted and cemented, fine to coarse grained sandstones. It contains also mica, glauconite and detrital lignite. The sandstone is interbedded with grey and black shales, limestones and sandy limestones. The H-1 formation locally is developed as clean sandstone without interbedded shales and limestone.

The minerology of the formation is presented in table below (Table 12.).

Table 12. Average minerals content in the H-1 formation.

Minerology of the H-1 formation [%]									
illite/ smectite	**illite/ mica**	**kaolinite**	**chlorite**	**quartz**	**k- feldspar**	**plagioclase**	**calcite**	**pyrite**	**total**
0,08	7,03	1,13	0,65	84,36	3,58	2,43	0,40	0,35	**100,00**

4.3.3. Fluids properties

Crude oil

Reservoir crude oil has gravity equal 40,6 °API and the viscosity 3,623 cP at 60°C. Unfortunately, the BN and AN were not established. The summary of the oil properties are demonstrated in Table 13.

Table 13. Crude oil properties- field V-1.

Crude oil properties	
Gravity [°API]	**Viscosity at 60°C [cP]**
40,6	3,6

Formation water

Concentration of salts presented in formation water is showed in tables 14. and 15. For calculation, density of the brine is equal to be 1,055 g/cm^3.

Table 14. Formation brine composition (salt content) - field V-1.

	CONCENTRATION	
	[g/l]	[mole/l]
NaCl	66,73	1,142
$CaCl_2$*$2H_2O$	10,43	0,071
$MgCl_2$*$6H_2O$	5,10	0,025
KCl	0,71	0,010
$BaCl_2$*$2H_2O$	0,30	0,001
LiCl	1,18	0,0005
$SrCl_2$*$6H_2O$	0,02	0,004

Table 15. Formation brine composition (ionic) - field V-1.

CONCENTRATION		
ion	[mole/l]	[ppm]
Na^+	1,213	26 427
Cl^-	1,355	45 540
Ca^{2+}	0,071	2 695
Mg^{2+}	0,025	578
K^+	0,010	353
Sr^{2+}	0,004	368
Br^{2+}	0,001	160
Li^+	0,0005	3
	TDS:	76 124

4.3.4. Evaluation of the initial wetting condition

Sandstone contains large amount of quartz and almost 9% of minerals is total clay amount. The average concentration of illite/mica is circa 7%. It is known, that illite has large CEC. It is significant fact, due to dependency of adsorption onto clays from their CEC. The amount of clay is smaller than in P-1 field. However, it may be sufficient to obtain increase of oil recovery after low-salinity waterflooding.

The reservoir rock contain little amount calcite (0,4%) that may have small influence on the concentration of Ca^{2+} cations. Calcite is the carbonate mineral, that chemical formula is $CaCO_3$. In aqueous environment it acts similar to anhydrite, calcite dissolves giving Ca^{2+} ions to the water phase. Still, the amount of calcite is too small to dramatically change the wettability to strongly water-wet.

The occurrence of plagioclase may have negative impact of pH on the initial wetting state. The average amount of plagioclase is 2,43%. Previously mentioned, that depending on salinity of the formation water plagioclase may have positive or negative impact on adsorption. In our reservoir, formation water has quite moderate salinity. It means that FW salinity is on the borderline and may affect pH in a negative or positive way. Probably the pH will be strived for crossing 7 units. Then adsorption of polar components will decrease. However, in experiments performed on Snorre cores plagioclase is accounted for c. 30% (Strand et al., 2014). In reservoir rock V-1 is less than 10% of that value. Probably, plagioclase will rise the pH value of the reservoir; however it will not be enough to stop adsorption of polar components.

The data about oil are scarce. There is no information about polar organic components content. Even, composition of crude oil is not available. In this situation we cannot be sure if adsorption of polar components will be compelling. It is believed that all crude oils contain some amount of polar components. There are existing three scenario of adsorption of surface-active organic compounds.

1. Acid number (AN) is larger than base number (BN) - this situation is rare, in sandstones reservoir basic components are most common polar material. Nonetheless, acidic components will be playing main role in adsorption, which

depends on pH of reservoir. Maximum adsorption is at pH circa 5. If the pH will be higher or lower than 5, adsorption will be decreasing in different rates.

2. Base number (BN) is larger than acid number (AN) - the most common situation. As was mentioned before, maximum adsorption occurs when pH is equal to 4. With increasing pH adsorption of basic materials decrease. Similar situation is when pH is below 4, however decline is sharper.
3. Acid and base number (AN, BN) is similar- both acidic and basic components will take part in adsorption.

The salinity of the formation water is moderate (76 124 ppm). Also concentration of active ions are not very high (Ca^{2+}- 2 695; Mg^{2+}- 578). It means, that adsorption of polar components will not be buffered by composition of formation water. Unfortunately, information about initial water saturation is unknown. In this situation we cannot be sure if amount of active ions will suddenly increase. However, we can assume that initial water saturation has average value for sandstone reservoirs that correspond to 25%. Small amount of calcite presented in reservoir rock will a little increase amount of calcium cations. The initial wettability condition probably will be more mixed-wet than water-wet.

The pH of the reservoir is also undefined. It is hard to say if the pH will be similar to common sandstone reservoir (6-7 pH) or if it will be lowered by sour gases. However, previously mentioned small amount of plagioclase may have impact on pH increase. Probably pH of the will be a bit higher than in reservoir P-1, it is expected that pH will not exceed 8. At pH equal to 8, adsorption of polar components is minimal.

The temperature of reservoir is 86°C. In literature most experiments was performed in temperature below 100°C. Adsorption of polar components are not sensitive to change in temperature due to their fast reaction and low activation energy (Aksulu et al., 2012) (only high-temperature, as was in P-1 field case, may have negative impact what was described in section 2.5.).

Conclusion

There are many uncertainties during evaluation of initial wetting state. There are a lot of factors that influence on wettability. If we assume that amount of polar components are sufficient to adsorb onto clay minerals and pH of the reservoir does not exceed 8 units, the wettability of the formation rock will be mix-wet. To eliminate unknowns, experiments to rate the AN, BN, composition of the oil and pH have to be performed.

4.3.5. Possibility of wettability alteration by low-salinity water injection

Referring back to influence of pH gradient on low-salinity effect, it has to be aware that with increasing pH gradient, oil recovery is enhanced. Presence of plagioclase in reservoir V-1 will increase the initial pH of the reservoir. After injection of “smart water” pH will rise, according to equation 11. (illustrated before). Overall, the pH gradient will be smaller due to high start point. Consequently desorption of polar components will be lower. Due to that, enhanced oil recovery will be reduced.

5. CONCLUSIONS

As the result of this work decision making scheme was prepared. Thanks to that, evaluation of using “smart water” injection as EOR method on selected fields could be achieved. Two fields were presented and taken as potential candidate for low-salinity waterflooding. Based on outlined above considerations, following conclusions was made:

- Initial wettability of field P-1 was confirmed as mixed-wet. Because of that, effects of low-salinity injection may be obtained.
- Temperature in field P-1 is equal to 140°C and, due to it will decrease effect of “smart water” flooding. Despite that, the field is considered as a good candidate for “smart water” flooding.
- Wettability of the field V-1 was assumed as mixed-wet. But in order to dispel doubts and unknowns exact oil properties and pH of the reservoir has to be tested.
- High pH of the reservoir V-1 may have negative impact on the mechanism of alteration wettability to water-wet. Desorption of polar component is increasing with high pH gradient.
- Evaluation the possibilities of using “smart water” injection on sandstones fields may be done without performing experiments. But in fact, they could confirm conclusions.

5.1. Further work

For field V-1 more information are needed to perform such evaluation more precisely, therefore additional data have to be provided. Amount of AN and BN should be investigated. In order to confirm presented opinion laboratory test has to be performed. Core flooding may supply evidence if presented fields have potential efficient smart-water flooding.

