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Magnus Halvorsen

ABSTRACT

The objective of the project is defined in two phases. The first phase is to study the effect of oil composition and carboxylic acids in the crude oil on the wetting condition and wettability alteration process using "Smart Water". It has been reported that the major types of acidic compounds in crude oil were identified as carboxylic acids, phenols, carbazoles, and amides. The phenols and carboxylic acids comprise the major portion of the acidic species. The water soluble components of the carboxylic material are a small fraction of the total amount of carboxylic acids in the crude oil. They play an important role in establishing the initial wetting condition by contributing to destabilize the water film between the rock and oil.

In this work, we have extracted water-soluble acids from a crude oil with high acid number (AN) to study the effect of these acidic materials on the wetting condition. Two crude oils have been prepared with almost the same acid number: the original oil, RES40 and synthetic crude oil containing only water-soluble acids termed EWS-oil. Two parallel cores were saturated and aged with each crude oil. The cores were subjected to spontaneous imbibition to study the oil displacement efficiency by "Smart Water". The potentiality of seawater as a wettability modifier has been investigated previously. The mechanism of wettability alteration has been proposed based on the interactions between the rock surface and the potential determining ions Ca^{2+}, Mg^{2+} and SO_4^{2-} present in seawater.

It was concluded that, not only the strength of the bonding of carboxylic material onto the calcite surface dictated by the carboxylic group, AN, is an important wetting parameter; but also the organic structure of the carboxylic material may have an impact on the wetting condition as well.

The second phase of the project is to study the application of Enzymes to improve the wetting condition towards water-wetness. An enzyme-based method has already been reported, which generates organic acids for a variety of acidizing applications such as a matrix acidizing, the stimulation of natural fracture networks, damage removal over long horizontal intervals. The generation of acid in-situ following placement of the fluid ensures the even delivery of acid over the whole of the treated zone.

Two cores were saturated and aged with the crude oil, RES40. After forced displacement with seawater depleted in sulfate and establishing residual oil saturation, the enzyme solution was injected into the cores and shut-in for 48 or 96 hours in an attempt to improve the wetting condition towards water-wetness. Later, the chromatographic wettability test was performed to monitor the change in the wetting condition. No improvement in the wetting condition and displacement efficiency was observed after enzyme injection.

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1 INTRODUCTION

1.1 Carbonates

It has been documented that close to 50% of the worlds proven petroleum reserves are located in carbonate formations [1]. One of the problems is the rather poor ultimate oil recovery factor from the rock, less than 30 %. The low recovery factor is mainly due to wettability and the fractured nature of these reservoirs.

Carbonates are a sub class of the chemical/biochemical sedimentary rocks. Carbonates originate by precipitation of minerals from water through different processes. Carbonate rock can again be divided into limestone or dolomite, depending on the mineralogy. The main difference is that limestone is containing more than 50 % of calcite while dolomites are composed of more than 50 % of the mineral dolomite [2].

"Chalk is classified as a limestone, and it originated from the deposition and sedimentation of calcareous skeletal debris from the unicellular planktonic algae coccolithophorid, plus a small amount of foraminiferal materiall [3]. The coccolithophorid algae consist of many spherical coccospheres (2-20 μm diameter), which are built up by coccolithic ring structures (3-15 μm diameter), which in turn are composed of ring fragments or platelets consisting of calcite crystals (0.25-1 μm diameter). Figure 1.1 shows clearly a coccolithic ring and ring fragments, intact and non-intact.

Chalk is finely grained and is usually highly porous because of small pores between the skeletal constituents, seen as the black spaces in Figure 1.1, but with low permeability because of the microscopic size of the constituents [4]".

Figure 1.1 Picture of chalk, taken by a scanning electron microscope (SEM), showing coccolithic rings, fragments and pore space.

1.2 Oil recovery

Production from a reservoir is often classified into three groups, primary, secondary and tertiary oil recovery. These three groups are most of the time dependant on whether it is in the beginning or late in the production time line.

1.2.1 Primary recovery

Primary oil recovery refers to the situation were only reservoir energy through different mechanisms is used for drainage of oil. There are no additional forces, only the pressure difference will make the oil flow up through the well. This primary recovery gives a rather low recovery factor, normally only 5-30 % of original oil in place (OOIP) can be produced.

1.2.2 Secondary recovery

Secondary oil recovery is usually applied after primary recovery, or started when the primary production is decreasing. It is all about adding forces to maintain the reservoir pressure. The pressure can be supported by injection of water or gas, with water the most common, to keep up the production of reservoir fluid or give a more efficient oil displacement. The recovery factor after this stage is a bit higher, usually in the rage of 30-50 % of OOIP [4].

1.2.3 Tertiary recovery

After both primary and secondary production there is still a lot of oil in the reservoir, so more techniques can be applied if economical. These methods are called tertiary oil recovery or enhanced oil recovery (EOR). The purpose of EOR is to extend the production lifetime of a field by support of waterflooding or different conventional methods. Bavière gave one definition of EOR: "*EOR consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers in order to induce new mechanisms for displacing oil*" [5]. This definition excludes all methods using mechanical energy to support the pressure and work like well stimulation, infill drilling and directional drilling. So the Norwegian petroleum directorate came up with a wider definition of increased oil recovery (IOR): "*Actual measures resulting in an increased oil recovery factor from a reservoir as compared with the excepted value at a certain reference point in time*". This includes all methods applied for increasing the lifetime of a reservoir, not planned at the beginning of production.

Tertiary hydrocarbon recovery can be divided into four processes.

-Mobility-control
-Chemical
-Miscible
-Thermal

Mobility-control is about adding polymers to the injection fluid. These polymers are capable of increasing the viscosity of the displacing fluid and thereby creating a better mobility ratio. The chemical process is an expensive flooding technique. By injecting a chemical like surfactants the interfacial tension between the injecting fluid and the reservoir fluid will decrease. This lowering can lead to mixing of the fluids and a higher recovery factor. Miscible processes are displacing hydrocarbons with a fluid that is miscible with the hydrocarbons. The displacing fluid will be able to mix with the reservoir fluid and create one phase together. The last process, thermal, is mainly based on the advantageous properties of heated hydrocarbons. With an increase in temperature inside a reservoir the viscosity of the hydrocarbons will decrease, which again will make the reservoir fluid flow easier.

1.3 Wettability in carbonates

In general, wettability can be described as the tendency one fluid has to spread on or adhere to a solid surface in the presence of another immiscible fluid [6]. Knowing the wettability of a reservoir is very important due to its affect on capillary pressure, relative permeability, irreducible saturations, electrical properties and for many EOR processes. Unlike sandstone reservoir, studies indicate that about 80-90% of the worlds carbonate reservoirs show a negative capillary pressure, in other words they are preferentially oil-wet. Chilinger and Yen did a survey on 161 samples from carbonate rock, they reported that 15 % were strongly oil-wet, 65 % were oil-wet, 12 % were in the intermediate class and 8 % were water-wet [7].

It is documented that almost 50 % of the proven hydrocarbon reserves are located in carbonates. These reservoirs usually shows a rather low recovery factor, at about 30 %, mainly because of the fractured nature of these reservoirs [8]. These fractured reservoirs is hard to produce from because injected water is likely to follow the larger fractures to the production wells, going past most of the oil in the rest of the matrix blocks. If the rock were water-wet, water would imbibe spontaneously and displace oil from the matrix block to the fracture network. This method does not work well as long as most carbonate reservoir is on the oil-wet side.

The carboxylic material, quantified as acid number (AN), present in the crude oil absorbs very strongly onto the positive sites of a chalk surface [9]. It is therefore the most important wetting parameter for carbonates. The water wetness of a rock surface will decrease as the AN increases. Within the carboxylic group there are some water-soluble components. These components are believed to play an important role in the initial wetting state because the water-soluble acids may contribute in destabilization of the water film [10].

A lot of studies have been made on carbonates, concerning improved recovery of petroleum. Research has shown that interaction between the chalk surface and the potential determining ions Ca^{2+}, Mg^{2+} and SO_4^{2-} are able to alternate the wettability of chalk at high temperature, and by that increase the oil recovery [8, 11].

2 THEORY

Principles and concepts that make it possible to produce hydrocarbons from reservoirs and fundamental concepts regarding EOR.

2.1 Displacement forces

There are several different forces acting on the fluid flow within a reservoir. The most influencing displacement forces are gravity, viscous and capillary force, which will be explained. In a spontaneous imbibitions process the active forces are gravity- and capillary forces. The interplay between these two forces is particular important in situations where the wettability approaches neutral or the interfacial tension decreases.

2.1.1 Gravity force

Gravity force is especially important in an oil and gas situation, where there is a great difference between the fluids and fluid phases. The dissimilar density of two or more fluids causes this force. The fluid with the lightest density will flow upwards relative to a denser fluid. Cole, 1969, expressed the force by formula 2.1 [12].

$$\Delta P_g = \Delta\rho * g * H \quad (2.1)$$

Where:

ΔP_g Pressure difference between oil and water due to gravity, [Pa]

$\Delta\rho$ Density difference between oil and water, [kg/m^3]

G Gravity acceleration, [9.8m^2/s]

H Height of the liquid column, [m]

2.1.2 Viscous force

In a porous medium the viscous forces are reflected in the magnitude of the pressure drop that occurs as a result of fluid flow through the porous medium. A simple approximation to calculate the viscous force is to think of the porous medium as a bundle of parallel capillary pipes. With this assumption, the pressure drop for a laminar flow through a single tube is given by formula 2.2, Poiseuille’s law [13].

$$\Delta P = -\frac{8\mu L\,\bar{v}}{r^2 g_c} \quad (2.2)$$

Where:

ΔP = Pressure drop across the capillary tube

μ = Viscosity of flowing fluid

L = Capillary tube length

$\bar{v}$ = Average velocity in the capillary tube

r = Capillary tube radius

g_C = Conversion factor

2.1.3 Capillary force

It is the capillary forces that make a fluid imbibe into thin capillary tubing. Example of this is the process where water rises up into plants and trees.

When there is a capillary tube or a rock pore channel with two immiscible fluids in contact with each other, the interface between the two fluids will be influenced by the adhesive force of the wetting fluid. The interface will curve, developing an asymmetric meniscus. This meniscus will be convex towards the wetting fluid and with an angle to the pipe wall named the contact angle.

"*Capillary pressure (Pc) can be defined as the molecular pressure difference across the interface of the two fluids*." The pressure difference is caused by electrostatic forces acting on both fluids. Electrostatic forces concern differences in both internal (cohesive) and external (adhesive) force. Another way to put this is to say that Pc is the difference in molecular pressure between the wetting- (W) and non-wetting (NW) fluid. See equation 2.3 [14].

$$P_c = P_W - P_{NW} \quad (2.3)$$

Capillary pressure across a meniscal interface

As mentioned earlier the interface between two fluids in a capillary pipe has a meniscal shape always convex towards the wetting fluid, which has a greater internal pressure. The shape of the meniscal can be characterized by two radii, see figure 2.1. The Laplace equation gives the relationship between the Pc and the different radii (See equation 2.4).

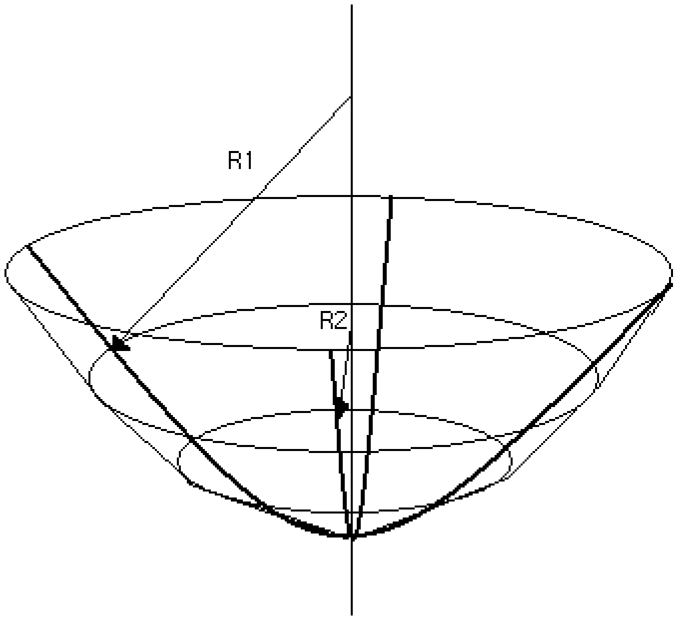


Figure 2.1 A meniscal interface, with its two radii of its curvature.

$$\Delta \mathrm{P} = \mathrm{P_C} = \sigma \left(\frac{1}{\mathrm{R_1}} + \frac{1}{\mathrm{R_2}} \right) \quad (2.4)$$

Where:

Pc	Pressure difference across the meniscal
σ	Interfacial tension
R1,R2	Two principal radii

If a meniscus has a hemispherical shape, or a spherical oil droplet is equal the pore size, then R1=R2=r and $\Delta P = 2\sigma/r$. As the other extreme, a planar interface will have R1 and R2 equal to infinity and therefore ΔP equal to zero [14].

