



*“The Effect of Formation Water Composition
on the Wettability Established Between
Carbonate Rocks and Crude Oil”*

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Life does not consist mainly

*– or even largely –
of facts and happenings.*

*It consists mainly of the storm, that is
forever blowing through one's head.*

–Mark Twain

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Educating the mind,

Without educating the heart,

Is no education at all.

–Aristotelis.

Abstract

Initial reservoir rock wetting conditions are of the main factors influencing the overall oil recovery (primary, secondary and tertiary). Depending on the conditions under which an oil field was formed, different rock/oil/brine systems have been established over millions of years. In this study, the effect that the composition of formation water has on the wetting state of Stevns Klint Chalk cores was examined. More specifically, for carbonate rocks it has been experimentally observed that the existence of Sulfate (SO_4^{2-}), Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) ions in the formation water contributes towards an improved oil recovery.

The fact that the active oil compounds (e.g. R-COO^-) are responsible for the mixed wet conditions justifies this observation, because these compounds serve as anchor molecules, creating a very strong bonding with the calcite surface. For high oil recovery to occur, the rock needs to be at least partially water-wet. In order to improve water-wetness, part of the oil active polar compounds must be removed by chemical reactions with injected water. Sulfate, Magnesium and Calcium ions operate as substituents of these oil active polar compounds, by creating symbiotic interactions with the rock surface. Sea water enriched in specific ions has been injected in several operators. For instance, in the Ekofisk field ($T_{\text{res}}=130^\circ\text{C}$) in the Norwegian sector injection of sea water enriched in Sulfate and Magnesium ions has been proved as an enhanced oil recovery fluid. Additionally, the high reservoir temperature (130°C), acts complementary for wettability alteration to take place.

To examine the effect of each ion separately on the wetting conditions, three Chalk cores, drilled from the same quarry were used. Each core was saturated with a brine enriched in one of the above three ions. Afterwards, a mixture of Heidrun field crude oil (60%) and Heptane (C_7) (40%) was flooded through the cores at 50°C . Effluent samples were collected and analyzed for negatively and positively charged polar compounds. For that reason, a potentiometric titrator was used and the properties related to the amount of negative and positive polar compounds are the Acid Number (AN) and the Base Number (BN) respectively. The cores were then aged at 50°C for two weeks to acquire a uniform polar compound distribution throughout each core. Afterwards, oil recovery wettability tests took place. More specifically, spontaneous imbibition and forced displacement processes were performed to the cores with Valhall Brine depleted in Sulphate (VB0S). Finally, Mild Cleaning procedure was conducted to restore the initial wetting state of the cores and compare the wetting state after the oil flooding and after the Mild Cleaning procedure. To measure the wettability of the cores, additional oil recovery wettability test (spontaneous imbibitions and chromatographic wettability test) took place, at ambient conditions.

The experimental results show that both Magnesium and Sulfate ions improve oil recovery, with Sulfate to bear the greatest impact. The effect of temperature on oil recovery wettability tests (at 20°C and 50°C) and the resulting wettability alteration is also discussed.

Περίληψη

Η αρχική διαβρεκτότητα των ταμιευτήρων πετρελαίου είναι μία από τις σημαντικότερες παραμέτρους που επηρεάζουν την συνολική ανάκτηση πετρελαίου (πρωτογενής, δευτερογενής και τριτογενής). Ανάλογα με τις συνθήκες δημιουργίας των ταμιευτήρων πετρελαίου, διαμορφώνονται σε διάστημα εκατομμυρίων ετών διαφορετικά συστήματα πετρώματος/πετρελαίου/άλμης. Στη συγκεκριμένη διπλωματική εργασία μελετήθηκε η επίδραση του νερού του σχηματισμού πάνω στην αρχική διαβρεκτότητα δοκιμών κιμωλίας, τα οποία προέρχονται από τον σχηματισμό Stevens Klint, της Δανίας. Πιο συγκεκριμένα, έχει παρατηρηθεί πειραματικά σε ασβεστολιθικά πετρώματα ότι η ύπαρξη θειϊκής ρίζας (SO_4^{2-}), κατιόντος μαγνησίου (Mg^{2+}) και κατιόντος ασβεστίου (Ca^{2+}) στο νερό του σχηματισμού επιδρούν ευεργετικά στην ανάκτηση πετρελαίου.

Η παρατήρηση αυτή αποδίδεται στο γεγονός ότι τα ενεργά πολικά συστατικά του πετρελαίου (π.χ. R-COO^-) είναι υπεύθυνα για τις καταστάσεις ενδιάμεσης διαβρεκτότητας, καθώς τα συγκεκριμένα πολικά συστατικά λειτουργούν σαν μοριακές «άγκυρες», δημιουργώντας πολύ ισχυρούς χημικούς δεσμούς στις ασβεστιτικές επιφάνειες. Για να επιτευχθεί υψηλή ανάκτηση πετρελαίου, το πέτρωμα του ταμιευτήρα πρέπει να είναι τουλάχιστον μερικώς υδατοδιαβρεκτό. Με στόχο τη βελτίωση της υδατικής προτίμησης του πετρώματος, μέρος αυτών των ενεργών πολικών συστατικών πρέπει να απομακρυνθούν. Τα ιόντα θείου, μαγνησίου και ασβεστίου λειτουργούν σαν υποκαταστάτες αυτών, δημιουργώντας συμβιωτικές αλληλεπιδράσεις με την επιφάνεια του πετρώματος. Θαλασσινό νερό, εμπλουτισμένο σε συγκεκριμένα ιόντα έχει εγχυθεί σε διάφορες εγκαταστάσεις. Για παράδειγμα, στο πεδίο Ekofisk ($T_{\text{res}}=130^\circ\text{C}$), του Νορβηγικού τομέα έχουν πραγματοποιηθεί εγχύσεις νερού το οποίο ήταν εμπλουτισμένο σε θειϊκή ρίζα και κατιόν μαγνησίου, οι οποίες απέδειξαν τη χρήση του συγκεκριμένου εμπλουτισμένου νερού, ως υγρό βελτίωσης της ανάκτησης πετρελαίου. Επιπλέον, η υψηλή θερμοκρασία του ταμιευτήρα (130°C), επιδρά ευεργετικά στην πραγματοποίηση διαβρεκτικής τροποποίησης.