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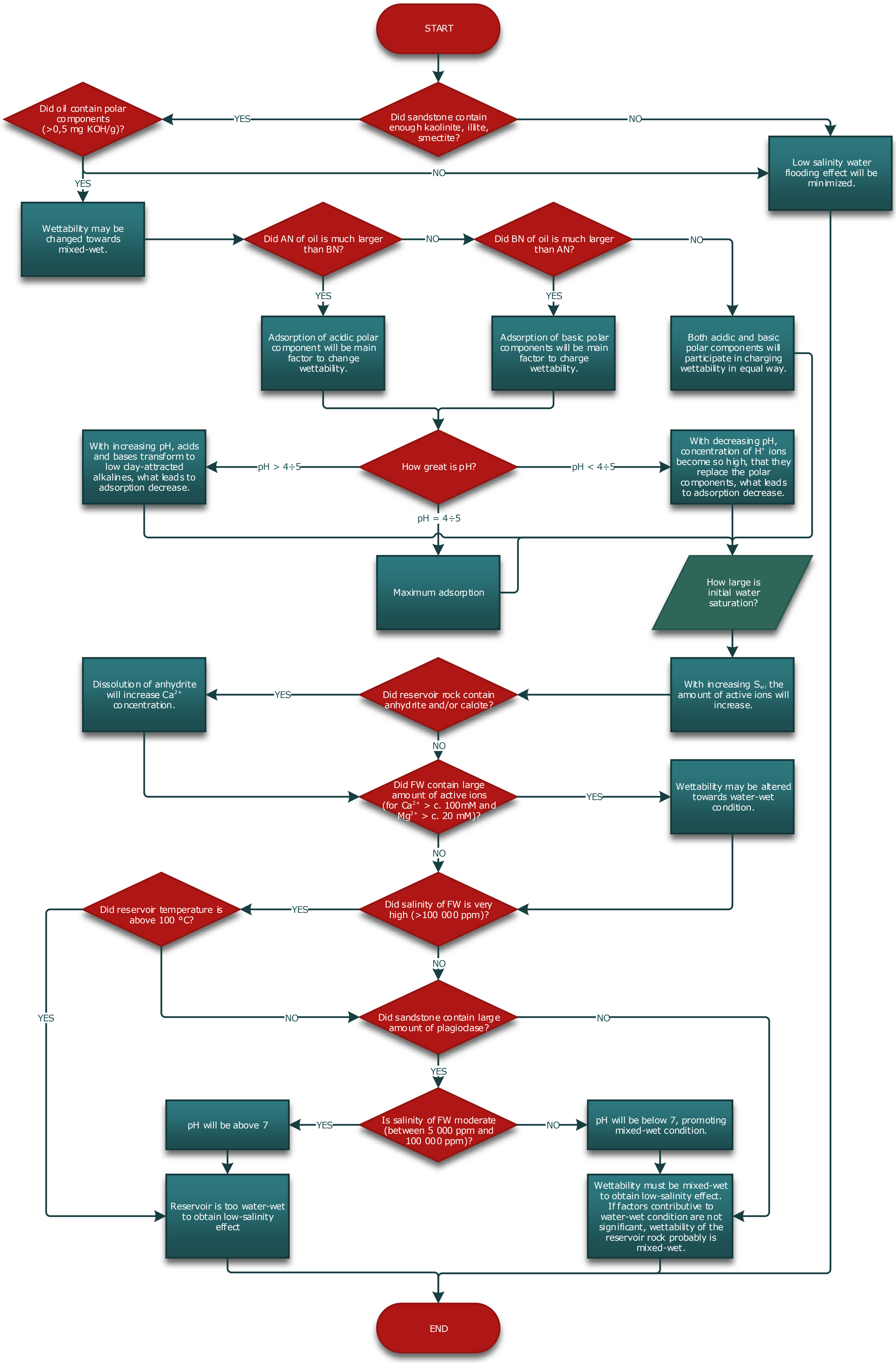
APPENDIX A


START
Did sandstone contain enough kaolinite, illite, smectite?
YES
NO
Did oil contain polar components (>0,5 mg KOH/g)?
NO
Low salinity water flooding effect will be minimized.
YES
Wettability may be changed towards mixed-wet.
Did AN of oil is much larger than BN?
NO
Did BN of oil is much larger than AN?
NO
YES
YES
Adsorption of acidic polar component will be main factor to change wettability.
Adsorption of basic polar components will be main factor to charge wettability.
Both acidic and basic polar components will participate in charging wettability in equal way.
With increasing pH, acids and bases transform to low clay-attracted alkalines, what leads to adsorption decrease.
pH > 4÷5
How great is pH?
pH < 4÷5
With decreasing pH, concentration of H$^+$ ions become so high, that they replace the polar components, what leads to adsorption decrease.
pH = 4÷5
Maximum adsorption
How large is initial water saturation?
With increasing S$_{wi}$ the amount of active ions will increase.
Dissolution of anhydrite will increase Ca^{2+} concentration.
YES
Did reservoir rock contain anhydrite and/or calcite?
NO
Did FW contain large amount of active ions (for Ca^{2+} > c. 100mM and Mg^{2+} > c. 20 mM)?
YES
Wettability may be altered towards water-wet condition.
NO
Did reservoir temperature is above 100 °C?
YES
Did salinity of FW is very high (>100 000 ppm)?
NO
YES
NO
Did sandstone contain large amount of plagioclase?
NO
YES
pH will be above 7
YES
Is salinity of FW moderate (between 5 000 ppm and 100 000 ppm)?
NO
pH will be below 7, promoting mixed-wet condition.
Reservoir is too water-wet to obtain low-salinity effect
Wettability must be mixed-wet to obtain low-salinity effect. If factors contributive to water-wet condition are not significant, wettability of the reservoir rock probably is mixed-wet.
END

APPENDIX B

Evaluation of using Smart Water to enhance oil recovery from Norwegian Continental Shelf sandstone reservoirs

Natalia Piotrowska
Stavanger, 2016

Universitetet
i Stavanger

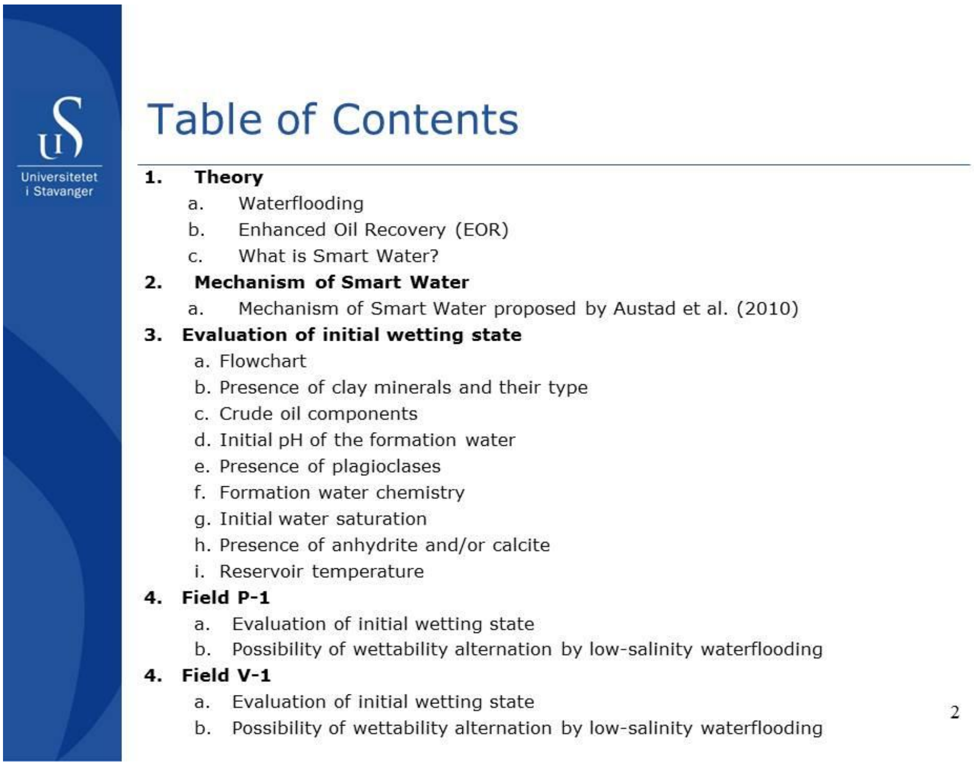


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Table of Contents

Waterflooding

- Secondary recovery method.
- Widely used in oil industry since 50’s of the XX country.
- The main objectives of the use of waterflooding are:
    - increasing reservoir pressure,
    - displacing the oil by viscous forces.

Enhanced Oil Recovery (EOR)

- In order to increase oil recovery, EOR method is implemented on reservoir.
- Applied after waterflooding, but also can be used from the very begging of the field production.
- EOR leads to altering the oil and/or rock properties and therefore improves the mobility of oil.
- Categories of EOR:
    - chemical
    - thermal
    - mobility-control
    - miscible

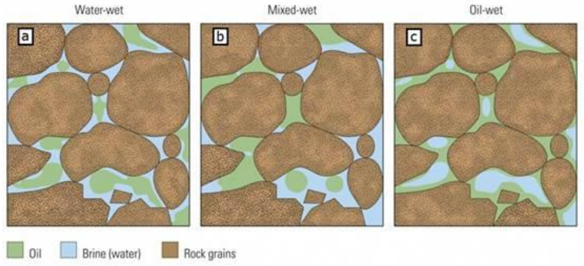
What is Smart Water?