Capillary pressure in a pipe

Figure 2.2 shows a drawing of a capillary tube containing two immiscible fluids with a meniscal interface between them. In this section, the wetting fluid is water and the non wetting fluid is oil. The radius of the pore channel or tube is r, R is the radius of the meniscus curvature and θ is the wetting angle. Assuming R1 and R2 are equal and called R, an equation for R can be calculated, see equation 2.5.

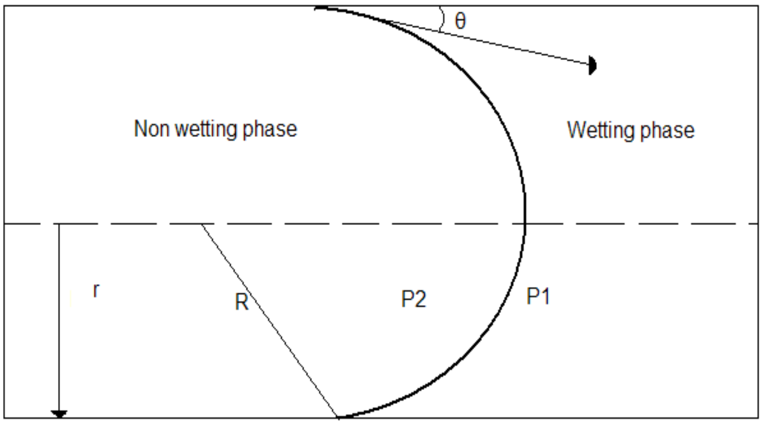


Figure 2.2 Idealized model of a pore channel, filled with two immiscible fluids.

$$R = \frac{r}{\cos\theta} \qquad (2.5)$$

By using equation 2.5 in equation 2.4 it leads to equation 2.6.

$$P_C = \frac{2\sigma_{OW}\cos\theta}{r} \qquad (2.6)$$

The equation for capillary pressure is dependent many parameters. Pc is dependent of the pore structure of the porous rock, since r is the radius of the pore. Pc is also a function of wettability and contact angle. Equation 2.6 shows that an increase in the interfacial tension for this example will give an increase in capillary pressure. The contact angle is the indication of wettability. This angle decides whether the capillary pressure is a negative or positive number. With a contact angle of the wetting fluid larger than 90°, the capillary number will become negative, and vice versa [14].

2.2 Wettability

Wettability is a rock property. Because of its great impact on the location, flow and distribution of the fluids in the reservoir it is an important factor for success of water flooding. "*The wettability of a solid can be defined as the tendency of one fluid to spread on, or adhere to, the solid`s surface in the presence of another immiscible fluid*" [14]. When two or more immiscible fluids are together in a pore, one of the fluids is usually more attracted to the solid and will adhere. The more attracted fluid will give name to the wetting phase.

If the system is at equilibrium the wetting fluid will be located at pore walls and in the smallest pores, while the other fluid will be in the pore bodies, see figure 2.3.

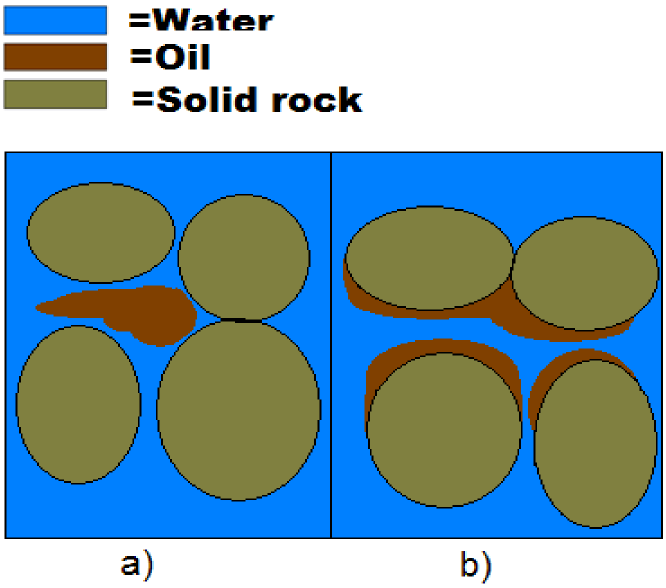


Figure 2.3 a) Water wet rock. a) Oil wet rock.

A way to evaluate the wettability is by measuring the contact angle. This is the angle (θ) between a solid and the two immiscible fluids, see figure 2.4. The contact angle shows the equilibrium between the interfacial tensions of the two fluids and their individual adhesive attraction to the solid. When looking at a system containing oil, water and a rock, the rock is preferentially water wet if θ<90°. If θ>90° the rock is preferentially oil wet. The wettability of the rock is called intermediate or neutral if the contact angle is equal to 90°, when this is the case the rock has no strong preference and both fluids could be the spreading fluid.

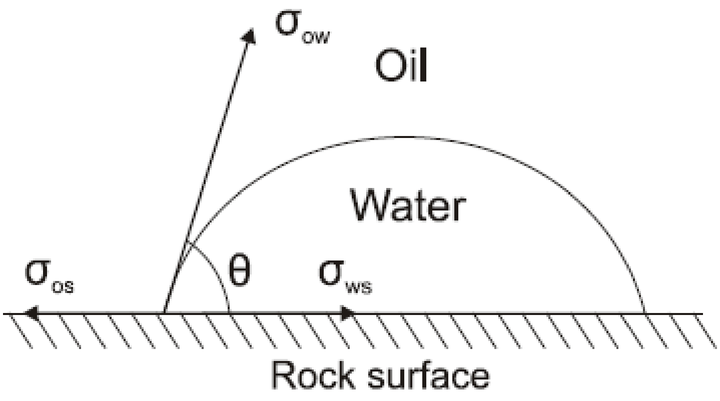


Figure 2.4 Contact angles between oil, water and rock [6].

There is a great diversity of reservoir, and not all have a uniform wettability as described. The wettability could be more heterogeneous. In some reservoir the wettability change from location to location, at some places the rock is strongly oil-wet while the rest is strongly water-wet. This situation is called fractional, spotted or dalmatian wettability. Another type of wettability, introduced by Salathiel, is the “mixed wettability”. Here the oil-wet surfaces make continuous paths through the largest pores, which contain all the oil, and fine pores and grain contacts are preferentially water-wet [4].

As mentioned the wettability is very important when producing oil from subterranean formations. Considering the effect of wettability on fluid distributions, one can imagine that relative permeability curves are strong functions of wettability. Figure 2.5 show a relative permeability curve as a function of water saturation. The saturation is again a function of rock properties, as pore distribution and wettability.

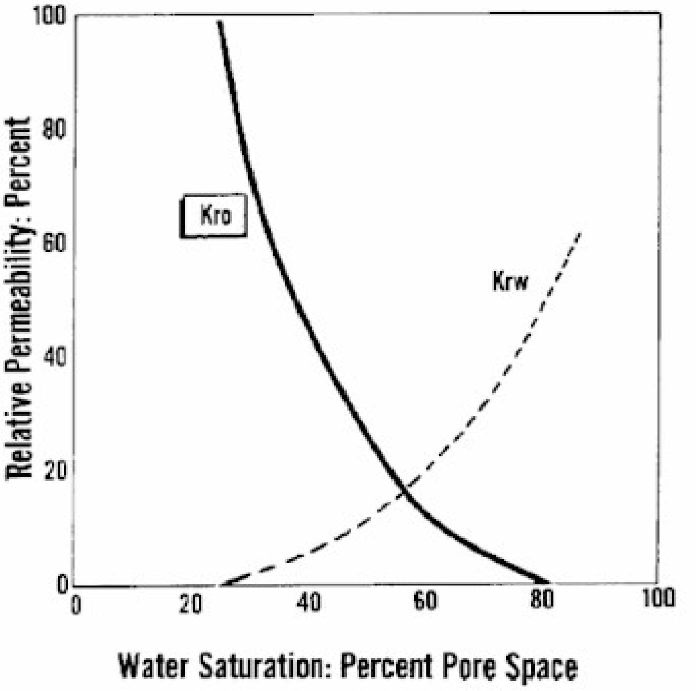


Figure 2.5 The relative permeability as a function of water saturation.

2.2.1 Wetting state of surfaces

Clean carbonate rocks are naturally water-wet. The migration of oil from the source rock made the wetting state change to more oil-wet by absorption of polar components from the crude oil onto the originally water-wet mineral surface [15]. The wetting state for a reservoir rock is related to the stability of the water film between the oil and rock. Electrostatic attraction between the crude oil/brine and the rock/brine interface tends to collapse the brine film and bring the crude oil in contact with the rock [16].

2.3 Wettability measurement methods

There are several different methods to measure the wettability of a rock. The type of measurement is divided into two groups, quantitative and qualitative. Methods to perform a quantitative measure of the wettability include contact angle measurement, Amott and the USBM (United States Bureau of Mines) method. Qualitative methods comprises imbibitions rates, microscope examination, relative permeability curves, permeability/saturation relationships, capillary pressure curves, displacement capillary pressure, reservoir logs, nuclear magnetic resonance and dye adsorption [4].

The methods used in this thesis is of the quantitative sort, wettability have been measured by spontaneous- and forced imbibitions (a part of the Amott) and by the Ion Chromatographic wettability test developed by Strand et al.2006 [17]. The two methods will be explained.

2.3.1 Amott method

The original Amott method measured the average wettability by imbibition and forced displacement (by centrifuging). The wetting fluid will normally imbibe spontaneous into a core or reservoir and displace the non-wetting fluid. A comparison of the spontaneous imbibition and the forced displacement ratio is used to reduce the influence of e.g. relative permeability, viscosity and initial saturation of the rock.

A complete Amott test gives two results, displacement by oil ratio (I_O) and displacement by water ratio (I_W). See equation 2.7 and 2.8.

The Amott method was modified into the Amott-Harvey test method. Figure 2.6 shows a full cycle of the Amott and Amott-Harvey test with its five steps.

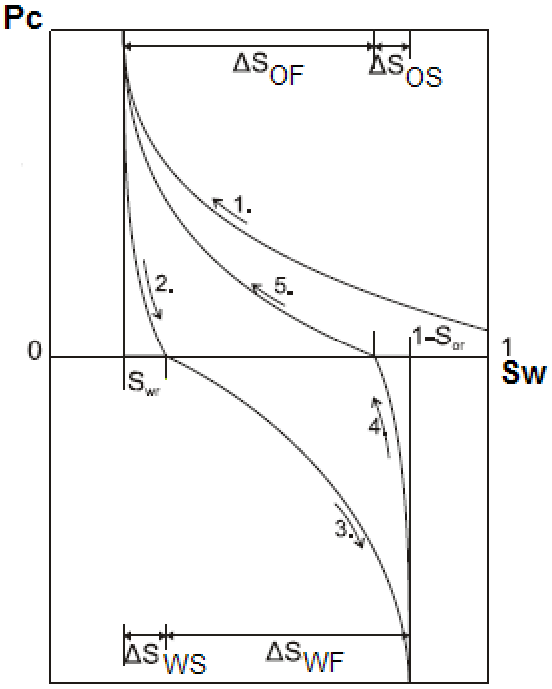


Figure 2.6 A typical capillary pressure curve for the Amott and Amott-Harvey test.

The five steps in the test cycle:

1. Primary drainage of water by oil to establish initial water saturation, S_{WI}
2. Spontaneous imbibition of water
3. Forced imbibition of water
4. Spontaneous imbibition (drainage) of oil
5. Forced imbibition (drainage) of oil

$$I_O = \frac{\Delta S_{OS}}{\Delta S_{OS} + \Delta S_{OF}} \quad (2.7)$$

$$I_W = \frac{\Delta S_{WS}}{\Delta S_{WS} + \Delta S_{WF}} \quad (2.8)$$

The Amott-Harvey combines I_O and I_W by the use of equation 2.9 to find a relative displacement index (I_{AH})

$$I_{AH} = I_W - I_O \quad (2.9)$$

This test will give a single value as the final answer, the value ranging from -1 for a completely oil-wet system to a value of 1 for a completely water-wet system. The index was later supplemented by stating that $-1 \leq I_{AH} \leq -0.3$ was an oil-wet system, $-0.3 < I_{AH} < 0.3$ was a neutral-wet system and $0.3 \leq I_{AH} \leq 1$ was a water-wet system.