Τρία δοκίμια κιμωλίας του σχηματισμού Stevens Klint, τα οποία είχαν διατηρηθεί από το ίδιο τεμάχιο, χρησιμοποιήθηκαν ώστε να εξεταστεί η επίδραση του κάθε ιόντος, χωριστά. Έπειτα, ένα μίγμα βαρέος πετρελαίου (Heidrum field) (60%) και επτανίου (C_7) (40%), εγχύθηκε μέσα από τα δοκίμια στους 50°C . Συλλέχθηκαν δείγματα πετρελαίου, τα οποία αναλύθηκαν ως προς τα θετικά και τα αρνητικά φορτισμένα πολικά συστατικά. Για τον λόγο αυτό, πραγματοποιήθηκε τιτλοδότηση δυναμικού (potentiometric titration), μια μέθοδος μέσω της οποίας εκτιμάται η διαφορά δυναμικού σε ένα διάλυμα, με τη χρήση ηλεκτροδίου, η οποία οφείλεται στην ύπαρξη πολικών συστατικών. Οι ιδιότητες που συνδέονται με την ποσότητα αρνητικά και θετικά φορτισμένων πολικών συστατικών ονομάζονται Acid Number (AN) και Base Number (BN), αντίστοιχα. Στη συνέχεια, τα δοκίμια τοποθετήθηκαν σε ειδική κλίνη στους 50°C για διάστημα δύο εβδομάδων, ώστε τα πολικά συστατικά να κατανεμηθούν σε όλη την επιφάνεια(, κάθε δοκιμίου). Πραγματοποιήθηκαν δοκιμές ανάκτησης πετρελαίου και μέτρησης της διαβρεκτότητας. Πιο συγκεκριμένα, διαδικασίες «αυθόρμητης αναρρόφησης» (spontaneous imbibition) και «εξαναγκασμένης εκτόπισης» (forced displacement) πραγματοποιήθηκαν, με χρήση άλμης του πεδίου Valhall, από την οποία είχε απομακρυνθεί το θείο. Τελικώς, ακολούθησε διαδικασία ήπιου καθαρισμού, με στόχο την αποκατάσταση της αρχικής διαβρεκτότητας των δοκιμών και τη σύγκριση της διαβρεκτότητας μετά την έγχυση πετρελαίου και μετά τη διαδικασία ήπιου καθαρισμού. Το επίπεδο διαβρεκτότητας μετρήθηκε μέσω δοκιμών ανάκτησης πετρελαίου και μέτρησης διαβρεκτότητας, σε συνθήκες περιβάλλοντος.

Τα πειραματικά αποτελέσματα έδειξαν ότι τα ιόντα μαγνησίου και θείου βελτίωσαν την ανάκτηση πετρελαίου, με το θείο να παρουσιάζει τη μέγιστη επίδραση. Η επίδραση της θερμοκρασίας στις δοκιμές ανάκτησης πετρελαίου και (στους 20°C και 50°C) και η προκαλούμενη μεταβολή της διαβρεκτότητας αποτιμήθηκε.

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1. Introduction

1.1 Reservoir rocks

There are three main types of reservoir's rocks: Sandstones, Dolomites and Limestones. Each type of rock has developed different properties and characteristics (e.g. porosity, permeability, wettability etc.), regulated mainly by the circumstances under which they were formed, the minerals they consist of and the grain structure that they exhibit.

Sandstone is a medium-grained clastic sedimentary rock, which is composed of sand particles, quartz, clay and other minerals, such as: hematite, ilmenite, feldspar, amphibole and mica. ^[6]

Dolomite belongs to the carbonate group. It is a sedimentary rock, which consists of the mineral dolomite $(Ca, Mg)(CO_3)_2$. Dolomite has the same environmental origin as limestone: warm, shallow marine environments. The difference is that the underground water where dolomite was formed was rich in Magnesium. That was how calcite was converted into dolomite. This chemical change is known as "dolomitization". In case a full alteration takes place, the whole rock is transformed into dolomite otherwise, dolomitic limestone is formed (partial alteration). ^[7]

Limestone is a sedimentary rock which consists of the mineral calcite $CaCO_3$. It is an organic rock, formed by the accumulation of shell, coral algal and fecal debris. It is formed in low-energy marine environments, where the organisms are capable to form calcium carbonate shells and skeletons, since the ocean water can easily provide the ingredients needed. When these animals die, their shells and skeleton debris accumulate as a sediment that under the proper conditions, might be lithified into limestone. ^[9]

It can also be formed by direct precipitation of calcium carbonate, from marine environments (lakes, oceans). This type of rock formation is considered chemically formed and it is less abundant, than biological limestones. ^[9]

In case evaporation takes place, precipitation of calcite occurs and the rock that is formed, belongs to the evaporate group. ^[9]

By definition, carbonate rocks contain at least 50% calcium carbonate in the form of calcite by weight. It can also be consisted of small particles of other minerals such as: quartz, feldspar, clay minerals, pyrite, siderite and other. ^[9]

Depending on the different compositions, appearance, the way that the rock was formed and other factors, many different names are used to describe a limestone. The most common varieties used are: chalk, coquina, fossiliferous limestone, lithographic limestone, oolitic limestone, travertine and tufa. ^[9]

1.2 Chalk's Mineralogy and formation

Chalk is the type of rock which will be examined and utilized during the course of this study. It is classified as biochemically produced sedimentary rock and when pure, it appears to have the same chemical composition as calcite (CaCO_3). Otherwise, impurities might be present, such as: clay, iron, magnesium etc. When pure, it is a white in colour, soft in touch, fine-grained, porous rock.