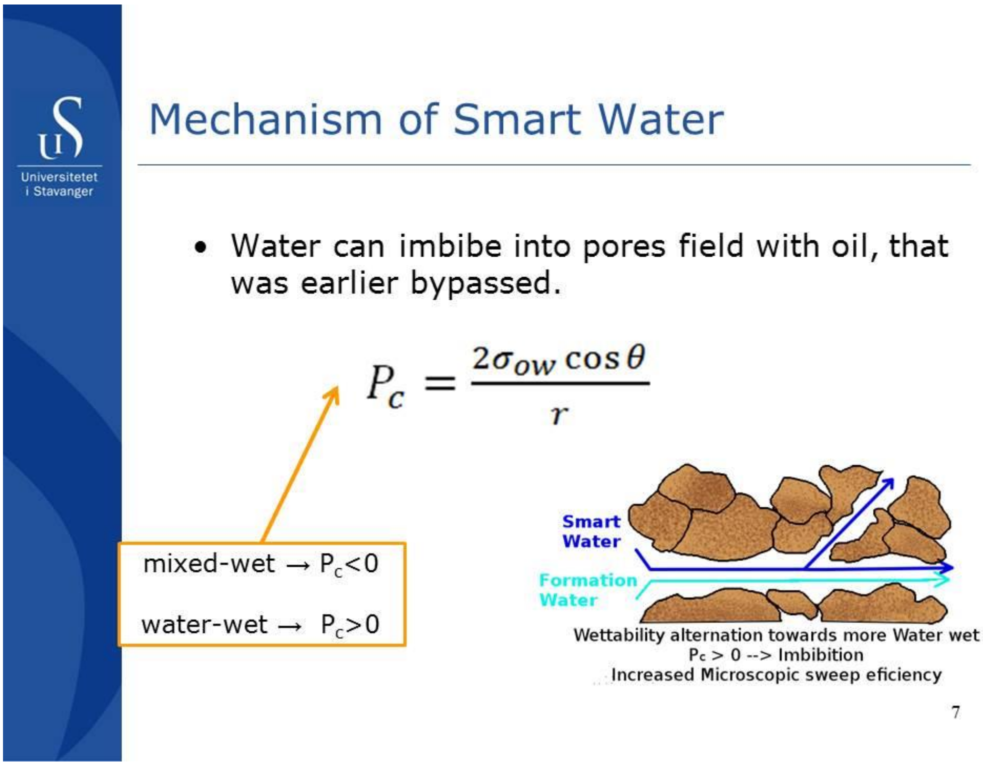
Modified injection water that has:

- **Low-salinity water-** usually between 1 000–2 000 ppm, but effect was also obtained using 5 000 ppm fluid.
- **Low concentration of active ions-** it was found out that lower concentration of active ions (Ca^{2+} and Mg^{2+}) than in formation water (FW) is necessary to obtain Smart Water effect.

Mechanism of Smart Water

- Main mechanism has not been established.
- Improve of oil recovery is achieved due to altering wettability from mixed-wet to more water-wet.
- Displacement efficiency of this EOR method is increased because of the lowering capillary pressure.





Mechanism of Smart Water

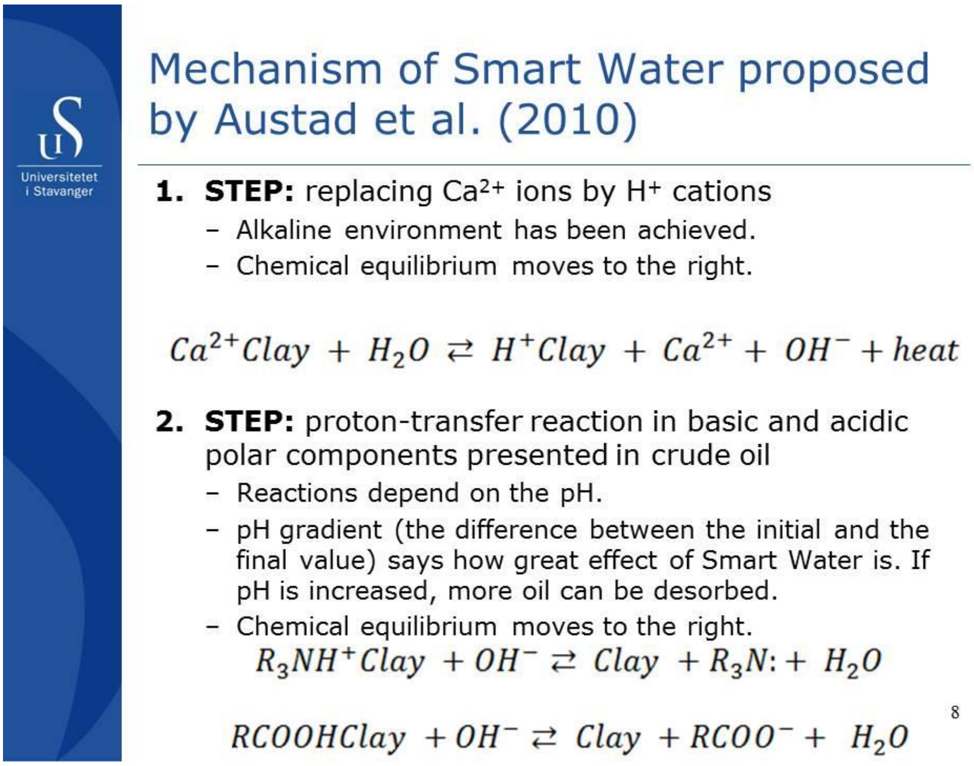
- Water can imbibe into pores field with oil, that was earlier bypassed.

$$P_c = \frac{2\sigma_{OW}\cos\theta}{r}$$

mixed-wet → $P_c<0$

water-wet → $P_c>0$

Wettability alternation towards more Water wet
$P_c > 0$ --> Imbibition
Increased Microscopic sweep eficiency



Mechanism of Smart Water proposed by Austad et al. (2010)

1. **STEP:** replacing Ca^{2+} ions by H^+ cations
   - Alkaline environment has been achieved.
   - Chemical equilibrium moves to the right.

$$Ca^{2+}Clay + H_2O \rightleftarrows H^+Clay + Ca^{2+} + OH^- + heat$$

2. **STEP:** proton-transfer reaction in basic and acidic polar components presented in crude oil
   - Reactions depend on the pH.
   - pH gradient (the difference between the initial and the final value) says how great effect of Smart Water is. If pH is increased, more oil can be desorbed.
   - Chemical equilibrium moves to the right.

$$R_3NH^+Clay + OH^- \rightleftarrows Clay + R_3N: + H_2O$$

$$RCOOHClay + OH^- \rightleftarrows Clay + RCOO^- + H_2O$$

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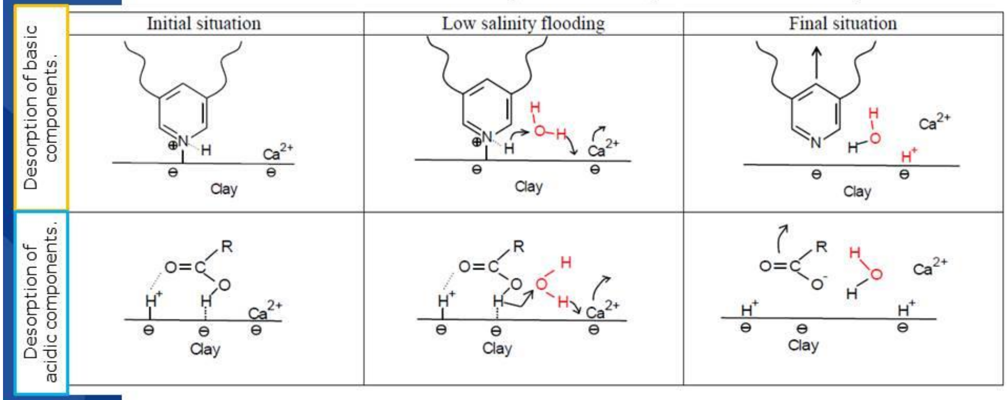
Mechanism of Smart Water proposed by Austad et al. (2010)