The Amott methods are insensitive near neutral wettability and do not distinguish well enough between degrees of strong water wetness [4]. It is however used a lot, because of it is easy to perform and gives a defined scale for the wettability.

2.3.2 Chromatographic wettability test

Most of the carbonate reservoirs are in the neutral to oil-wet region and therefore in the insensitive range using methods like Amott.

This test was developed by Strand et al. 2006 to characterize the wetting state of a porous chalk core by the fraction of surface area covered by one of the two fluids, i.e. water or oil. It is based on chromatographic separation between sulfate, SO_4^{2-}, and the tracer thiocyanate, SCN^- during a core flooding. The difference between the two water-soluble components is that SO_4^{2-} will adsorb to the water-wet chalk surface, while SCN^- will not adsorb.

The procedure for doing a chromatographic test starts with an oil saturated core. The core is first flooded with brine containing neither sulfate nor tracer down to residual oil saturation (S_{OR}). Second the flooding fluid is changed to brine containing equal content of sulfate and tracer. The produced effluent is collected in fractions by a fraction collector and analyzed for the ionic compositions of SO_4^{2-} and SCN^-.

The core wetness is computed by plotting relative ion concentration against pore volume injected, and calculating the area between the effluent curves. The calculated area is proportional to the area contacted by water during the flooding process. Figure 2.7 is an example of this computation, showing the relative ion concentration as a function of pore volume injected. In this figure both a reference core and the investigated core are plotted. It also shows the respective areas calculated. The final wetting index (WI) is calculated by equation 2.10, and describes the fraction of water-wet surface inside the core.

$$WI = \frac{A_{WET}}{A_{REF}} \qquad (2.10)$$

Where:

A_{WET} is the area between sulfate and tracer for the core aged in oil, while A_{REF} is the area between sulfate and tracer in a core assumed to be totally water-wet. Both areas are calculated using the trapezoidal rule [17].

Characterization:

WI = 0 is completely oil-wet

WI = 0.5 in neutral wetting state

WI = 1 is completely water-wet

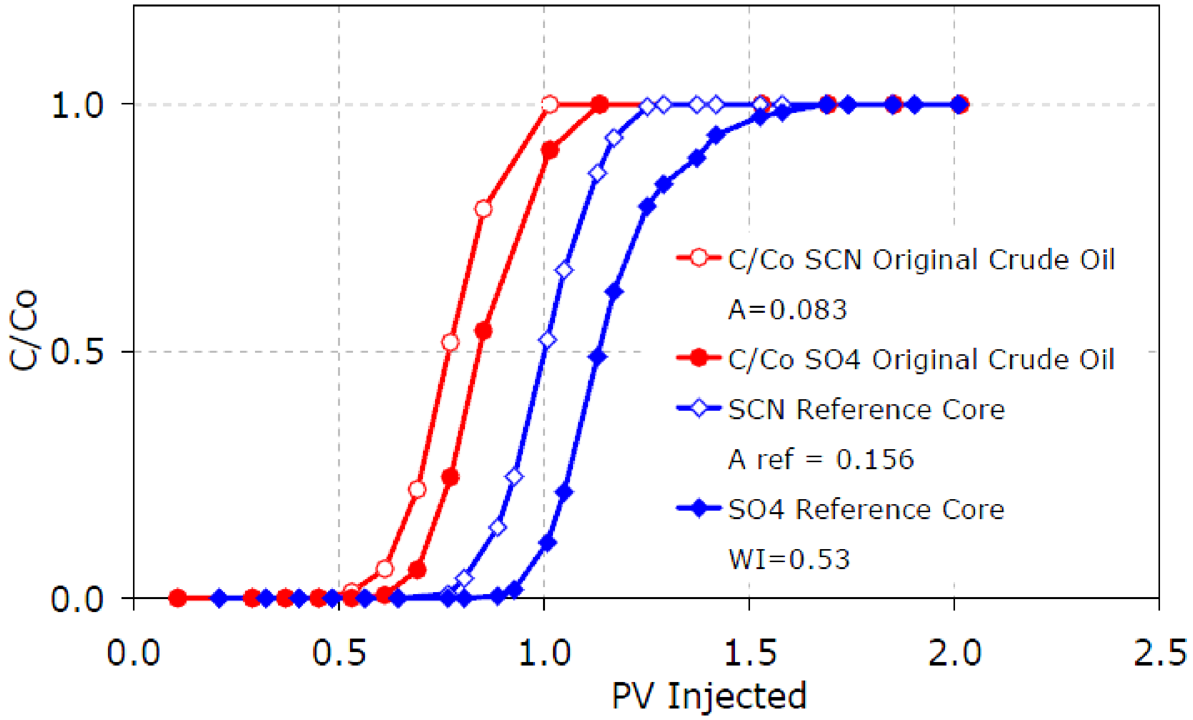


Figure 2.7 Typical plot of wettability test on chalk core, this one resulting in neutral wettability.

2.4 EOR from carbonates reservoir

Enhanced oil recovery (EOR) is very important since after primary and secondary recovery there is still a great volume of hydrocarbons left in the reservoir. If water injected does not have the same composition as the original brine, and higher recovery is expected, it can be thought of as a tertiary recovery method. The Ekofisk field in Norway had initially an estimated recovery of 17 %. Today the prediction is increased to 50-55 %, which is well above most carbonate reservoirs with a recovery below 30 % [4]. The reasons for the success of the Ekofisk field recovery are mainly the highly fractured nature and injection of seawater.

EOR from carbonates faces great difficulties. Unfavorable wetting conditions in carbonates makes the spontaneous imbibition hard, and for that reason less oil is expelled from the pores. Another reason is the fractured nature of carbonate reservoirs. The matrix has a very low permeability, while fractures in the rock have better permeabilities. About 50 times better actually. Fluid injected into a reservoir will always follow the path with the lowest resistance, meaning it flows through the fractures and not the matrix. Oil produced will be the oil originally residing in the fractures, which in some cases is only a couple per cent of OOIP. The oil stored in the matrix is passed by the injected fluid [15].

To be able to produce more oil, the injected fluid will have to enter the neutral-wet matrix blocks. In order to imbibe the matrix a capillary pressure threshold, expressed by the Leverett J-function (equation 2.11), must be overcome, or maybe lowered.

$$P_C = \sigma\sqrt{\frac{\varphi}{k}}J^* \qquad (2.11)$$

Where:

P_c = capillary pressure
σ = interfacial tension between oil and water
φ = porosity
k = permeability
J^* = dimensionless entry pressure (often 0.25)

This pressure threshold can be broken by viscous- or gravity forces. Another possibility is to lower the barrier by reducing the interfacial tension (IFT) between the fluids using methods like surfactant flooding, gas injection, miscible gas injection or by simply alternate the wetting state of the rock [15]. This thesis use surfactant- and seawater flooding to alter the wettability and increase the recovery rate, so these two will be described.

2.4.1 Surfactant flooding

The injection of surfactants into oil reservoirs was originally aimed to mobilize the capillary trapped oil after water flooding, to increase the recovery [18]. Surfactants work in a way that lowers the interfacial tension between water and oil, and deforms the trapped oil droplets so that these can be mobilized and displaced through the throats by viscous forces [13]. According to equation 2.11 a lowering of the IFT will reduce the capillary threshold pressure, making it easier to imbibe the matrix blocks. However, a lowering of IFT will also lower the Pc according to equation 2.6, so the oil recovery rate may increase or decrease, but the final recovery factor tends to increase by surfactant flooding.

Alternative effect of surfactant flooding is wettability alteration. Where surfactants make the rock more water-wet, in that way also to increase the capillary force and enhance the imbibition [19].

The biggest limitation of surfactant flooding may be that as an EOR method it is quite expensive.

2.4.2 Injection of seawater into chalk reservoirs

The final goal of seawater injection as a tertiary recovery process is to get more oil produced from the reservoir. As mentioned earlier, to be able to produce more oil, injected water must enter the matrix blocks and not only flow through the fractures. Increased spontaneous imbibition is a process that can make this happen in chalk at low water-wetness. So to sum it up: Improved oil recovery is possible if the injected fluid can change the wetting condition towards a more water-wet state.

"*The wettability of carbonates is dictated by the stability of the water film between the rock and the oil phase, which is related to the Zeta-potentials of the oil-water and water-rock interfaces*" [20]. The charge of the water-rock interface is determined by the pH and the actual potential determining ions present in the formation water. With a pH of about 8 and a high concentration of Ca^{2+} in the initial brine, the surface charge of the chalk become positive. Carboxylic material, quantified by acid number, AN (mgKOH/g), present in the oil is negatively charged and will adsorb to the chalk surface, making the rock oil-wet.

The wetness of carbonate reservoir is mainly governed by the acid number of the crude oil, since the carboxylic group will adsorb onto the chalk surface. The water wetness increases as the AN decreases. Reservoir temperature also makes an impact, the acid number of the crude oil decreases due to decarboxylation as the reservoir temperature increases [21].

Injected seawater has the ability to alter the wettability of the rock by interaction. A reaction has been proposed by Zhang et al.2007 and is shown in figure 2.8. The original formation water differs from the injected seawater in composition. The initial brine usually has a high concentration of Ca^{2+} and a negligible SO_4^{2-} concentration, while in seawater the concentration of SO_4^{2-} is about double the Ca^{2+} concentration [11]. The potential determining ions SO_4^{2-} adsorbs on the chalk surface and lowering the positive charge density. Due to less electrostatic repulsion, more Ca^{2+} can attach to the rock surface and displace some of the carboxylic material (see fig. 2.8 A). The seawater also contains a lot of Mg^{2+} ions. At temperature higher than 90-100°C Mg^{2+} ions are able to substitute the Ca^{2+} ions from the chalk surface. Thus, Mg^{2+} should be able to displace the Ca^{2+} linked to the carboxylic material, making the rock surface more water-wet (see fig. 2.8 B).

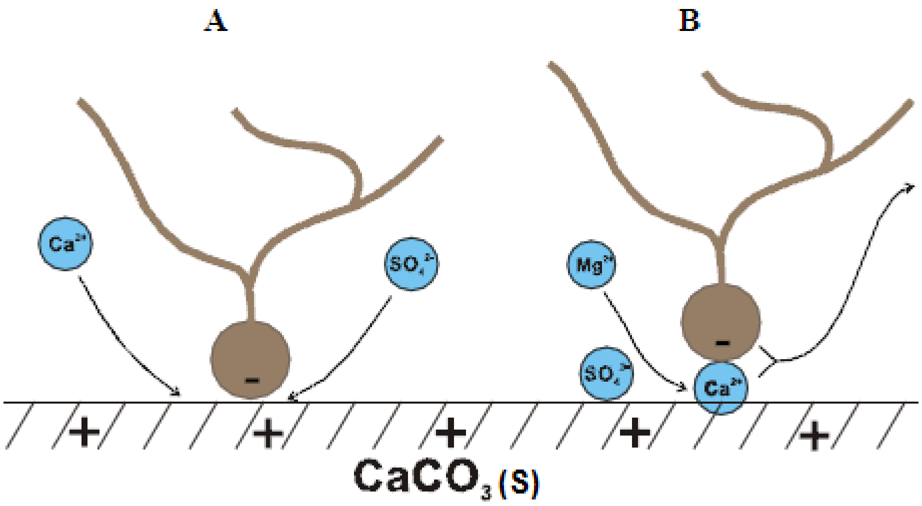


Figure 2.8 Seawater interacts with Chalk. A) SO42- and Ca2+ are active at lower temperature. B) At higher temperature, when SO42-, Ca2+ and Mg2+ are active.

Seawater can change the wettability in chalk towards more water-wet. To alter it, the potential determining ion SO_4^{2-} must interact with Ca^{2+} or Mg^{2+}. Both the imbibition rate and oil recovery increases with increasing reservoir temperature due to stronger adsorption of sulfate and calcium ion onto the chalk surface [20].

3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Rock materials

Outcrop Stevns Klint chalk from a quarry nearby Copenhagen, Denmark was used as the porous medium. The Stevns Klint is of Maastrichian age and is a soft and highly porous material. The porosity is about 45-50 % and the permeability is relative low, in the range of 1-3 mD. This chalk has a specific area about 2m^2/g [17]. A cleaned limestone reservoir core was tested together with chalk cores in the application of enzymes part.

3.1.2 Crude oils

The biodegraded Heidrun crude oil with AN=2.78 and BN=0.74 mgKOH/g was used as the base crude oil. This oil was sampled from a new well during a well-test. Two types of crude oils were used in the experiment: RES40 Oil and EWS-Oil (synthetic crude oil containing only water-soluble acids).