Most of the world-wide chalk deposits, were formed during the Cretaceous period. Cretaceous' period extend from approximately 145 to 66 million years ago and appears as the last period of the Mesozoic Era. Cretaceous marks the beginning of dinosaurs' extinction, also known as the Great Extinction, during which the conditions were suitable for petroleum to be formed. During this geologic period, which spans 79 million years, great changes occurred to the earth's tectonic landmass. The two "supercontinents": Gondwana (to the South) and Laurasia (to the North) separated from each other. As a result, the South Atlantic Ocean joined the North Atlantic Ocean (mid-oceanic ridge was formed) and smaller continents started to form (e.g. Africa, South America, Antarctica connected with Australia etc.) [1]. The Tethys Sea started to disappear as Africa moved North towards Eurasia.[3] This tectonic displacement led to a sea level elevation thus, creating inland seas. That geological event is called **Marine Transgression** and created proper geological conditions for Chalk (CaCO_3) to form, since deeper sea sediments were being deposited on top of continentally-derived beach sediments (sand). As a result, the sequence of rocks which was formed from bottom to top is: sand-shale-limestone. [8]

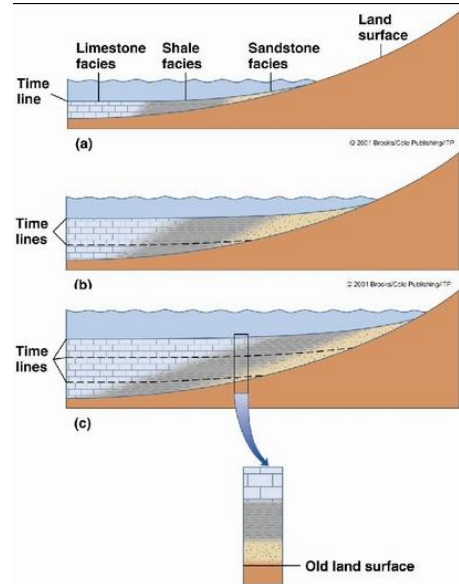


Figure 1.1: Schematic Illustration of Marine Transgression event [8]



Figure 1.2: Visible fossil on a chalk core

has a low concentration in magnesian calcite, which makes the rock very chemically and mineralogy stable.

Additionally, Chalk was formed in low-energy marine environments, mainly from calcareous shells, remains of microscopic marine organisms, such as foraminifers, or from the calcareous remains of numerous types of marine algae, planktonic skeletons. That is the reason why Cretaceous Chalk has low impurities, which can be recognized by the white or light grey colour it usually has. It is a soft limestone with a very fine texture and its' biogenic origin is usually revealed by the presence of fossils on the rocks surface. [9] It

1.3 North Sea Chalk Reservoirs

According to Hardman R. F. P. ^[10], the creation of North Sea Chalk reservoirs was a result of fortunate circumstances, which will be analyzed below. Initially, during the Cenomanian period, the deposition of Chalk started under the gradually rising sea level (Marine Transgression). As it has been mentioned, those times were characterized by warm weather, allowing coccolithophorid algae and coccoliths population to increase. As it has been pointed out by Bromley (1979) and Hardman & Kennedy (1980), the particle settling took place mainly as entire or disintegrating fecal pellets. They suggest that the coccoliths were too small to settle by themselves. After settling, sea/wave current could not affect the formation, much and after “chalk mud/ooze” became dewatered, erosion could take place only by intense current or “land-slips”.

Furthermore, because of Marine Transgression that took place at the North Sea, from the Upper Turanian to the Lower Santonian times and during the Maastrichtian period, terrestrial material (e.g clay) was reduced or disappeared from the North Sea Chalk formations thus increasing the purity of the formation. In case Chalk contains more than 5% of clay, its compaction is affected. More specifically, when compaction takes place, clay prevents the formation of the initial open framework of the rock, as it works as an adhesive material (cement). In addition, the degree of compaction is greater compared to pure chalk because the clay flakes rotate normal to the stress. Additionally, the clay minerals have the ability to absorb magnesium ions, leading to carbonate precipitation (might create dolomite $[(Mg,Ca)(CO_3)_2]$). So, in the case of North Sea section re-deposition of clays in the form of cement and overgrowths, was not to a great extent, hence pure chalk formed. (Hardman, 1982).

Another fortunate factor, according to Hardman and Kennedy (1980), that led to oil reservoirs formation was that during the early diagenesis (compaction and burrowing), about 50% of the initial water quantity inside the porous medium dropped off. Due to this dewatering effect, coccospheres and coccolith scales were broken and fractures were created. As a result, oil migration and oil saturation were able to take place. Additionally, due to geological factors, diagenesis did not reduce the porosity of the rock. Normally, diagenesis reduces porosity from approximately 50% at the sea bed to 10% at depth between 3000 and 4000m. (Hardman, 1982) For instance, Valhall oil Field, which is located in the Norwegian sector of the North Sea, has approximately 50% porosity at a depth of 2500m.