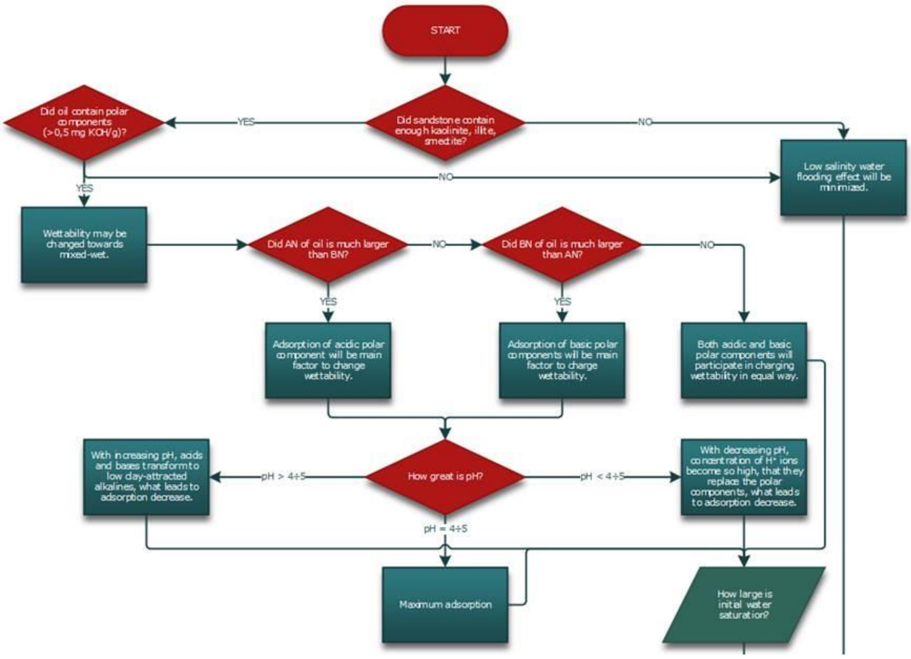
Schematic mechanism of polar components desorption:



Reservoir rock initially has to be mixed-wet, mechanism altering the wettability towards water-wet.

THEREFORE, INITIAL WETTABILITY HAS TO BE EVALUATED.

Evaluation of initial wetting state- flowchart


START

Did sandstone contain enough kaolinite, illite, smectite?

Did oil contain polar components (>0,5 mg KOH/g)?

Low salinity water flooding effect will be minimized.

Wettability may be changed towards mixed-wet.

Did AN of oil is much larger than BN?

Did BN of oil is much larger than AN?

Adsorption of acidic polar component will be main factor to change wettability.

Adsorption of basic polar components will be main factor to charge wettability.

Both acidic and basic polar components will participate in charging wettability in equal way.

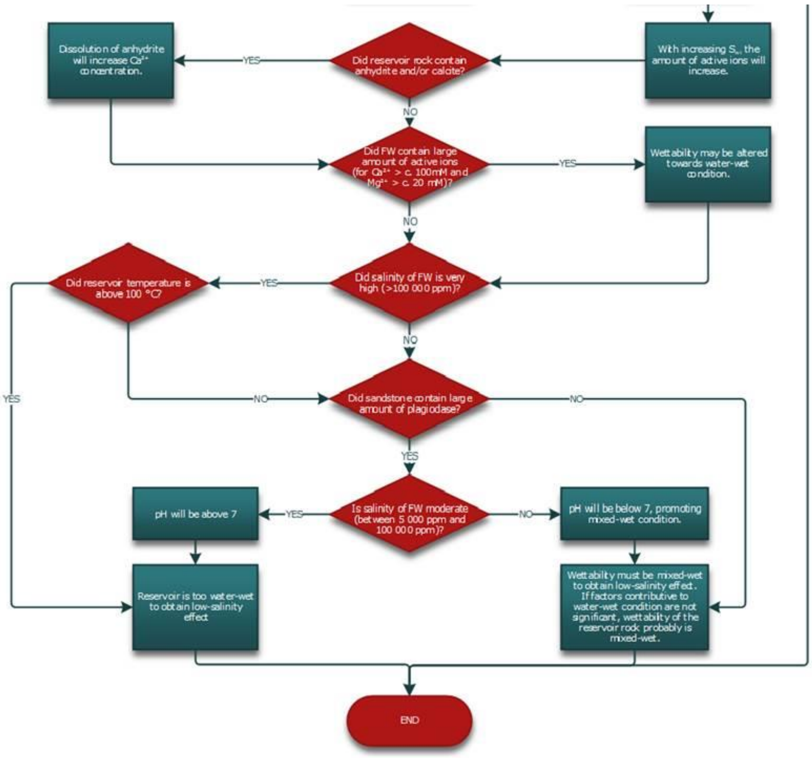
How great is pH?

With increasing pH, acids and bases transform to low clay-attracted alkalines, what leads to adsorption decrease.

With decreasing pH, concentration of H⁺ ions become so high, that they replace the polar components, what leads to adsorption decrease.

Maximum adsorption

How large is initial water saturation?



Dissolution of anhydrite will increase Ca^{2+} concentration.

YES

Did reservoir rock contain anhydrite and/or calcite?

With increasing S_w, the amount of active ions will increase.

NO

Did FW contain large amount of active ions (for Ca^{2+} > c. 100mM and Mg^{2+} > c. 20 mM)?

YES

Wettability may be altered towards water-wet condition.

NO

Did reservoir temperature is above 100 °C?

YES

Did salinity of FW is very high (>100 000 ppm)?

NO

YES

NO

Did sandstone contain large amount of plagioclase?

NO

YES

pH will be above 7

YES

Is salinity of FW moderate (between 5 000 ppm and 100 000 ppm)?

NO

pH will be below 7, promoting mixed-wet condition.

Reservoir is too water-wet to obtain low-salinity effect

Wettability must be mixed-wet to obtain low-salinity effect. If factors contributive to water-wet condition are not significant, wettability of the reservoir rock probably is mixed-wet.

END

Evaluation of initial wetting state

1. Presence of clay minerals and their type:

- Clay minerals has large cation exchange capacity (CEC), which allows adsorption of ions or polar components onto negatively charged surface.
- Different types of clay minerals vary in CEC.
- Clay minerals organized by CEC increase:

kaolinite < illite < montmorillonite.

Evaluation of initial wetting state

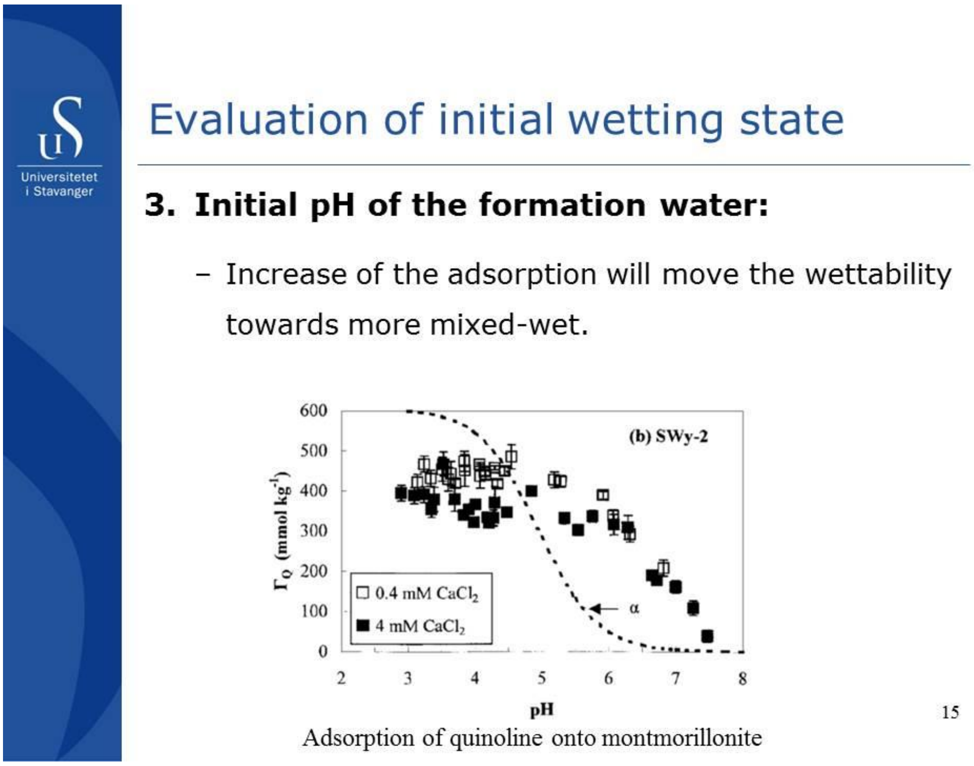
2. Crude oil components:

- Polar components are determined by acid number (AN) and base number (BN).
- Crude oil has to consist sufficient amount of polar components, which is above 0,5 mg KOH/g.
- Adsorption of polar components onto mineral surface can change the wettability of the sandstone towards mixed-wet.