RES40 Crude Oil

The RES-40 oil was made by diluting the base oil, Heidrun oil, with 40 vol % n-heptane. The mixture was centrifuged and filtered through a 5 µm Millipore filter.

RES40-0

This crude oil was prepared by adding 10 wt% silica gel to RES-40 crude oil in two steps. After stirring the mixture on a magnetic stirrer for 6 days, the mixture centrifuged to separate the crude oil and silica gel. The crude oil was filtered through 0.8 Millipore filter and the AN and BN was measured to be zero at the end of the test.

EWS-Oil

EWS-Oil is synthetic oil containing only water-soluble carboxylic acids with a known specific composition. The crude oil was prepared by adding the concentrated water-soluble acids to a crude oil depleted in charged organic materials, RES40-0.

The properties of the crude oils are given in table 3.1. Densities were measured with a DMA 4500 Density Meter and the viscosities by a Physica UDS 200 viscosimeter. A Mettler Toledo DL55 autotitrator was used to measure the acid and base number for all the different oils. This method involves potentiometric titrations using an internal standard. The method used were developed by Fan and Buckley [22], which are modified variations of ASTM D2896 for base number and ASTM D664 for acid number titration,[23, 24].

Table 3.1 Oil properties, measured at room temperature.

Oil type	Viscosity [cP]	Density [g/cm3]	AN [mgKOH/g]	BN [mgKOH/g]
HEIDRUN	20,47	0,886	2,78	0,74
RES40	3,17	0,809	1,9	0,42
RES40-0	2,44	0,801	0	0
EWS-oil	--	0,809	1,9	0

3.1.3 Brines and seawater

Synthetic formation brine and seawater were made similar to Valhall brine (VB0S), and SW. Chromatography analysis was performed using SW0T and SW½T. During spontaneous imbibition, VB0S and SW were applied as the imbibing fluid. The brine was made by adding different salts to distilled water, stirred magnetically, and filtered through a 0.22 µm filter before use. The composition and density of the brines are given in table 3.2.

Table 3.2 Brine and seawater composition [mole/L].

	VB0S	SW	SW0T	SW1/2T
HCO_3^-	0.009	0.002	0.002	0.002
Cl^-	1.066	0.525	0.583	0.538
SO_4^{2-}	-	0.024	-	0.012
SCN^-	-	-	-	0.012
Mg^{2+}	0.008	0.045	0.045	0.045
Ca^{2+}	0.029	0.013	0.013	0.013
Na^+	0.997	0.450	0.460	0.427
Li^+	-	-	-	0.012
K^+	0.005	0.010	0.010	0.022
TDS [g/l]	62.83	33.39	33.39	33.39
Density [g/cm^3]	1.042	1.024	1.024	1.024
Ionic strenght	1.112	0.657	0.643	0.645

3.1.4 Enzyme

The enzyme fluid used was made by adding 7.5 wt% of the bio-surfactant to SW0T. The fluid was magnetically stirred before use.

3.1.5 Chemicals

Silica Gel with a grade 60 was used for the removal of all the acids from the crude oil, it is supplied by Fluka chemical. The n-heptane used for dilution had 98 % purity, and was supplied by VWR international. Dichloromethane, CH_2Cl_2, used for the back-extraction of the water-soluble acids had a purity of 99.8 % and was delivered by VWR international.

3.2 Core preparation

The cylindrical cores were drilled out from the block by an oversized bit. Then they were shaved down to a diameter of ~38.1 mm in a lathe and cut to a length of ~70 mm with a diamond saw. The cores were placed in a Hassler cell for cleaning, see Figure 3.1. The cleaning process is according to the method described by Puntervold et al. [25]. The cores were first flooded by 250 ml distilled water at a rate of 0.2 mL/min at 50 °C. A confining pressure of 25 bars was applied. This process was done to remove the easily soluble salts, especially SO_4^{2-}. Sulfate free cores were confirmed by a batch test by adding Ba^{2+} ions to the effluent: $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(S)$.

After drying the cores at 90 °C to constant weight, for about 24 hours, the cores were evacuated and saturated with formation water, and the pore volume was determined. Weight before and after saturation and the density of formation fluid were used to calculate the porosity of the different cores by formula 3.1 and 3.2. The core data are given in table 3.3.

$$V_P = \frac{m_{WET} - m_{DRY}}{\rho_{FLUID}} \quad (3.1)$$

$$\varphi = \frac{V_P}{V_B} * 100\% \quad (3.2)$$

V_P indicates the pore volume. m_{WET} and m_{DRY} are weights of core saturated and dry, respectively and ρ is the density of the formation water. φ is the porosity in percent and V_B is the bulk volume.

Table 3.3 Core properties with remarks.

Core ID	L [mm]	D [mm]	PV [cm^3]	φ [%]	S_{WI} [%]	S_{OI} [%]	Crude oil	Experiment
MH#1	70,2	38,1	36	45	10	90	EWS	S.I. @110°C
MH#2	70,6	38,0	36	46	11	89	EWS	S.I. @110°C
MH#3	70,2	38,1	36	45	11	89	RES40	S.I. @110°C
MH#4	70,2	38,1	36	46	10	90	RES40	S.I. @110°C
LSSK#8	69,7	38,1	36	46	10	-	-	-
LSSK#11	69,9	38,1	36	45	11	-	-	-
EZ#1	69,0	38,1	36	46	13	87	RES40	Enzyme
EZ#2	70,0	38,1	37	47	12	88	RES40	Enzyme
EZ#3	70,0	38,1	37	47	12	-	RES40	Enzyme
EZ#4	66,9	38,1	36	47	9	-	RES40	Enzyme
CA-02-02	-	-	-	-	-	-	Reservoir oil	Enzyme

Figure 3.1 Picture of a Hassler cell.

The initial water saturation, S_{WI}, of 10% was obtained by draining the cores on a porous plate using water saturated N_2 gas, figure 3.2. Figure 3.3 shows how the saturation decreased as the pressure in the porous plate increased. The pressure was increased gradually to ~7 bars. The cores were then saturated and flooded with the actual crude oil; 1.5 PV of oil in each direction at 50 °C using a Hassler core holder with a confining pressure not exceeding 25 bars. Prior to aging, the cores were wrapped in Teflon tape to avoid unrepresentative adsorption of acidic material onto the core surface. The cores were aged in the actual crude oil at 90 °C for 4 weeks. Table 3.3 gives the core data and remarks on the individual cores.

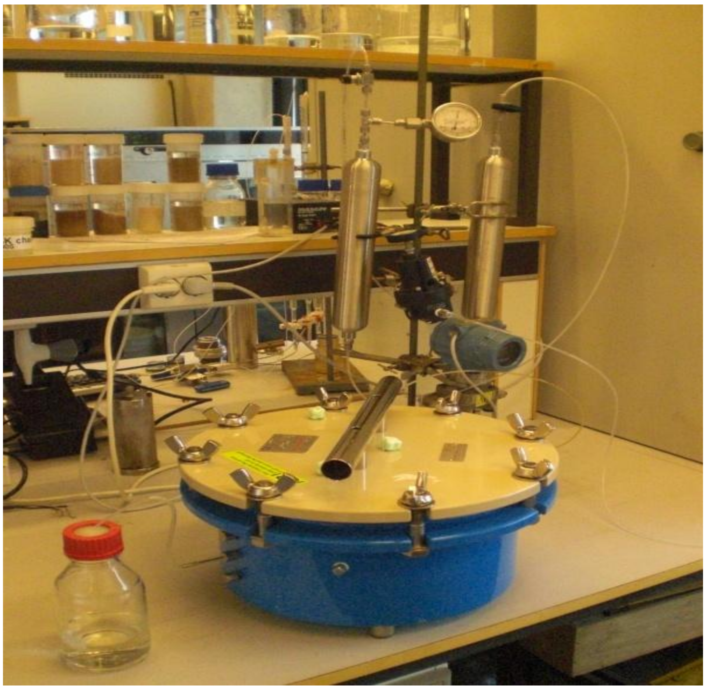


Figure 3.2 Picture of the porous plate setup used for establishing S_{WI}.

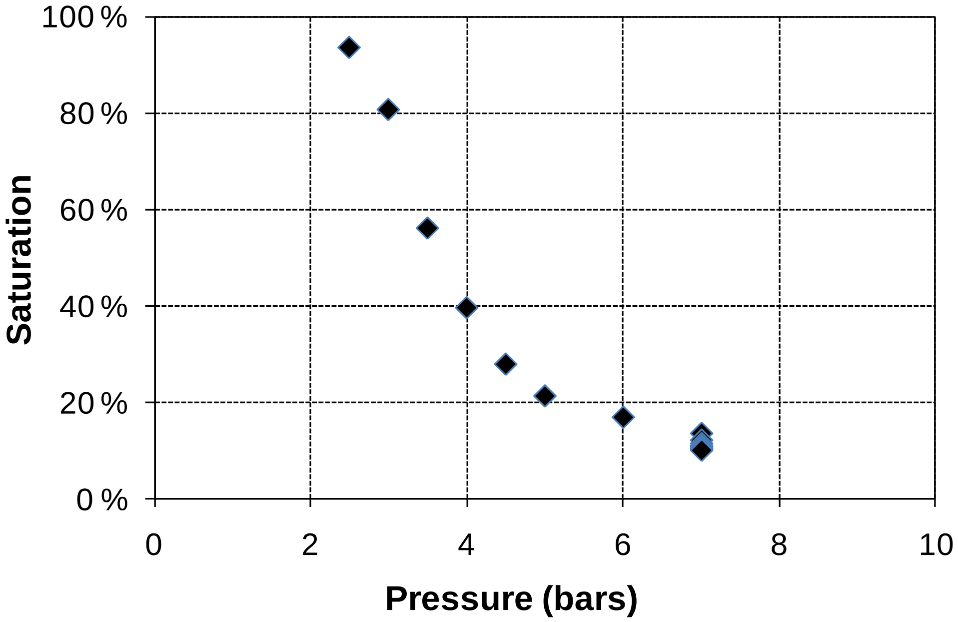


Figure 3.3 Obtaining SWI as the pressure in the porous plate increased.

3.3 Extraction of water-soluble carboxylic acid fraction

A procedure for the extraction of the total acid fraction has been described previously, Fathi et. al. The extraction of carboxylic acid was performed using pure Heidrun oil, AN=2.78 mgKOH/g, and DW in the W/O volume ratio of 2.0. The pH was increased from about 6 to 10, by adding small volumes of 1.0M sodium hydroxide (NaOH) solution during stirring for 24 hours. All pH-values were measured with a Mettler Toledo pH-meter.

After the wanted pH was obtained, the mixture was centrifuged to separate the oil and water phase with water soluble acids.

Acid back extraction:

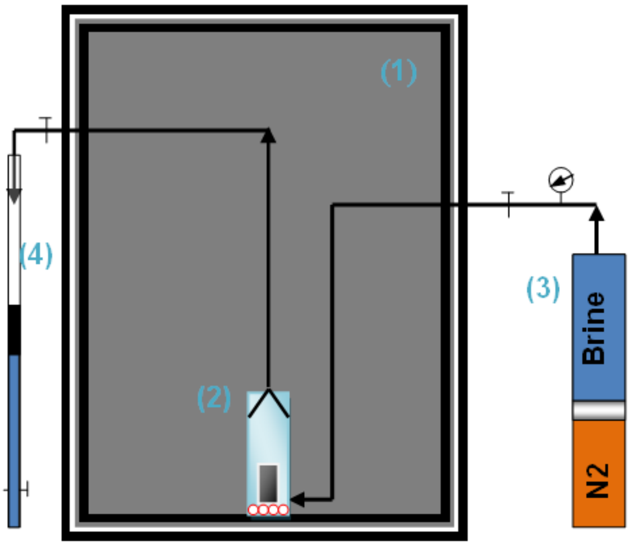
The pH in the water phase with water-extractable acids was adjusted to 2 by adding small volumes of concentrated hydrochloric acid (3M HCl), while it was stirring, over a time period of 24 hours.

The acids were back-extracted using dichloromethane, CH_2Cl_2, in a mixing ration of 1:1. The water phase and the dichloromethane phase containing the water-soluble acids were separated and the acid extraction was concentrated by evaporation at 40 ºC.

The concentrated water-soluble acids were added to the crude oil depleted in the carboxylic group with AN and BN of zero, RES40-0. The synthetic oil termed EWS-Oil was filtered through a 5 µm Millipore filter and the AN and BN were determined to be 1.9 and 0.0. mgKOH/g, respectively. All the EWS-oil was then mixed with Valhall formation water in the same ratio as the initial saturations, i.e. ≈10 vol% water. After equilibrating the solution under stirring for 24h, the pH was determined to be 7.0.