As burial continued, lithification and loss of porosity would occur, but the presence of magnesium ions led to oil “supersaturation”. As a result, over-pressuring and oil

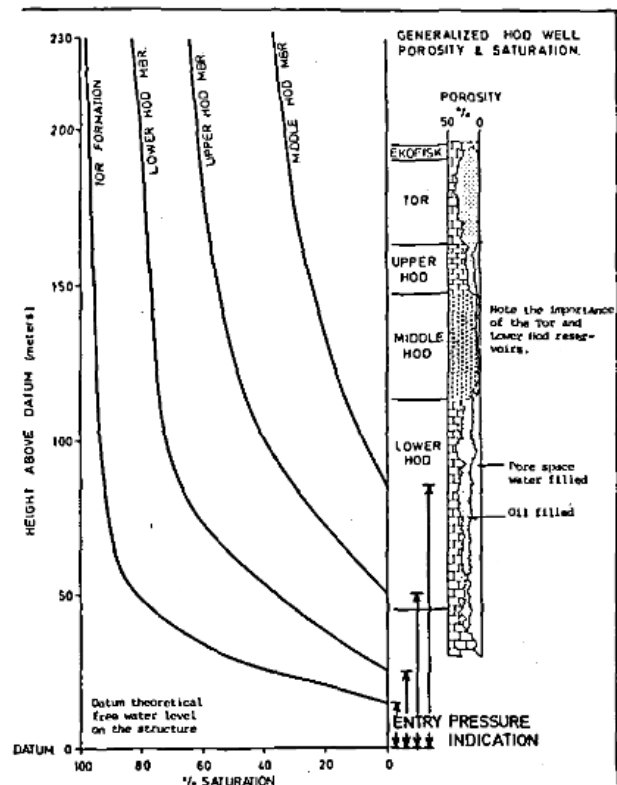


Figure 1.3: Oil Saturation-Pressure for different average rock formations (The Hod fields reservoirs (After Hardman and Kennedy 1980))

emplacement “protected” the formations and retarded the diagenesis. In case of further compaction, weakly-bonded coccoliths are crushed and porosity is mechanically reduced even more and led to size reduction and was immediately susceptible to further rapid solution.

Generally, due to the composition of the porous medium (grain size, fine grained, spherical shape), right after burial, the chalk rock has high porosity (45%-50%) and low permeability (1-3mD). Due to this fact, it forms a reservoir with micro-pores. In order for fluid to enter into the porous medium, adequate pressure differential is needed. Beneath these hydrocarbon fields, thick “beds” of Kimmeridge and Oxford Clay source rocks lay, formed in the Tertiary period. During the Oligocene, fractures were created, due to the structural growth and as a consequence hydrocarbons escaped. The amount of hydrocarbons which were generated started to accumulate within the structural openings.

Due to these fractures and hydrocarbons’ density (buoyancy), hydrocarbons were able to enter into the chalks’ formations (reservoirs). In order for hydrocarbons to displace the already resident fluid, a given pressure differential was required. As shown in Figure 1.3, depending on the formation, a different “entry pressure” must be applied. Specifically, formations with higher amount of sand and clays, exhibit lower oil saturation. Additionally, the Diagram in Figure 1.3 shows that the lower the initial pressure needed, the higher the oil saturation.

2. Oil Properties and Oil Recovery

Crude oil is a complex mixture of: hydrocarbons (H/C), Nitrogen (N), Oxygen (O), Sulfate (S) and other elements and compounds. Depending on the different ways these compounds are connected, crude oil exhibits different chemical and physical properties.

In order to design the oil exploitation in the most efficient way, the oil characteristics need to be known. Some of the main oil properties are: molar mass (M), equilibrium coefficients (K-value) at given temperatures and pressures, density (d, API index), UOP index, viscosity (μ), PVT (Pressure/Volume/Temperature) parameters (B_o , B_g , R_s , R_v), GOR and compressibility factor (c).

Molar mass (M) is defined as the mass of one mol of a substance and it is expressed in [g/mol]. It is calculated as the sum of the atomic masses of each atom.

Equilibrium coefficient (or K-value) is defined for each individual component, at given temperature and pressure conditions as the ratio of its molecular fraction in the vapor phase to its molecular fraction in the liquid phase:

$$K_i = \frac{y_i}{x_i} \quad [2.1]$$

Specific Gravity: for a gas mixture of H/C is defined as the ratio of the density of the mixture to the density of dry gas at standard conditions. On the other hand, for a liquid mixture of H/C, the density of the mixture is divided to the density of water at ambient conditions (60°F, 14.696psia).

API is an index correlated to the specific gravity of H/C and is defined as:

$$API = \frac{141.5}{\text{specific gravity (@60°F)}} - 131.5 \quad [2.2]$$

According to the equation above, the higher the specific gravity of an H/C mixture the lower the API index.

UOP Index is an index correlated with the boiling point and the specific gravity, which is used in order to characterize the H/C. The classes are

Table:

Class	UOP
Mixture of paraffinic	12.5-13
Rich in naphthenic	11-12
Rich in aromatics	9-11

Viscosity of a fluid is a property that defines the resistance of the fluid to be gradually deformed by shear or tensile stress (flow). It is expressed as: a) Dynamic (absolute) viscosity (μ) and b) kinematic viscosity (ν).

a) **Dynamic viscosity (μ)** is expressed as:

$$\mu = \frac{\tau}{\gamma} \quad [2.3]$$

Where,

- μ : dynamic viscosity [$\text{N}\cdot\text{s}/\text{m}^2$]
- τ : shearing stress in fluid [N/m^2]
- γ : shear rate [s^{-1}] ($\gamma = dc/dy$)
 - dc : unit velocity [m/s]
 - dy : unit distance between layers [m]

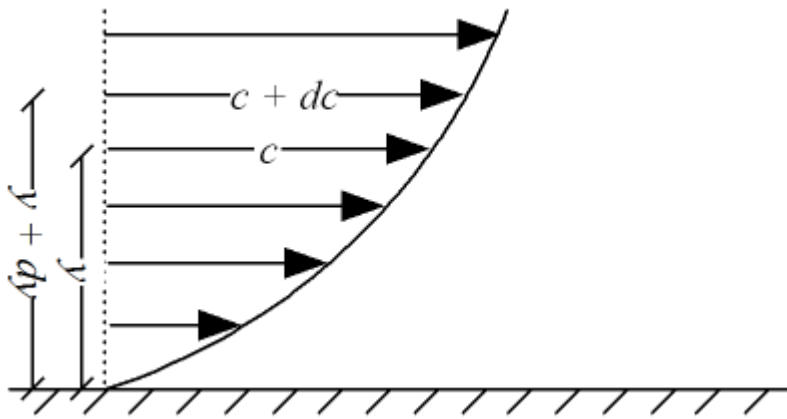


Figure 2.1: Illustration of the shearing stress between the layers of a non-turbulent fluid in straight parallel lines. (www.engineeringtoolbox.com)

b) **Kinematic viscosity (ν)** is defined as the ratio of dynamic viscosity to the density of the fluid:

$$\nu = \frac{\mu}{d} \quad [2.4]$$

Where,

- ν : kinematic viscosity [m^2/s]
- μ : absolute viscosity [$\text{N}\cdot\text{s}/\text{m}^2$]
- d : density of the fluid [kg/m^3]

Kinematic viscosity depicts the thickness of the fluid.