Evaluation of initial wetting state

3. Initial pH of the formation water:

- Adsorption of polar components depends on the pH.
- If the pH is equal to 4÷5 adsorption will reach the maximum.
- If the pH is lower than 4÷5, adsorption decreases. Concentration of H^+ ions became high and are replacing the polar components.
- If the pH is higher than 4÷5, polar components transform to their alkaline forms, that have lower attraction towards clay minerals.



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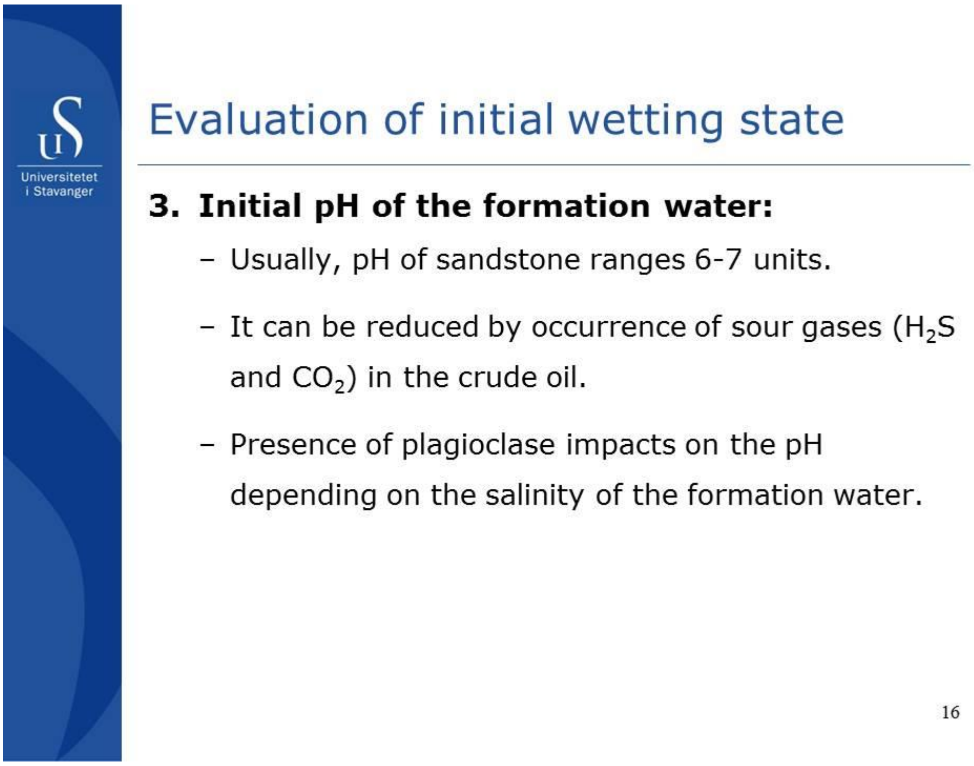
Evaluation of initial wetting state

3. Initial pH of the formation water:

- Increase of the adsorption will move the wettability towards more mixed-wet.

Adsorption of quinoline onto montmorillonite



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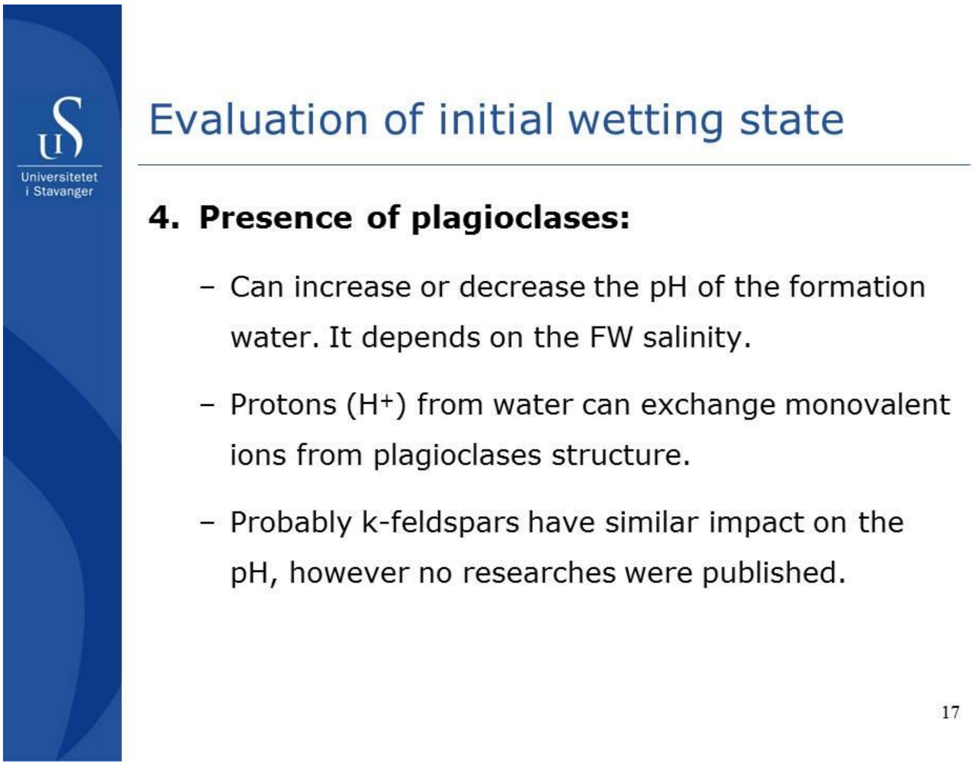
Evaluation of initial wetting state

3. Initial pH of the formation water:

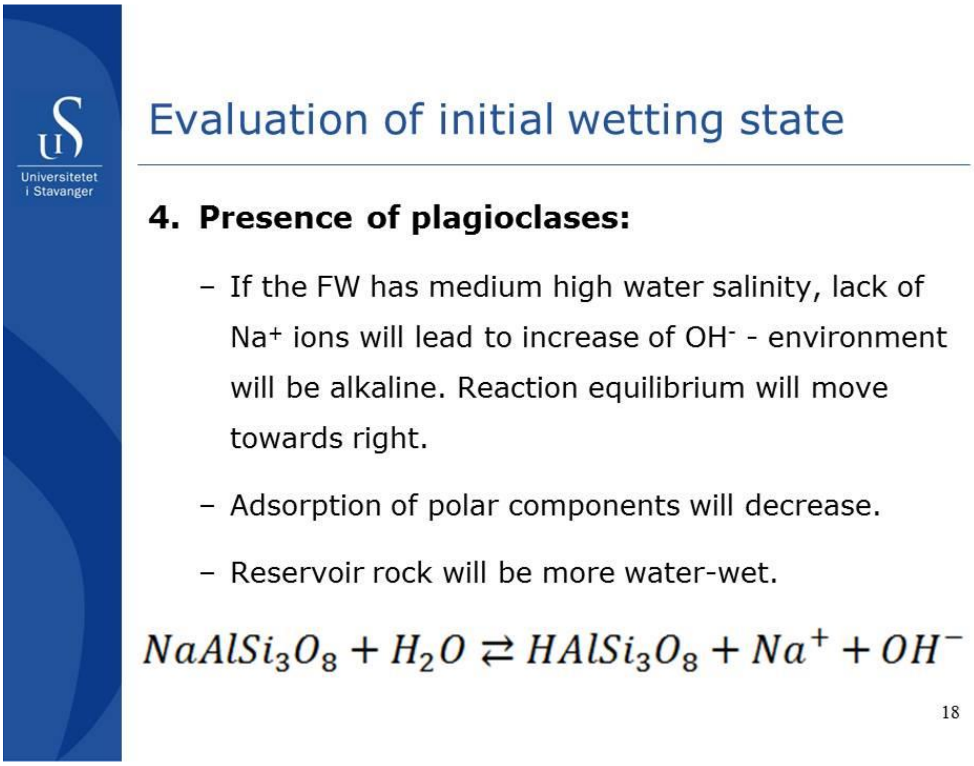
- Usually, pH of sandstone ranges 6-7 units.
- It can be reduced by occurrence of sour gases (H_2S and CO_2) in the crude oil.
- Presence of plagioclase impacts on the pH depending on the salinity of the formation water.



Evaluation of initial wetting state

4. Presence of plagioclases:

- Can increase or decrease the pH of the formation water. It depends on the FW salinity.
- Protons (H^+) from water can exchange monovalent ions from plagioclases structure.
- Probably k-feldspars have similar impact on the pH, however no researches were published.