3.4 Spontaneous imbibition (SI)

The aged cores were immersed in the imbibing fluid in sealed steel cells. The spontaneous imbibition tests were performed at a 110 ºC, with a back pressure of 10 bars to avoid boiling of the fluids. The produced oil during the test was collected in a burette, and oil recovery was determined versus time as a percentage of original oil in place, %OOIP. Figure 3.4 shows the setup used in the spontaneous imbibition.



(1) Heating chamber

(2) Steel imbibition cell (with a coning top and marble balls beneath the core to keep the core immersed in the imbibing fluid)

(3) Piston cell to provide a backpressure of 10bars (imbibing fluid at the top and compressed nitrogen gas at the bottom)

(4) Burette for collecting and measuring the produced oil

Figure 3.4 Spontaneous imbibition setup [10].

3.5 Forced displacement

In the phase-2 of this work, the cores were subjected to forced displacement before introducing the Enzyme solution for wettability modifications. A Hassler core holder was used for the forced displacement tests. The core was placed in a rubber sleeve and mounted in the core holder with a confining pressure of ~25 bars and back pressure of 10 bars. The injection rate was 1PV/D and 0.2 ml/min, and the temperature during the forced displacement was 50 ºC. The produced fluid was collected in a burette and oil recovery was determined as %OOIP versus injected pore volumes, PV.

3.6 Chromatographic wettability test

The chromatographic wettability test for carbonates developed by Strand et al.2006 [17] was used to determine the increase in the water-wet area after injecting enzyme solution with a shut-in period of 48 or 96 hrs. In order to determine the water-wet fraction, the core was placed in a core holder with a confining pressure of 25 bars and flooded with the brine without SO_4^{2-} and tracers, SW0T, at a rate of 1PV/D, followed by a rate of 0.20 ml/min to establish residual oil saturation. Next, the core was flooded with at least 2.0 PV of SW½T brine (containing SO_4^{2-} and the tracers SCN^- and Li^+) at a rate of 0.20 ml/min. The effluent was collected in fractions of 1-4 ml by using a fraction collector, figure 3.5. The fractions were diluted 200 times by a Gilson Gx-271 Liquid Handler and analyzed for concentration of SO_4^{2-} and tracer, SCN^-, using Dionex ICS-3000 Ion Chromatograph. The concentration relative to the initial concentration was plotted against injected pore volume. The area between the tracer curve and the sulfate curve is directly proportional to the water-wet area inside the core because the chromatographic separation only takes place at the water-wet sites. The area ratio between the tracer and sulfate curves of the sample, A_{WET}, and a reference cleaned water wet core, A_{REF}, is a measure of the water-wet fraction of the sample, WI:

$$WI = \frac{A_{WET}}{A_{REF}} \qquad (3.3)$$

Where:

WI = 0 is completely oil-wet

WI = 0.5 is neutral wettability

WI = 1 is completely water-wet.

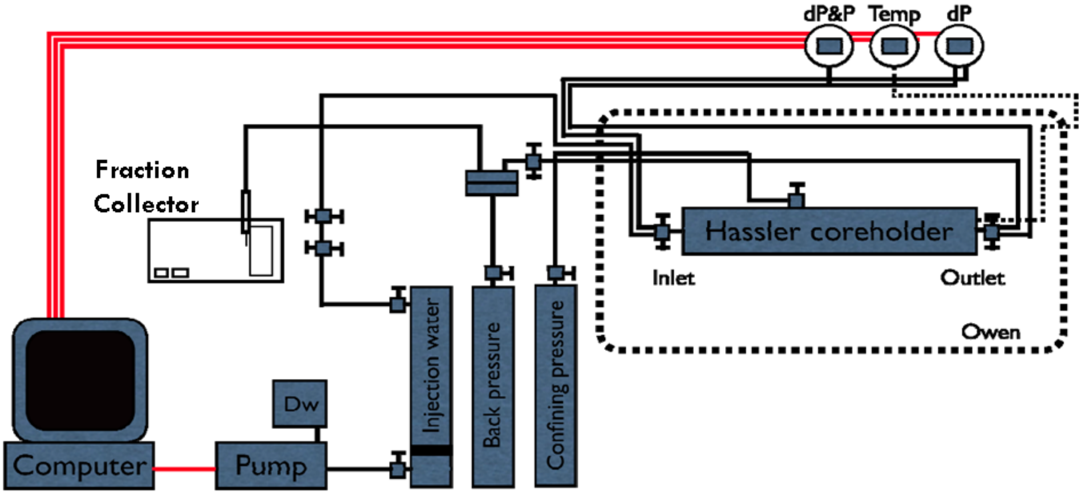


Figure 3.5 Experimental setup for the wettability test.

4 RESULTS AND DISCUSSION

Phase-1: The Effect of Water-Soluble Acids

4.1 Extractable water-soluble acids

The water-soluble components of the carboxylic materials in the crude oil are believed to be a small fraction of the total amount of acids present. The amount of extractable water-soluble acids in the crude oil has been quantitatively studied previously using an auto-titrator in a two phase titration mode [10]. The amount of extractable water-soluble acids is a function of pH and water-oil ratio. For a specified crude oil at a predetermined pH=10.0, the decrease in the AN can be determined as a function of the volumetric W/O ratio, as shown in Figure 4.1. The AN of the crude oil decreases as the W/O volume ratio increases, and the variation is greater at low values of the W/O ratio.

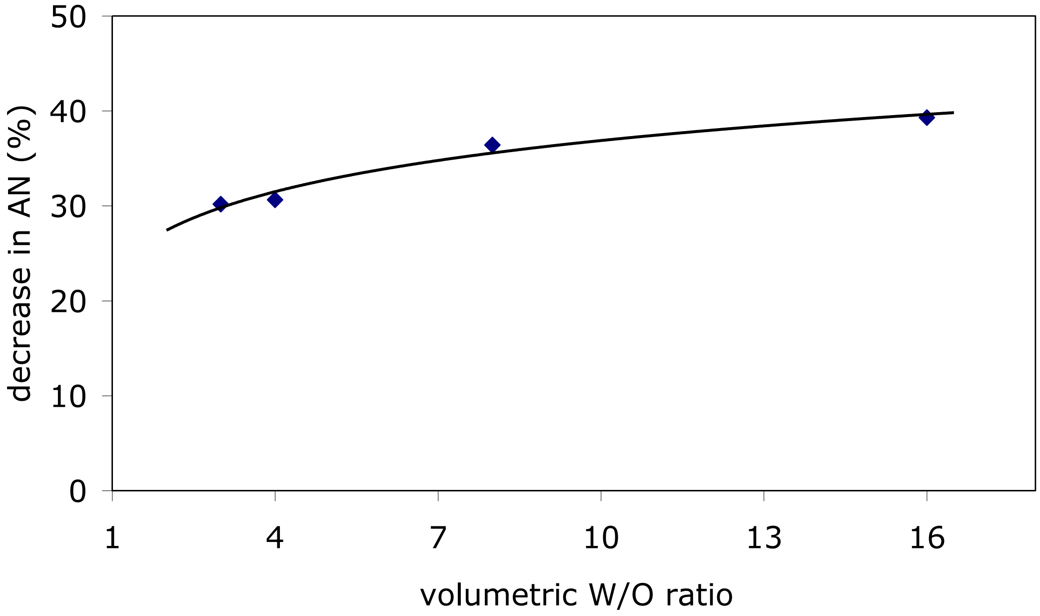


Figure 4.1 The AN of the crude oil decreases as the W/O volume ratio increases, and the variation is greater at low values of the W/O ratio [10].

At a given W/O ratio of 4.0, the amount of extractable carboxylic acids can be determined at different pH-values. As shown in Figure 4.2, the AN decreased 5-30% when pH increased from 8 to 10 [10].

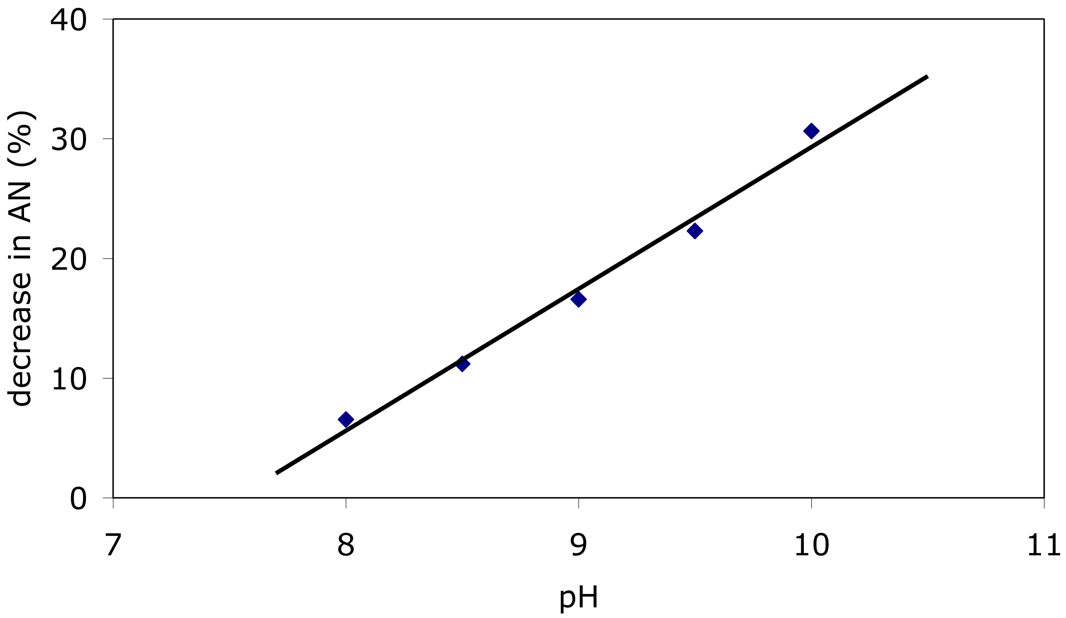


Figure 4.2 Percent decrease in AN as a function of pH at W/O = 4.0. [10].

For this study, the extraction of water-soluble carboxylic acids from the crude oil was performed at pH=10 and W/O ratio of 2.0. Figure 4.3 shows how the pH increased as a function of adding more NaOH to the mixture.

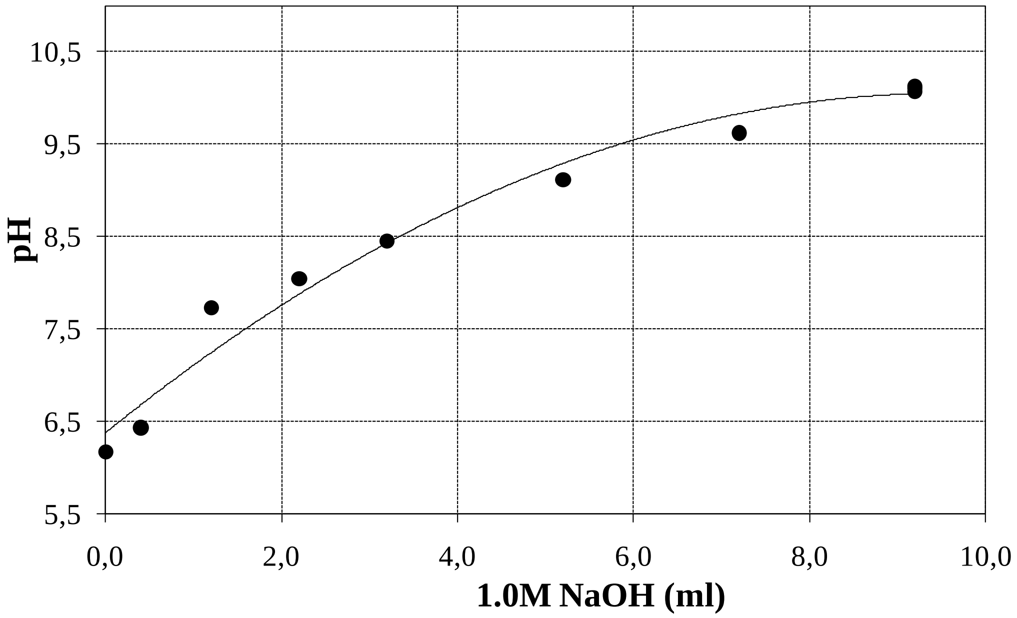


Figure 4.3 pH vs. NaOH added.

The acids then were back-extracted from the aqueous phase as described in the previous chapter. Figure 4.4 shows the pH decrease as a function of adding HCl to the aqueous phase. The extracted water-soluble acids were added to a crude oil depleted in carboxylic group (RES40-0). The final acid number of the synthetic oil, EWS-oil, was measured to be 1.9 mg KOH/g while the BN was zero.