PVT parameters

Depending on the pressure and temperature conditions under which the oil reservoir was formed, the oil acquires different volume and properties. Some of the main oil properties are presented below.

Oil Formation Volume Factor (FVF or B_o) is defined as the ratio of liquid oil volume at reservoir conditions (where gas is dissolved) over the volume of oil at ambient conditions after the dissolved gas is released.

$$B_o = \frac{V_{oil}^{@P_{res}}}{V_{oil}^{@P_{atm}}} \quad [2.5]$$

Gas Formation Volume Factor (B_g) is defined as the volume of gas, at reservoir conditions [bbl] that one gas volume unit occupies at ambient conditions [scf].

$$B_g = 0.0282 * Z \frac{T}{P} \quad [\text{ft}^3/\text{scf}] \quad [2.6]$$

Where:

- T: Temperature [Rankin]
- P: Pressure [psia]

Solution gas/oil ratio (R_s) is defined as the volume of gas at standard conditions that dissolves into one STB of oil under reservoir conditions and is expressed as standard cubic feet per stock-tank barrel [scf/STB].

Gas/Oil ratio (GOR) is defined as the volume of produced gas at ambient conditions, divided by the volume of produced oil at ambient conditions.

$$GOR = \frac{V_{gas}^{@P_{atm}}}{V_{oil}^{@P_{atm}}} \quad [2.7]$$

Isothermal Compressibility oil Factor (c_o)

The compressibility factor expresses the ability of a fluid to be compressed. Especially for unsaturated oil reservoirs, this factor defines the amount of expansion that accompanies the pressure drop that occurs during the oil exploitation.

The isothermal compressibility factor under these conditions is defined as:

$$c_o = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad [2.8]$$

In saturated oil conditions, below the bubble point pressure, oil isothermal compressibility is defined from oil and gas properties to account for gas coming out of solution. The corresponding saturated oil compressibility is defined as: ^[32]

$$c_o = -\frac{1}{B_o} \left[\left(\frac{\partial B_o}{\partial p} \right)_T - B_g \left(\frac{\partial R_s}{\partial p} \right)_T \right] \quad [2.9]$$

2.1 Classification of crude oil polar components

It is well known that in general crude oil is a non-polar substance although depending on its' quality, origin and geologic history, it may contain polar compounds. The method used to divide in the lab the oil polar components, into groups, is called **SARA fractionation**. More specifically, this method splits the crude oil components according to their polarity. It has been named that way by the initial letters of the crude oil components: Saturates, Aromatics, Resins and Asphaltenes. The **Saturates** fraction consists of non-polar compounds (linear, branched and cyclic saturated H/C-paraffin). **Aromatic** components are associating with low reactivity and polarity since they consists of non-saturated cyclic H/C. **Resins** and **Asphaltenes**, are both polar, also known as heteroatoms (NSO). The difference is that asphaltenes are insoluble in excess of heptane (C₇), whereas resins are miscible.

Depending on the relative percentage of each group, an oil is characterized as: Heavy oil, Light oil or Intermediate oil. The classification can be illustrated graphically as shown in Figure 2.2.

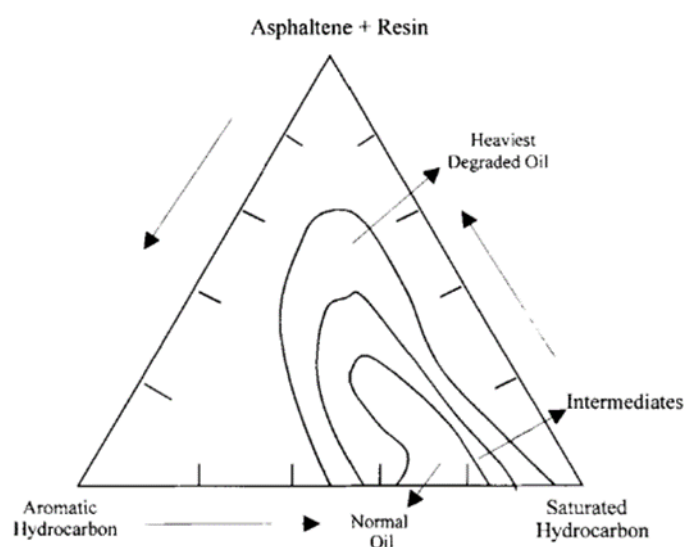


Figure 2.2: Crude oil components classification (IFP)

2.2 Reservoir Fluid Types

Depending on the circumstances under which a rock reservoir was formed, different rock/oil/brine systems are formed, with respect to the brine composition and the hydrocarbon fluid that the rock retains. Below, the different reservoir fluid types will be analyzed.