Evaluation of initial wetting state

4. Presence of plagioclases:

- If the FW has medium high water salinity, lack of Na^+ ions will lead to increase of OH^- - environment will be alkaline. Reaction equilibrium will move towards right.
- Adsorption of polar components will decrease.
- Reservoir rock will be more water-wet.

$$NaAlSi_3O_8 + H_2O \rightleftarrows HAlSi_3O_8 + Na^+ + OH^-$$

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Evaluation of initial wetting state

4. Presence of plagioclases:

- If the FW is high-salinity, high amount of monovalent ions will lead to moving chemical equilibrium towards right.
- Amount of H^+ ions will increase and environment will be acidic. Lowering the pH will enhance adsorption of polar components.
- Reservoir work will be more mixed-wet.

$$HAlSi_3O_8 + Na^+ \rightleftarrows NaAlSi_3O_8 + H^+$$

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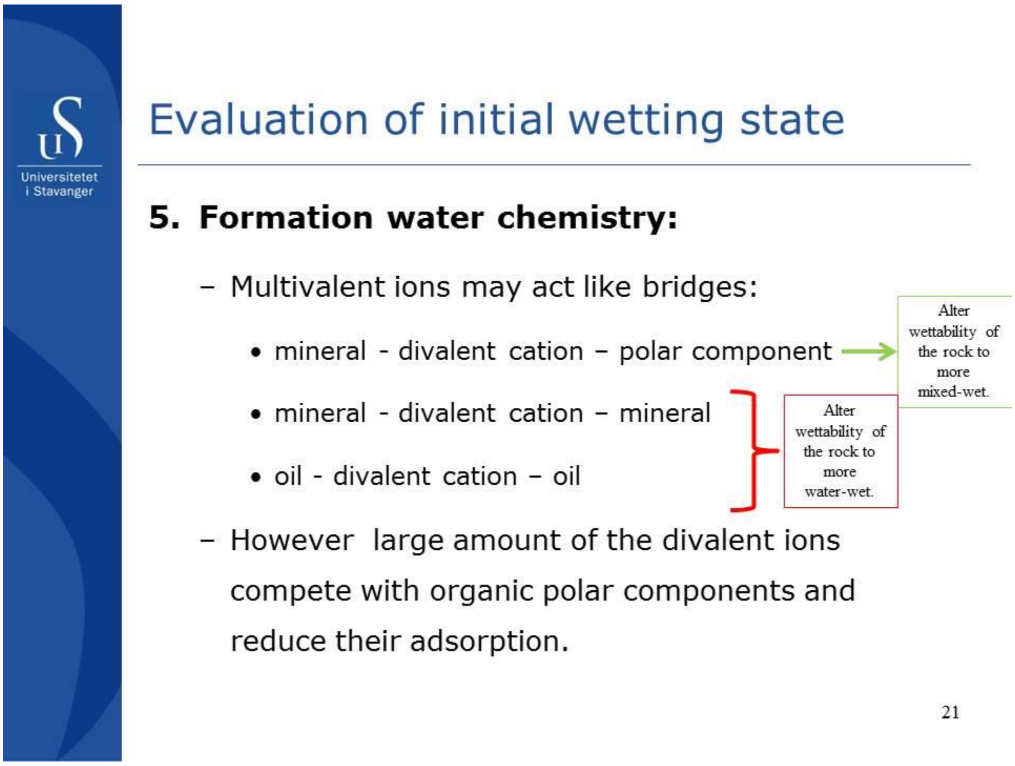
Evaluation of initial wetting state

5. Formation water chemistry:

- Formation water salinity has impact if in the reservoir rock plagioclases are present (previous section).
- If the salinity of the FW will be high (100 000 ppm) in very high reservoir temperature (above 100°C), the reservoir rock will be too water-wet.
- Presence of the active ions (Ca^{2+}, Mg^{2+}) can effect in the adsorption of polar components.



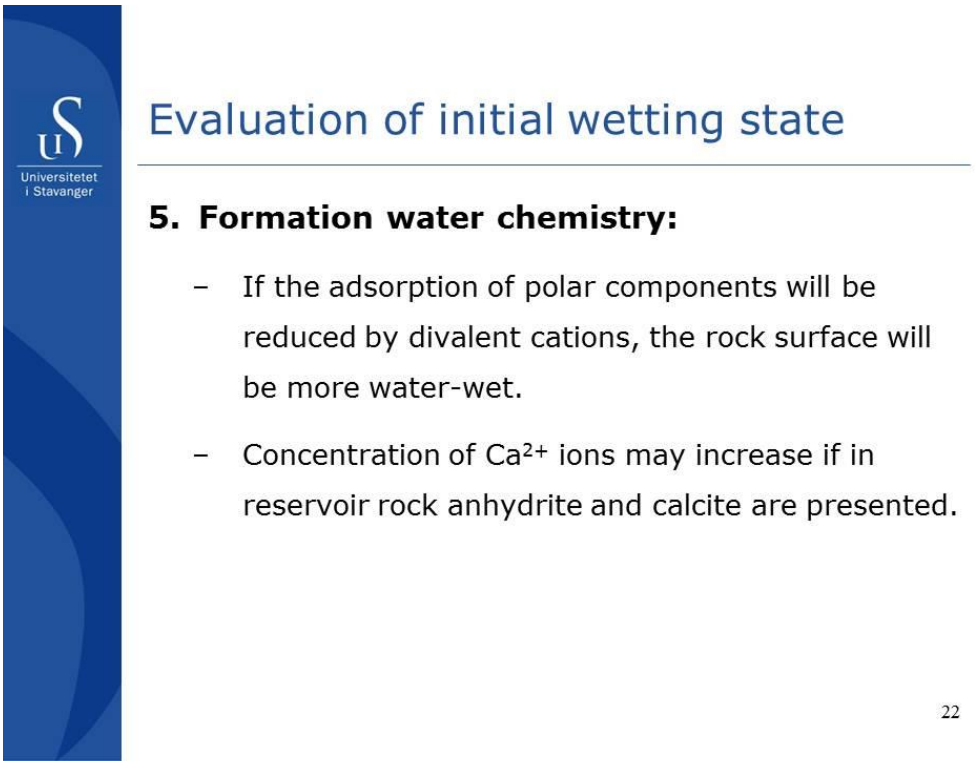
Evaluation of initial wetting state

5. Formation water chemistry:

- Multivalent ions may act like bridges:
  - mineral - divalent cation – polar component
  - mineral - divalent cation – mineral
  - oil - divalent cation – oil
- However large amount of the divalent ions compete with organic polar components and reduce their adsorption.

Alter wettability of the rock to more mixed-wet.

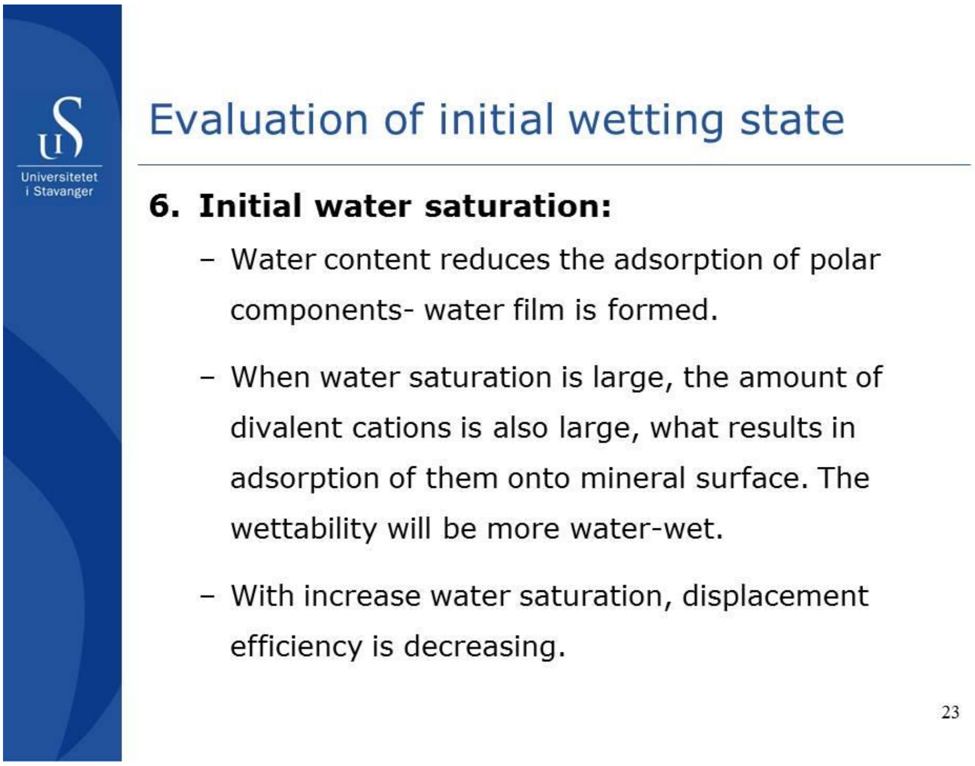
Alter wettability of the rock to more water-wet.