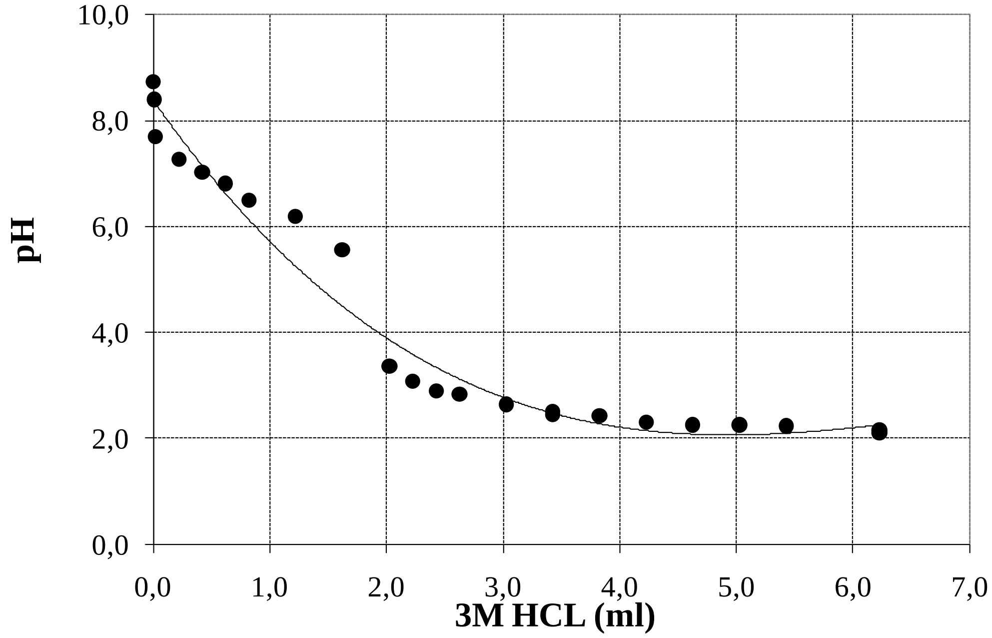


Figure 4.4 pH vs. HCl added.

4.2 Oil displacement efficiency

The effect of water-soluble acids on the displacement efficiency was studied by spontaneous imbibition at 110ºC. Two parallel spontaneous imbibitions test were performed for both RES-40 and EWS-oil after the cores had been aged for four weeks at 90 ºC in their respective crude oils.

The spontaneous imbibition was initiated with formation brine (VB0S) as the imbibing fluid, Figure 4.5. When using formation brine as the imbibing fluid, there was a clear difference in the oil recovery. The oil recovery from the cores containing RES40 oil was in average 18.5 % of OOIP after 14 days. On the other hand, from the cores containing EWS-oil (crude oil containing only water-soluble acids) the average oil recovery of 14.5 % of OOIP was achieved after 14 days. The difference in the recovery from two test series was around 4 % of OOIP. The imbibition curves were very reproducible in both test series, Figure 4.5. Due to the lack of SO_4^{2-} in the formation water; the VB0S was not able to induce wettability modification during the imbibing process. The oil recovery at this initial step is therefore mainly related to thermal expansion, capillary forces and initial wettability conditions. The AN is the most important wetting parameter for carbonates. The carboxylic group adsorbs very strongly onto the positive sites of a calcite surface making the rock surface less water-wet. The AN is the same for both crude oils, AN=1.9 mg of KOH/g, which is quite high. The apparent initial low recovery factor for the cores containing EWS-oil may indicate that the rock surface is less water-wet compared to the cores containing RES-40 oil.

After 14 days and reaching the production plateau with the formation brine, the imbibing fluid was switched to seawater. There was an immediate jump in the oil recovery in both test series, Figure 4.5. The increased oil recovery by SW is related to the ability of SW to improve the water wetness. The mechanism responsible for the wettability alteration by seawater is described in the previous chapter, 2.4.2. The potential determining ions present in seawater, Ca^{2+}, Mg^{2+}, and SO_4^{2-}, have great influence on the surface charge of chalk and the interactions between the chalk surface and the ions Ca^{2+}, Mg^{2+} and SO_4^{2-} present in seawater, are responsible for the wettability modification of chalk. There was a significant difference in the ultimate oil recovery factor after 68 days between two test series, Figure 4.5. The average oil recovery after 68 days was 49 % and 36 % of OOIP for RES40 and EWS-crude oil, respectively. The difference in the oil recovery factor after wettability modification by seawater was 13 %. The significant difference in the oil recovery indicates that the organic structure of the carboxylic material plays a role on the wettability alteration process as well. EWS-oil contains only water-soluble carboxylic acids. The lower water wetness of this crude oil, from an imbibition point of view, may indicate that the water film between the rock and the oil is more easily broken with water-soluble acids present in the crude oil and more acidic material are adsorbed to the carbonate surface.

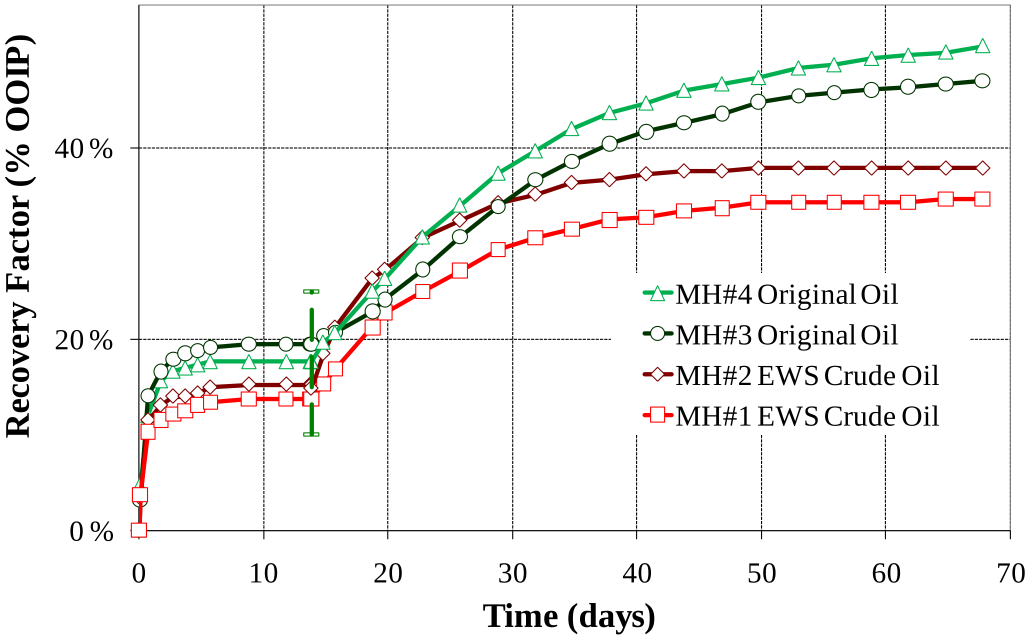


Figure 4.5 Spontaneous imbibition into chalk cores saturated with different crude oils, RES-40 and EWS-oil. The graph shows recovery factor as a function of time at a temperature of 110°C. The green vertical line indicates the change in imbibing fluid from VB0S to “smart water”.

The effect of water-soluble acids in crude oil has been studied previously by Fathi et al., 2010. They have tested two crude oils: Original Oil (O.O.) and a crude oil depleted in water-soluble acids namely Treated Oil (T.O.). The results from the spontaneous imbibition using formation brine and seawater are shown in Figure 4.6. The test materials and conditions are identical to this work. They have reported a significant difference in the oil recovery for the two test series when using formation brine (VB0S) as the imbibing fluid. The oil recovery from the cores containing treated oil (depleted in water extractable acids) was about 22% OOIP after 12 days, and the imbibition curves were very reproducible. From the imbibition curves for the cores containing the original oil, the oil recovery was well below the recovery from the cores containing treated oil. After 12 days, the average recovery was about 16% OOIP, Figure 4.6. When the imbibing fluid was changed to SW, there is an immediate increase in oil recovery for both series. The slope of the imbibition curve for the cores containing the treated oil is higher than that for the cores with the original oil. The difference in the imbibition rate can indicate that the carboxylic material from the treated oil is more easily displaced than that from the original oil. The oil recovery after about 70 days is also different, about 56% and 43% of OOIP for the treated and the original oil, respectively.

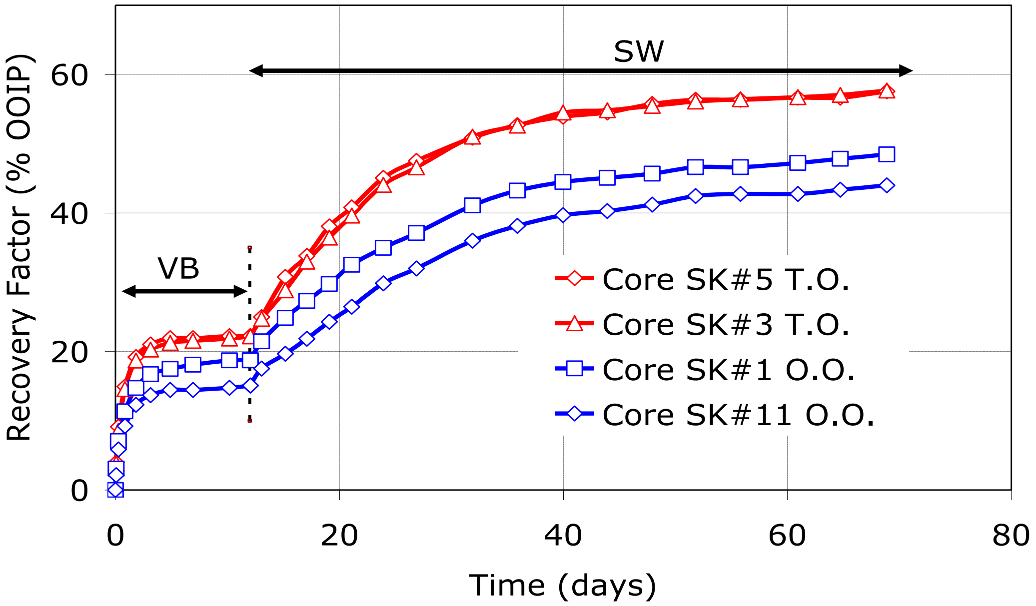


Figure 4.6 Spontaneous imbibition into chalk cores saturated with different crude oils, original and treated oil. Spontaneous imbibitions was performed by formation brine, VB, followed by seawater, SW, as the imbibing fluid at 110 °C, SWI=10% [10].

The results from this work together with the previous study, Fathi et al., indicate that the chemical properties of the acids present in the crude oil are very important wetting parameters. It was concluded that even though the strength of the bonding of carboxylic material onto the calcite surface is mostly dictated by the carboxylic group, the organic structure of the carboxylic material will have influence on the initial wetting and wettability alteration process as well.

4.3 Displacement efficiency

The second phase of the project is to study the application of Enzymes to improve the wetting condition towards more water-wetness. An enzyme-based method has already been reported, which generates organic acids for a variety of acidizing applications such as a matrix acidizing, the stimulation of natural fracture networks, damage removal over long horizontal intervals. The generation of acid in-situ following placement of the fluid ensures the even delivery of acid over the whole of the treated zone. Two cores were saturated and aged with the crude oil, RES-40. The cores were subjected to forced displacement with seawater depleted in sulfate (SW0T) at 50 °C to establish residual oil saturation.

For the core EZ#1, the injection rate was 1PV/D at the start of the test followed by a rate of 0.2 ml/min, figure 4.7. The recovery factor of 69% of OOIP was achieved after ~ 3.5PV injection. After performing an initial chromatographic wettability test, the enzyme solution was injected into the core and shut-in for 48 hours at 50 °C in an attempt to improve the wetting condition towards more water-wet. Later, seawater without SO_4^{2-} was injected at a rate a 0.2 ml/min to wash-out the enzyme solution. No extra oil was recovered during clean-out procedure, figure 4.7. Finally, the chromatographic wettability test was performed to monitor the change in the wetting condition.