In general, high pressure and temperature, increase the attractive forces and the kinetic energy of the molecules, in a solution. More specifically, in an hydrocarbon mixture, as temperature increases, the repulsion forces are also developed, hence the molecules in the solution tend to develop repulsive forces. As a result, the equilibrium established in the system is regulated by the interaction between the attractive and repulsive forces. ^[3]

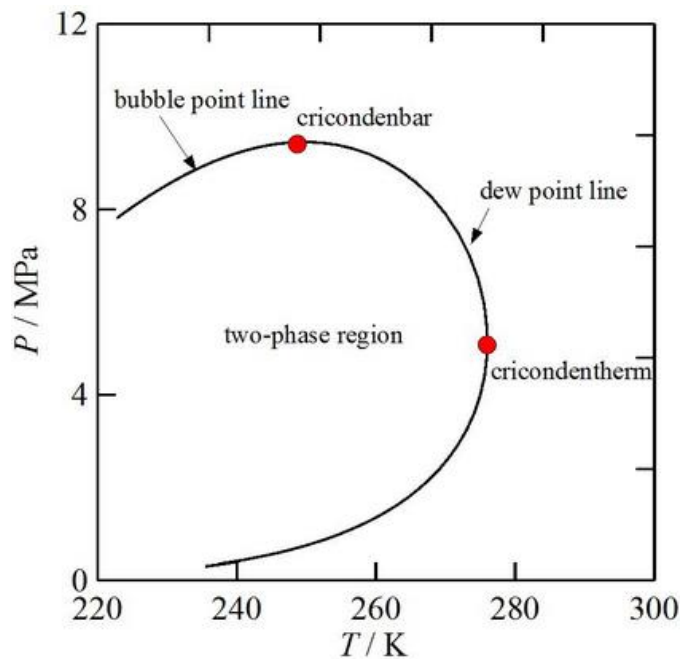


Figure 2.3: Typical phase envelope

These conditions result to different reservoir fluid types which are expressed graphically through the **phase envelope** (Diagram 1). The phase envelope is a thermodynamic diagram which is described by the composition of pressure, temperature values for which phase change will occur.

Let's assume an one substance system, then the properties below, belong to the phase envelope and can be defined as:

- Dew point: point which for specific P,T conditions the first (liquid) droplet of oil appears.
- Bubble point: point which for specific P,T conditions the first bubble appears.
- Saturation points: are called the dew point and the bubble point.
- Critical point: is the point on P,T graph where the geometric loci of dew and bubble points converge.

For values of P,T, inside and on the line that defines the envelope, the mixture appears to be on two-phase equilibrium, whereas on any other point the mixture exists as one-phase.

Depending on the pressure, temperature conditions, the origin of the organic matter and the composition of the mixture, the reservoir fluids are classified into five (5) categories:

1. Dry Gas
2. Wet Gas
3. Gas Condensate
4. Volatile Oil
5. Black Oil

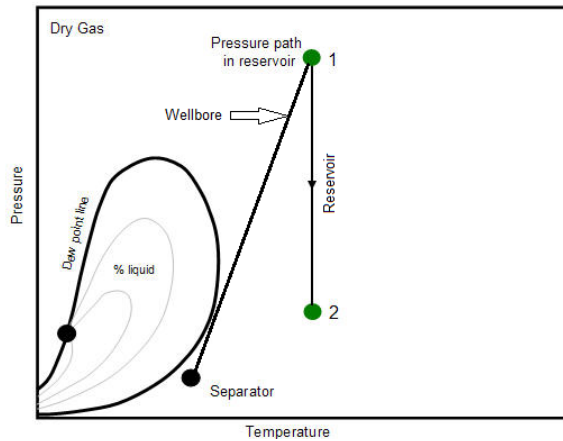


Figure 2.4: Typical phase envelope of Dry gas reservoir [4]

Dry Gas:

Due to the high temperature and pressure conditions that occurred during the catagenesis, the heavier hydrocarbon molecules broke down to lighter. The graph shows that in case of reservoir exploitation, this type of reservoir will only produce dry gas, since, by reducing the pressure during production, under stable temperature, the mixture which will be produced will be in single phase. Due to the fact that the points that depict the production are on the right hand side of the critical point, the phase is gas. [3]

Wet Gas:

It is noticed that the phase envelope is being shifted to the right, with respect to the previous one. That occurred due to the fact that the mixture of hydrocarbons (H/C) has higher concentration of heavier H/C. As pressure drops, during the reservoir exploitation, only gas is produced. The difference with the dry gas reservoir is that since the point "separator" shown on the graph is inside the phase envelope, liquid will be formed at ambient conditions in the separator. The amount of liquid to be condensed depends on the initial composition of the effluent. [3]

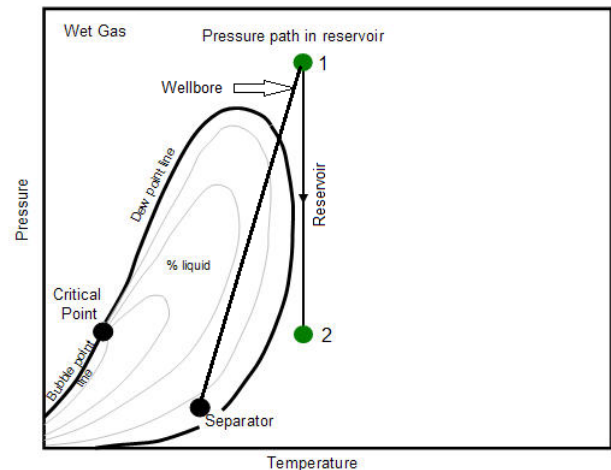


Figure 2.5: Typical phase envelope of Wet Gas reservoir [4]

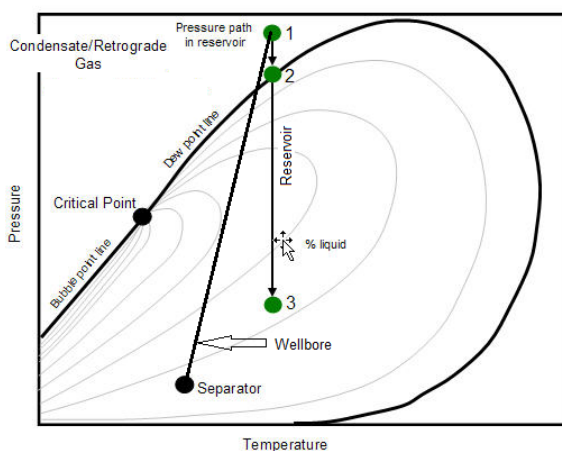


Figure 2.6: Typical phase envelope of Gas Condensate reservoir [4]