Evaluation of initial wetting state

5. Formation water chemistry:

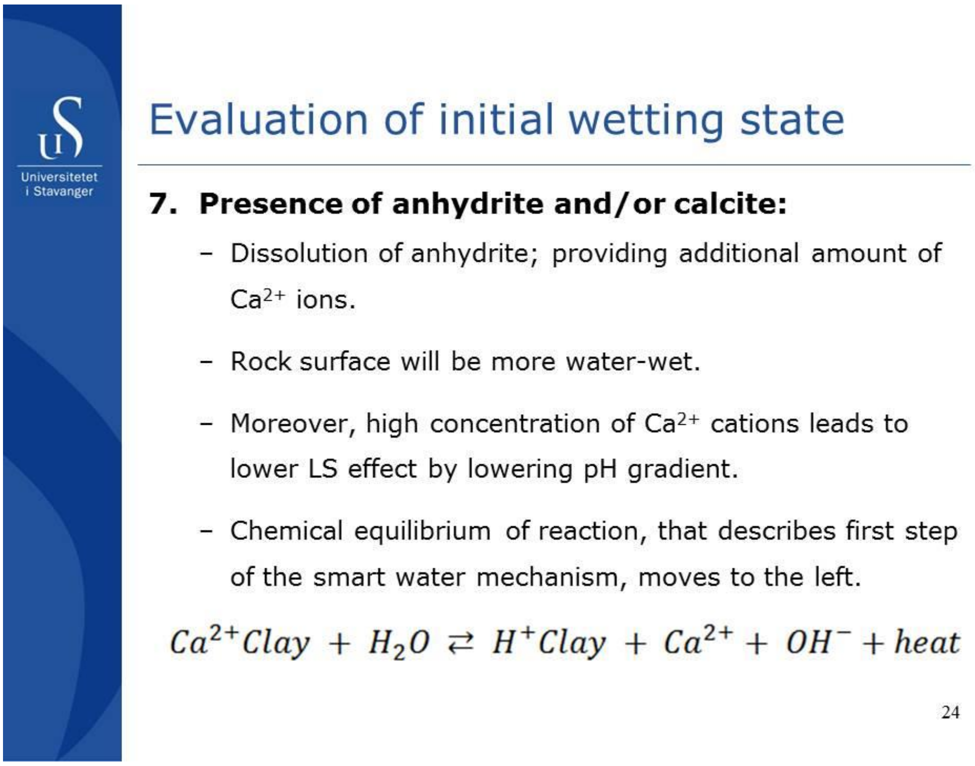
- If the adsorption of polar components will be reduced by divalent cations, the rock surface will be more water-wet.
- Concentration of Ca^{2+} ions may increase if in reservoir rock anhydrite and calcite are presented.



Evaluation of initial wetting state

6. Initial water saturation:

- Water content reduces the adsorption of polar components- water film is formed.
- When water saturation is large, the amount of divalent cations is also large, what results in adsorption of them onto mineral surface. The wettability will be more water-wet.
- With increase water saturation, displacement efficiency is decreasing.

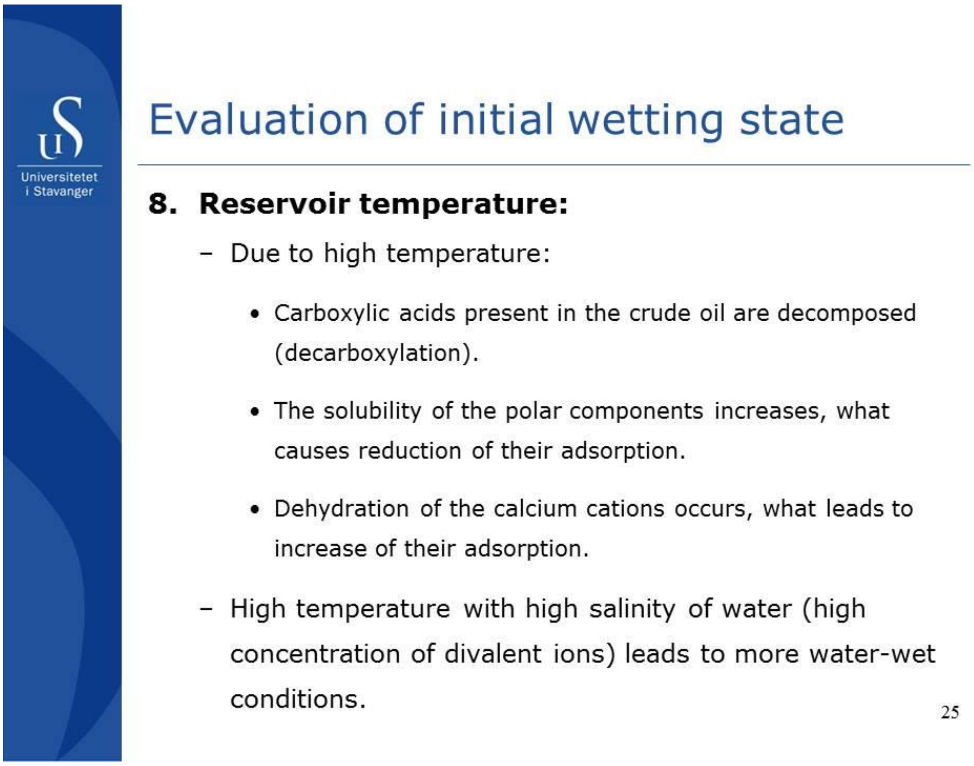


Evaluation of initial wetting state

7. Presence of anhydrite and/or calcite:

- Dissolution of anhydrite; providing additional amount of Ca^{2+} ions.
- Rock surface will be more water-wet.
- Moreover, high concentration of Ca^{2+} cations leads to lower LS effect by lowering pH gradient.
- Chemical equilibrium of reaction, that describes first step of the smart water mechanism, moves to the left.

$$Ca^{2+}Clay + H_2O \rightleftarrows H^{+}Clay + Ca^{2+} + OH^{-} + heat$$



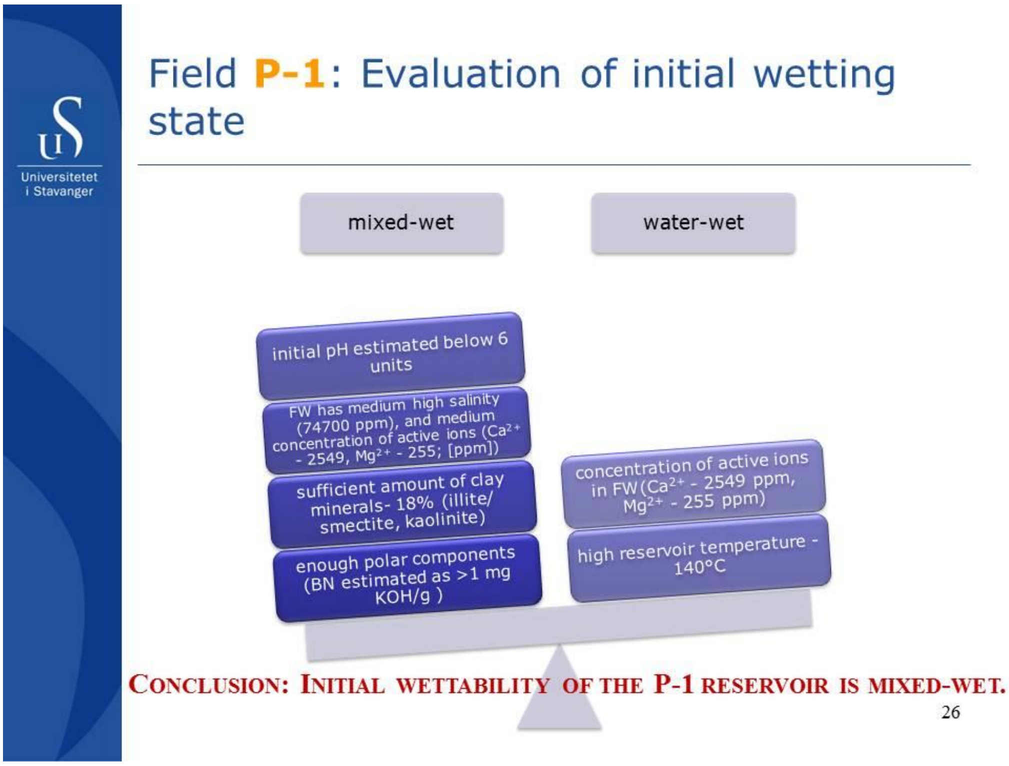
Evaluation of initial wetting state

8. Reservoir temperature:

– Due to high temperature:

- Carboxylic acids present in the crude oil are decomposed (decarboxylation).
- The solubility of the polar components increases, what causes reduction of their adsorption.
- Dehydration of the calcium cations occurs, what leads to increase of their adsorption.