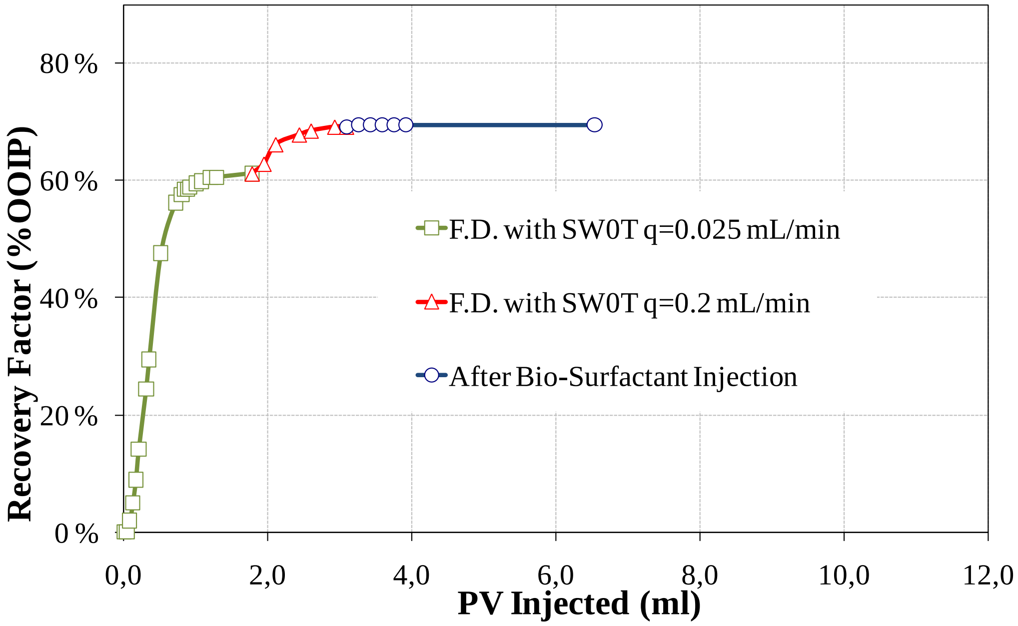


Figure 4.7 The recovery factor of core EZ#1 as a function of PV injected. The injected fluid was SW0T at different injection rate and SW0T containing 7.5 wt% of bio-surfactants.

Core EZ#2 was tested in the same way as core EZ#1. The core was flooded with SW0T at a higher rate of 0.2 ml/min at 50 °C. The ultimate oil recovery factor of 76% of OOIP was obtained after ~8PV, figure 4.8. The enzyme solution was introduced into the core and the system was shut-in for 96 hours at 50 °C. No extra oil production was observed due to the enzyme injection.

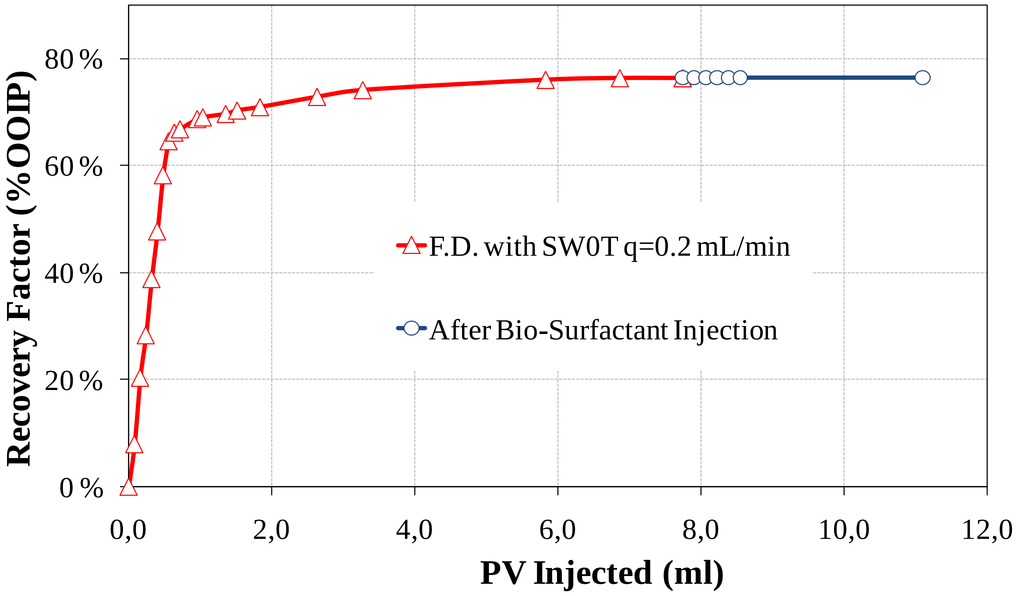


Figure 4.8 The recovery factor of core EZ#2 as a function of PV injected. The injected fluid was SW0T and SW0T containing 7.5 wt% of bio-surfactants.

For the reservoir core the same line of actions was performed, giving the same results. No more oil production was observed after forced displacement by enzymes.

The two chalk cores gave a final recovery factor of 69 and 76 %, which is quite high. The reason for higher ultimate recovery in core EZ#2 may be related to a higher injection rate. The bio-surfactants (enzyme) used did not increase the oil production from the mixed-wet chalk cores or from the preferentially oil-wet reservoir core.

4.4 Chromatographic wettability test

To study the potentiality of enzyme on modifying the wettability condition of the rock materials, the chromatographic wettability test was performed both in the initial condition and also after treatment with the enzyme solution. The chromatographic wettability test for carbonates developed by Strand et al. [17] was used to determine the increase in the water-wet area.

Two chalk cores, EZ#1&2, and one reservoir core were used to study the change in the wetting condition by application of enzyme solution. At the residual oil saturation during forced displacement by SW0T, the core was flooded with at least 2.0 PV of SW½T brine (containing SO_4^{2-} and the tracers SCN^- and Li^+) at a rate of 0.20 ml/min. The effluent was collected in fractions of 1-4 ml by using a fraction collector. The fractions were analyzed for concentration of SO_4^{2-} and tracer, SCN^-, using Dionex ICS-3000 Ion Chromatograph. The concentration relative to the initial concentration was plotted against injected pore volume. The area between the tracer curve and the sulfate curve is directly proportional to the water-wet area inside the core because the chromatographic separation only takes place at the water-wet sites. The calculated chromatographic separation areas are given in table 4.1 and in figure 4.9-4.11. The initial chromatographic separation area was 0.084 and 0.093 for the chalk cores, EZ#1 and 2, respectively. For the reservoir core tested, the chromatographic area was calculated to be 0.069.

All three cores were exposed to the enzyme solution and another chromatographic wettability test was performed after a specified shut-in period for each core. The enzyme solution was cleaned out by flooding the core with SW0T at a rate of 0.2 ml/min. The core was then flooded with SW½T brine (containing SO_4^{2-} and the tracers SCN^- and Li^+) at a rate of 0.20 ml/min. The effluent was collected using a fraction collector and analyzed for concentration of SO_4^{2-} and tracer, SCN^-. The chromatographic separation area was decreased to 0.031 and 0.015, for EZ#1 and EZ# 2, respectively. The reservoir core demonstrated the same behavior and the area decreased to 0.013, table 4.1 and figure 4.9-4.11.

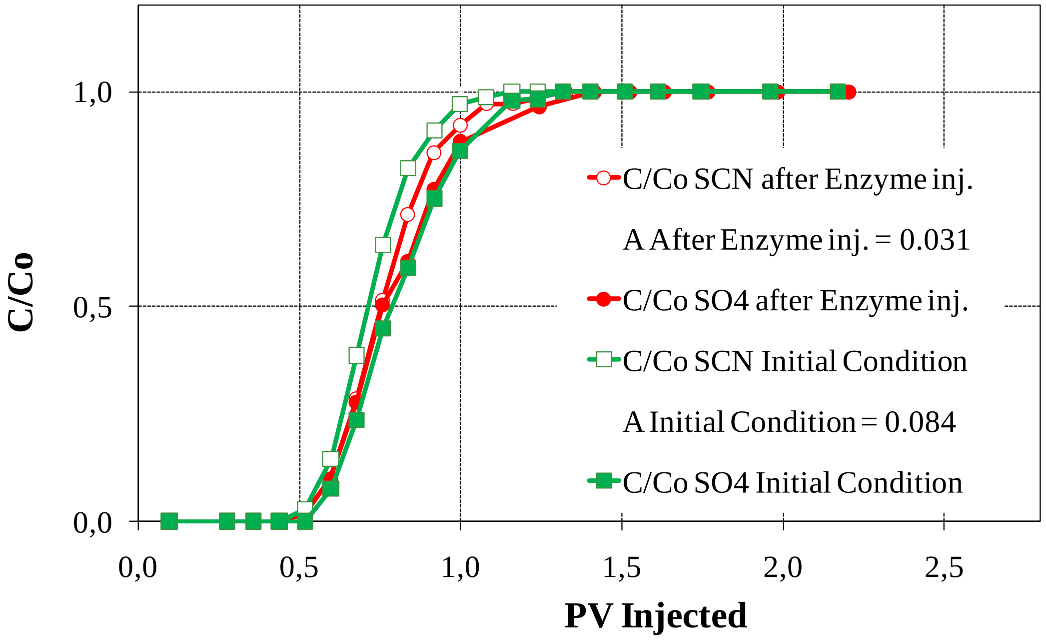


Figure 4.9 Chromatographic separation curves showing the normalized initial and final area in core EZ#1.

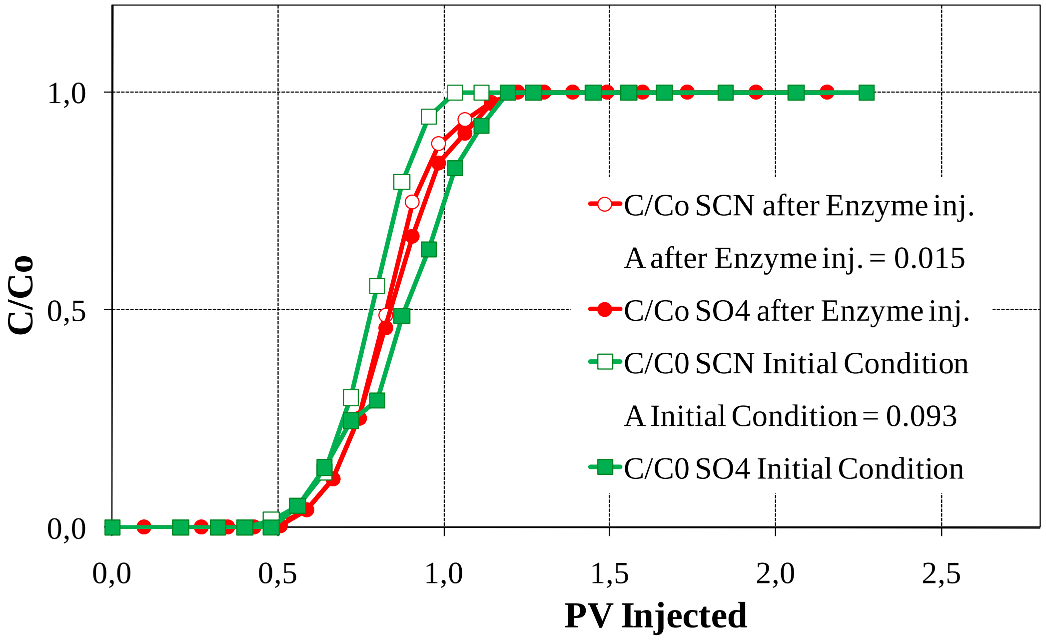


Figure 4.10 Chromatographic separation curves showing the normalized initial and final area in core EZ#2.

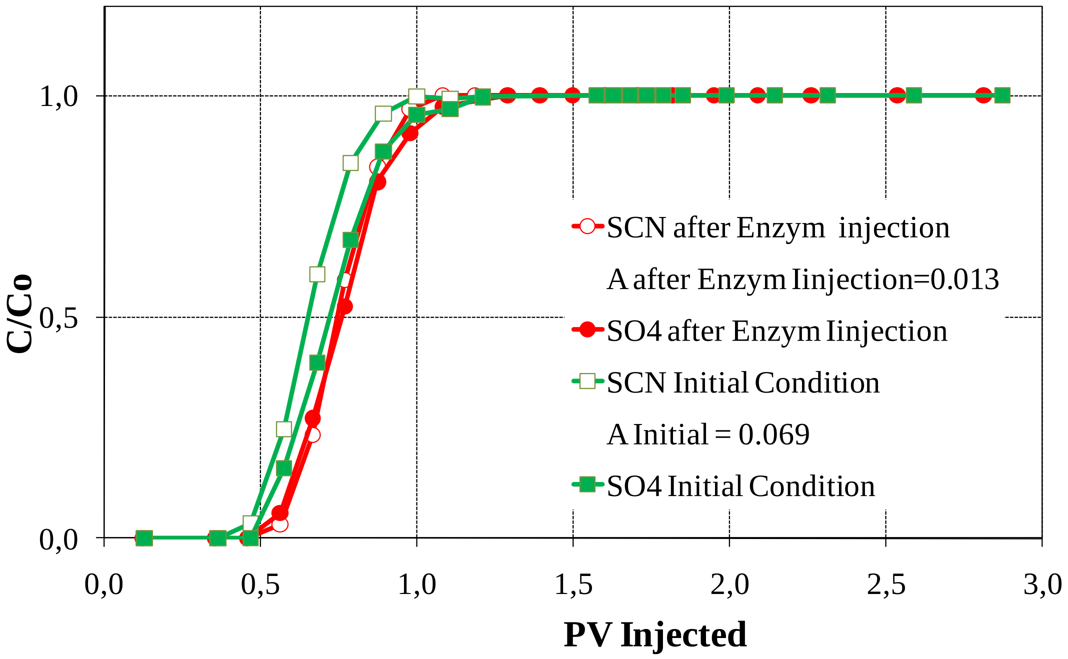


Figure 4.11 Chromatographic separation curves showing the normalized initial and final area in core CA-02-02.