Gas Condensate:

It is a type of reservoir fluid which has heavier H/C compounds compared to a Wet Gas fluid type. It is easily noticed that part of the hydrocarbons produced will be liquid and part will be gas, since the temperature of the reservoir (T_{res}) is higher than the critical temperature (T_c). The percentage of each phase depends on the amount of heavier H/C in the mixture. The fluid in the separator will also be both liquid and gas. [3]

Volatile Oil:

This type of fluid contains an even higher concentration of heavier H/C, with respect to the previous one. Its phase envelope is more shifted to the right and the reservoir temperature (T_{res}) is lower than the critical temperature (T_c). Hence, the fluid produced will be mostly liquid. At point 2, the bubble point (B_p) is reached, which means that gas will be produced. Inside the separator, both gas and liquid will be produced. [3]

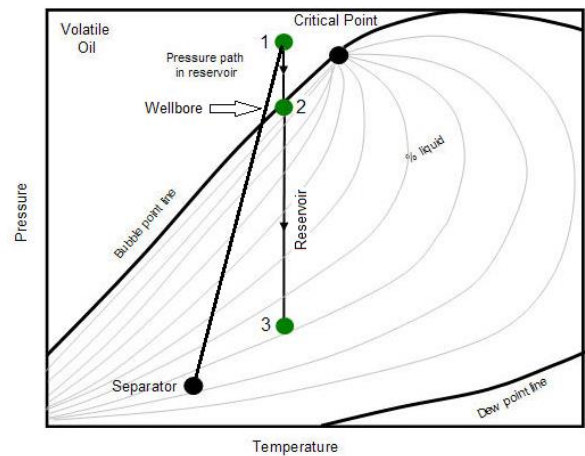


Figure 2.7: typical phase envelope of Volatile Oil reservoir [4]

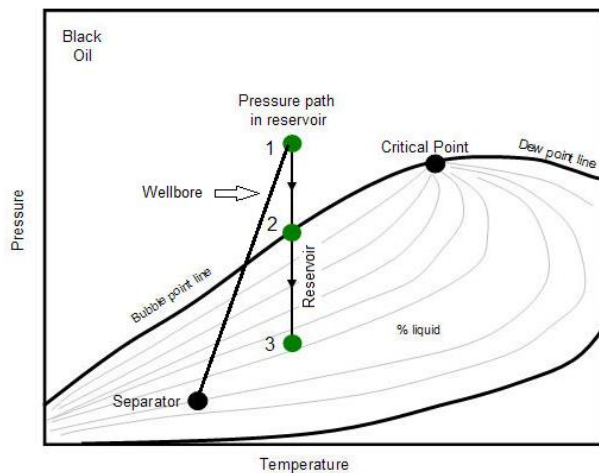


Figure 2.8: Typical phase envelope of Black oil reservoir [4]

Black Oil:

This type of fluid has low concentration of volatile components. For gas to form, the reservoir pressure needs to be decreased significantly. [3]

2.3 Oil Recovery Methods

Oil recovery is defined as the oil extraction process that takes place in the field. Initially, oil arrives to the surface due to pressure difference between the reservoir (high pressure) and the atmosphere (1atm). In this stage, pump jacks or other artificial lift devices might be used, to stabilize the system and maintain a stable oil recovery. This stage is called **Primary Oil Recovery** and usually only 5% to 15% of OOIP is recovered. ^[2]

The following stage of recovery is **Secondary Oil Recovery**. During this process, gas or water is injected, so more oil is being displaced and forced to flow through the perforations. Typically, an additional 30% of the oil's reserves can be produced. However, from this stage and on recovery requires expertise and well trained professionals (at the field) and researchers (at the laboratory). ^[2]For that reason many different techniques have been developed in order to increase the recovery beyond the secondary stage's one. These methods are called **Tertiary Oil Recovery** ones, known also as **Enhanced Oil Recovery (EOR)** ones. In contrast with the previous two stages, these methods aim to alter the properties either of the rock or of the hydrocarbons, with purpose to enhance the oil recovery. The three most commonly applied EOR techniques are: ^[2]

- Thermal Recovery: Is a technique which aims to reduce the viscosity of the oil, usually by introducing steam inside the reservoir. As a result, the oil's ability to flow is enhanced.
- Gas injection: by this method, natural gas, nitrogen or carbon dioxide, is injected inside the reservoir. The gases are able to expand, reduce the oil viscosity by dissolving and push oil to be produced.
- Chemical flooding: many different chemicals have been found to act complementary, with respect to the recovery. Some of them are: polymers, surfactants, alkaline, micellar, emulsion etc. All these chemicals aim to alter the rock and fluid interactions and increase the oil recovery.
- Other EOR methods: microbial EOR, foam, low salinity water injection, water alteration gas injection.

3. Fundamentals of Fluid Flow

3.1 Fluid Flow inside the porous medium

There are three main forces that interact with each other and are involved in the flow of fluids through a saturated porous medium. Those are: Capillary action, viscous forces and hydrostatic forces. Each one is examined separately in the paragraphs 3.1.1, 3.1.2 and 3.1.3.

3.1.1 Capillary Action

Capillary action is the result of surface tension and adhesive forces. At liquid-air interfaces, the surface tension is caused by cohesion within the liquid (e.g. net effect). ^[1] In Figure 3.1, the capillary action is illustrated. For liquid to rise in a tube, the adhesive force needs to be greater than the cohesive forces.