– High temperature with high salinity of water (high concentration of divalent ions) leads to more water-wet conditions.



Field **P-1**: Evaluation of initial wetting state

mixed-wet

water-wet

initial pH estimated below 6 units

FW has medium high salinity (74700 ppm), and medium concentration of active ions (Ca^{2+} - 2549, Mg^{2+} - 255; [ppm])

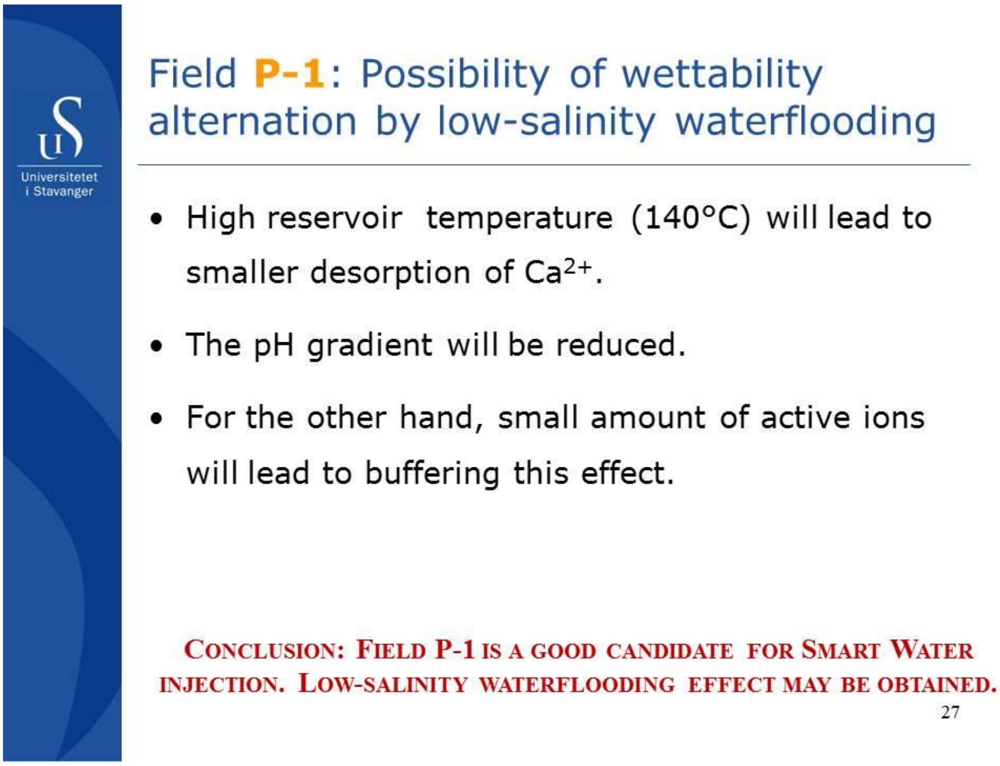
sufficient amount of clay minerals- 18% (illite/ smectite, kaolinite)

enough polar components (BN estimated as >1 mg KOH/g)

concentration of active ions in FW (Ca^{2+} - 2549 ppm, Mg^{2+} - 255 ppm)

high reservoir temperature - 140°C

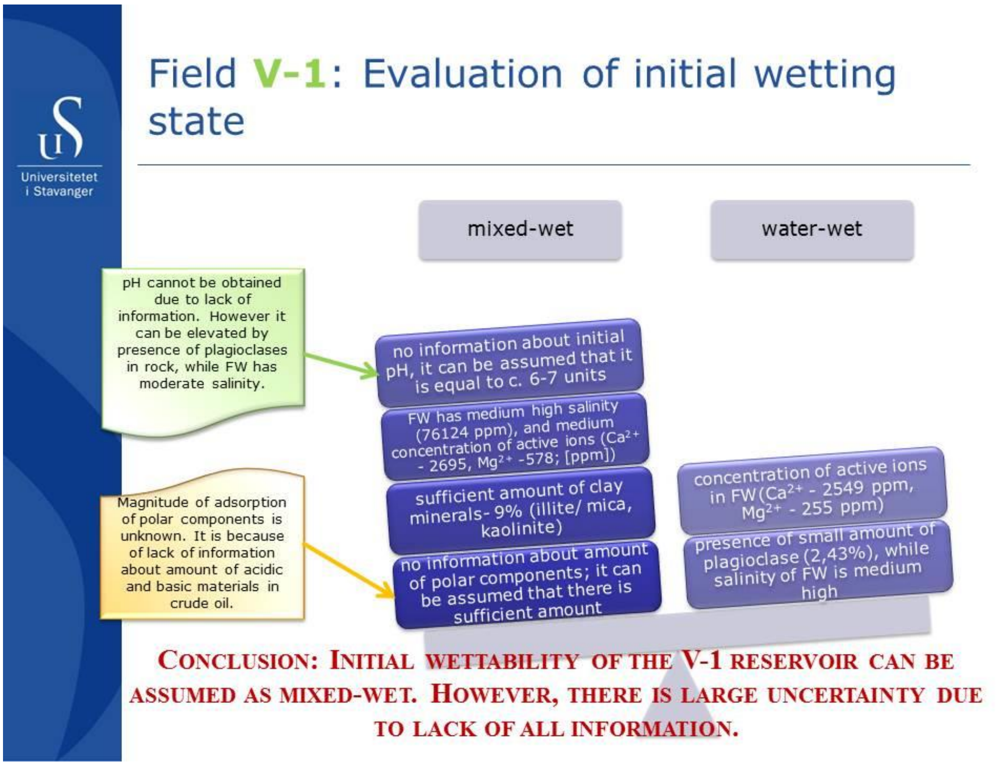
CONCLUSION: INITIAL WETTABILITY OF THE P-1 RESERVOIR IS MIXED-WET.



Field **P-1**: Possibility of wettability alternation by low-salinity waterflooding

- High reservoir temperature (140°C) will lead to smaller desorption of Ca^{2+}.
- The pH gradient will be reduced.
- For the other hand, small amount of active ions will lead to buffering this effect.

CONCLUSION: FIELD P-1 IS A GOOD CANDIDATE FOR SMART WATER INJECTION. LOW-SALINITY WATERFLOODING EFFECT MAY BE OBTAINED.



Field **V-1**: Evaluation of initial wetting state

mixed-wet

water-wet

pH cannot be obtained due to lack of information. However it can be elevated by presence of plagioclases in rock, while FW has moderate salinity.

no information about initial pH, it can be assumed that it is equal to c. 6-7 units

FW has medium high salinity (76124 ppm), and medium concentration of active ions (Ca^{2+} - 2695, Mg^{2+} -578; [ppm])

sufficient amount of clay minerals- 9% (illite/ mica, kaolinite)

no information about amount of polar components; it can be assumed that there is sufficient amount

Magnitude of adsorption of polar components is unknown. It is because of lack of information about amount of acidic and basic materials in crude oil.

concentration of active ions in FW (Ca^{2+} - 2549 ppm, Mg^{2+} - 255 ppm)

presence of small amount of plagioclase (2,43%), while salinity of FW is medium high

CONCLUSION: INITIAL WETTABILITY OF THE V-1 RESERVOIR CAN BE ASSUMED AS MIXED-WET. HOWEVER, THERE IS LARGE UNCERTAINTY DUE TO LACK OF ALL INFORMATION.

Field **V-1**: Possibility of wettability alternation by low-salinity waterflooding

- Presence of the plagioclases in reservoir rock and medium high saline formation water leads to increase of pH.
- The pH gradient will be reduced due to higher starting point (initial pH of the reservoir will be relatively high).
- Desorption of polar components will be lower.
- Due to high uncertainty, explicit conclusions cannot be drawn.

THANK YOU ☺

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