Table 4.1 Calculated areas between the tracer and sulfate curve for initial and final condition.

Core ID	Initial area	Shut-in [hours]	Final area
EZ#1	0.084	48	0.031
EZ#2	0.093	96	0.015
CA-02-02	0.069	48	0.013

The potentiality of enzyme application for wettability modification can be depicted in the increased water-wet fraction. From the results of this work, it seems that the enzyme solution tested was not able to increase the water-wetness and did not contribute to any extra oil recovery. These results clearly show that the chromatographic area was decreased for all the tested cores after treatment with the enzyme solution. The enzymes somehow made the rock surface less reactive for water adsorption.

The cores EZ#1&2 were saturated with RES40 with AN=1.9 and BN=0.4 while CA-02-02 was saturated with reservoir oil having AN=0.11 and BN=0.65. For both cases, with high and low AN, the enzymes did not contribute to any increase in the water-wet surface fraction.

Table 4.1 indicates that the final calculated area is dependent on the enzyme shut-in time. EZ#2 had twice the shut-in time compared to EZ#1 and showed a lower calculated final area.

This indicates that a longer shut-in time of these enzymes made the rock surface less reactive for water adsorption.

5 CONCLUSION

Phase-1: The Effect of Water-Soluble Acids.

The experiment has compared the spontaneous imbibition in a core saturated with original oil with a core saturated with EWS-oil (crude oil containing only water-soluble acids). This study has shown that the wetting properties of chalk are influenced by the chemical properties of the acids in the crude oil.

- Spontaneous imbibitions with formation water confirmed that cores saturated with crude oil only containing water-soluble acids gave a lower ultimate recovery factor.
- The spontaneous imbibition indicated that water-soluble acids make the core less water-wet, and that water-soluble acids affect the initial water film between the rock and oil.
- After 68 days the final average recovery factor from RES40 and EWS-oil were 49 and 36 %OOIP with SW as the imbibing fluid.

Phase-2: Application of Enzyme for Wettability Improvement.

The application of enzymes for wettability improvement was tested by forced displacement and “shut-in” of enzymes on cores with residual oil saturation. A chromatographic wettability test was performed before and after enzyme injection to see if the water-wet fraction had increased.

- The forced displacement by enzymes gave no improvement in recovery factor.
- The chromatographic wettability tests before and after enzyme injection proved the enzymes not capable of altering the rock wetness towards more water-wet.
- The enzymes made the chromatographic areas decrease, making the rock surface more oil-wet.

6 NOMENCLATURE

A	Adsorption area
AN	Acid number, mgKOH/g
BN	Base number, mgKOH/g
C/C_o	Relative concentration of ions
D	Core diameter, cm
DCM	Dichloromethane
DW	Distilled water
EOR	Enhanced oil recovery
EWS	extracted-water-soluble acids
IFT	Interfacial tension, mN/m
L	Core length, cm
O.O.	Original oil
OOIP	Original oil in place
PV	Pore volume
RES40-0	Oil depleted in acids
S_{WI}	Initial water saturation, %
S_{OI}	Initial oil saturation, %
S_{OR}	Residual oil saturation, %
SW	Synthetic seawater/ "smart water"
SW0T	Synthetic seawater without SO_4^{2-}
SW1/2T	Synthetic seawater where the concentration of SCN^- and SO_4^{2-} is 0.012 mole/l
T.O.	Treated crude oil
TDS	Total dissolved solids, g/l
VB	Valhall formation brine
VB0S	Valhall formation brine without SO_4^{2-}
WI	Water-wet surface fraction
m_{DRY}	Core weight dry, g
m_{WET}	Core weight wet, g
W/O	Water oil ratio
Φ	Porosity, %
μ	Viscosity, cp
ΔWI	Change in water-wet surface fraction

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APPENDIX A) SPONTANEOUS IMBIBITION

After aging for 4 weeks in 90°C, test temperature was 110°C. Imbibing fluids were VB0S and SW. $S_{WI}\approx 10$ % and $S_{OI}\approx 90$ %. Backpressure=10 bars.

	Cum. Oil Recovery (ml)				Recovery Factor (%OOIP)			
	EWS-Crude Oil		RES-40		EWS-Crude Oil		RES-40	
Time (days)	MH # 1	MH # 2	MH # 3	MH # 4	MH # 1	MH # 2	MH # 3	MH # 4
0	0	0	0	0	0 %	0 %	0 %	0 %
0	1,2	1,1	1	1,4	4 %	3 %	3 %	5 %
1	3,3	3,7	4,5	3,6	10 %	12 %	14 %	12 %
2	3,7	4,2	5,3	4,7	12 %	13 %	17 %	16 %
3	3,9	4,5	5,7	5	12 %	14 %	18 %	17 %
4	4	4,5	5,9	5,1	12 %	14 %	18 %	17 %
5	4,2	4,6	6	5,2	13 %	14 %	19 %	17 %
6	4,3	4,8	6,1	5,3	13 %	15 %	19 %	18 %
9	4,4	4,9	6,2	5,3	14 %	15 %	19 %	18 %
12	4,4	4,9	6,2	5,3	14 %	15 %	19 %	18 %
14	4,4	4,9	6,2	5,3	14 %	15 %	19 %	18 %
14	4,4	4,9	6,2	5,3	14 %	15 %	19 %	18 %
14	4,4	4,9	6,2	5,3	14 %	15 %	19 %	18 %
15	4,9	6,1	6,5	5,9	15 %	18 %	20 %	20 %
16	5,4	7	6,6	6,2	17 %	21 %	21 %	21 %
19	6,8	8,7	7,3	7,5	21 %	26 %	23 %	25 %
20	7,3	9	7,7	7,9	23 %	27 %	24 %	26 %
23	8	10,1	8,7	9,2	25 %	31 %	27 %	31 %
26	8,7	10,7	9,8	10,2	27 %	32 %	31 %	34 %
29	9,4	11,3	10,8	11,2	29 %	34 %	34 %	37 %
32	9,8	11,6	11,7	11,9	31 %	35 %	37 %	40 %
35	10,1	12	12,3	12,6	32 %	36 %	39 %	42 %
38	10,4	12,1	12,9	13,1	32 %	37 %	40 %	44 %
41	10,5	12,3	13,3	13,4	33 %	37 %	42 %	45 %
44	10,7	12,4	13,6	13,8	33 %	38 %	43 %	46 %
47	10,8	12,4	13,9	14	34 %	38 %	44 %	47 %
50	11	12,5	14,3	14,2	34 %	38 %	45 %	47 %
53	11	12,5	14,5	14,5	34 %	38 %	45 %	48 %
56	11	12,5	14,6	14,6	34 %	38 %	46 %	49 %
59	11	12,5	14,7	14,8	34 %	38 %	46 %	49 %
62	11	12,5	14,8	14,9	34 %	38 %	46 %	50 %
65	11,1	12,5	14,9	15	35 %	38 %	47 %	50 %
68	11,1	12,5	15,0	15,2	35%	38%	47%	51%

APPENDIX B) FORCED DISPLACEMENT

Core EZ#1: After aging for 4 weeks at 90 °C, T=50 °C, injected brines were SW0T and SW0T+bio-surfactants. The surfactants were injected at q=0.1ml/min. OOIP=30.24 ml. PV=36.55ml.

					Cum. Oil Rec. [ml]	RF [%OOIP]
q [ml/min]	t [min]	Vol Inj. [ml]	Corr. Vol. Injec. (ml)	PV Inj	EZ#1	EZ#1
0,025	0	0,00	0,00	0,00	0	0 %
0,025	60	1,50	1,50	0,04	0	0 %
0,025	120	3,00	3,00	0,08	0,6	2 %
0,025	180	4,50	4,50	0,12	1,5	5 %
0,025	240	6,00	6,00	0,16	2,7	9 %
0,025	300	7,50	7,50	0,21	4,3	14 %
0,025	450	11,25	11,25	0,31	7,4	24 %
0,025	510	12,75	12,75	0,35	8,9	29 %
0,025	750	18,75	18,75	0,51	14,4	48 %
0,025	1050	26,25	26,25	0,72	17	56 %
0,025	1170	29,25	29,25	0,80	17,4	58 %
0,025	1230	30,75	30,75	0,84	17,7	59 %
0,025	1290	32,25	32,25	0,88	17,7	59 %
0,025	1340	33,50	33,50	0,92	17,8	59 %
0,025	1460	36,50	36,50	1,00	18	60 %
0,025	1580	39,50	39,50	1,08	18,1	60 %
0,025	1760	44,00	44,00	1,20	18,3	61 %
0,025	1880	47,00	47,00	1,29	18,3	61 %
0,025	2600	65,00	65,00	1,78	18,5	61 %
0,2	0,00	65,00	65,00	1,78	18,5	61 %
0,2	30,00	71,00	71,00	1,94	19	63 %
0,2	60,00	77,00	77,00	2,11	20	66 %
0,2	120	89,00	89,00	2,44	20,5	68 %
0,2	150	95,00	95,00	2,60	20,7	68 %
0,4	180	107,00	107,00	2,93	20,9	69 %
0,2	210	113,00	113,00	3,09	20,9	69 %
0,1	0	113,00	113,00	3,09	20,9	69 %
0,1	60	119,00	119,00	3,26	21	69 %
0,1	120	125,00	125,00	3,42	21	69 %
0,1	180	131,00	131,00	3,58	21	69 %
0,1	240	137,00	137,00	3,75	21	69 %
0,1	300	143,00	143,00	3,91	21	69 %
0,1	1260	239,00	239,00	6,54	21	69 %

Core EZ#2: After aging for 4 weeks at 90 °C, T=50 °C, injected brines were SW0T and SW0T+bio-surfactants. The surfactants were injected at q=0.1ml/min. OOIP=31.4 ml. PV=37.56ml.

					Cum. Oil Rec. [ml]	RF [%OOIP]
q [ml/min]	t [min]	Vol Inj. [ml]	Corr. Vol. Injec. (ml)	PV Inj	EZ#2	EZ#2
0,2	0	0,00	0,00	0,00	0	0 %
0,2	15	3,00	3,00	0,08	2,5	8 %
0,2	30	6,00	6,00	0,16	6,4	20 %
0,2	45	9,00	9,00	0,24	8,9	28 %
0,2	60	12,00	12,00	0,32	12,2	39 %
0,2	75	15,00	15,00	0,40	15	48 %
0,2	90	18,00	18,00	0,48	18,3	58 %
0,2	105	21,00	21,00	0,56	20,3	65 %
0,2	120	24,00	24,00	0,64	20,8	66 %
0,2	135	27,00	27,00	0,72	21	67 %
0,2	180	36,00	36,00	0,96	21,6	69 %
0,2	195	39,00	39,00	1,04	21,7	69 %
0,2	255	51,00	51,00	1,36	21,9	70 %
0,2	285	57,00	57,00	1,52	22,1	70 %
0,2	345	69,00	69,00	1,84	22,3	71 %
0,2	495	99,00	99,00	2,64	22,9	73 %
0,2	615	123,00	123,00	3,27	23,3	74 %
0,2	1095	219,00	219,00	5,83	23,9	76 %
0,2	1290	258,00	258,00	6,87	24	76 %
0,2	1455,00	291,00	291,00	7,75	24	76 %
0,1	0,00	291,00	291,00	7,75	24	76 %
0,1	60,00	297,00	297,00	7,91	24	76 %
0,1	120,00	303,00	303,00	8,07	24	76 %
0,1	180,00	309,00	309,00	8,23	24	76 %
0,1	240,00	315,00	315,00	8,39	24	76 %
0,1	300,00	321,00	321,00	8,55	24	76 %
0,1	1260,00	417,00	417,00	11,10	24	76 %