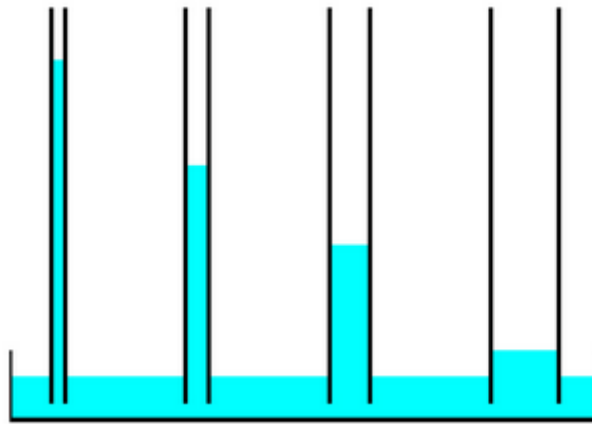


Figure 3.1: Capillary action on tubes

The height of the column is given by Jurin's Law:

$$h = \frac{2\gamma \cos(\theta)}{\rho g r} \quad [3.1.1.1]$$

Where,

- h: height of a liquid column [m]
- γ : liquid-air surface tension [N/m²]
- θ : contact angle [degrees]
- ρ : density of the fluid [kg/m³]
- g: local acceleration due to gravity (9.81m/s²)
- r: radius of the tube [m]

The capillary pressure is defined as the difference between the pressure prevailing the non-wetting phase and the pressure in the wetting phase (view Chapter 4. Wettability):

$$P_c = P_{non\ wetting} - P_{wetting} \quad [3.1.1.2]$$

According to the Young-Laplace equation, the capillary pressure is given by the equation^[3]:

$$P_c = \frac{2\gamma \cos(\theta)}{r_c} \quad [3.1.1.3]$$

Where,

- P_c : capillary pressure [N/m³]
- γ : interfacial tension [N/m²]
- θ : contact angle [degrees]
- r_c : effective radius of the interface [m]

Capillary pressure can serve both as opposing force, for the fluid most imbibed onto the surface (wetting phase) or as driving force for the non-wetting phase, since due to the surface tension cause by the pressure difference between the wetting and non-wetting phase (eq. 3.1.1.2), the non-wetting phase tends to acquire the least surface area possible (eq. 3.1.1.3).^[3] It is important for the capillary pressure to be known, in order to properly estimate certain core properties (e.g. wettability, relative permeability) and optimize the oil recovery.

3.1.2 Viscous Forces

Let's assume a fixed (not moving) plate and a plate moving due to a force F (Figure 3.2). Between the two plates, there is a fluid. By moving the plate with a velocity v , the first layer of the fluid closer to the plate will start moving. The stronger the force applied on the plate, the more layers gradually move. At the bottom, the fluid will remain stagnant until all the layers above have started moving.

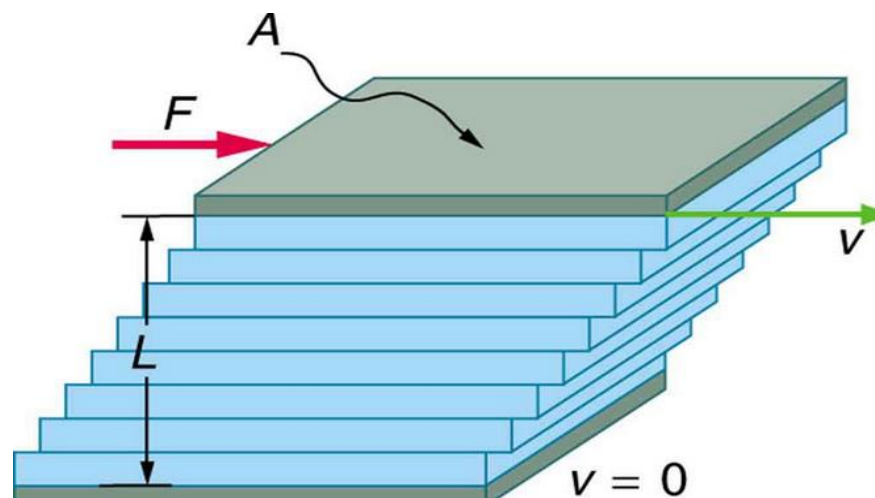


Figure 3.2: Illustration of viscous force during fluid flow (source: https://cnx.org/contents/pCk_wk3i@5/Viscosity-and-Laminar-Flow-Poi)

The force applied on the upper plate is called viscous force, and is defined as:

$$F_{viscous} = \eta * A \frac{\Delta v_x}{\Delta y} \quad [3.1.2.1]$$

Where,

- F_{viscous} : viscous forces [N]
- η : kinematic viscosity [$\text{N}\cdot\text{s}/\text{m}^2$]
- A : area [m^2]
- Δv_x : velocity difference at x-axis [m/s]
- Δy : Displacement difference between the two plates [m]

Depending on the correlation between the inertial and the viscous forces, Reynold's Number is defined:

$$Re = \frac{\text{Inertial Force}}{\text{Viscous Force}} \quad [3.1.2.2]$$

$$Re = \frac{(\text{mass}) * (\text{acceleration force})}{(\text{dynamic viscosity}) * \left(\frac{\text{velocity}}{\text{distance}}\right) * (\text{Area})} \quad [3.1.2.3]$$

$$Re = \frac{\rho * u * L}{\mu} \quad [3.1.2.4]$$

Where,

- Re : Reynold Number
- ρ : density [kg/m^3]
- u : velocity of the fluid [m/s]
- L : characteristic linear dimension [m]
- μ : dynamic viscosity [$\text{N}\cdot\text{s}/\text{m}^2$]

It is noted that the inertial force defines the force that is opposite in direction to an accelerating force on a body.

Reynold's Number is used to determine the flow regime of the fluid within the porous medium. Depending on its value the flow is characterized as shown in Table 1:

Table 1: Flow classification regarding Re number

Flow Types	Re
Laminar flow	<2300
Intermediate flow	2300-4000
Turbulent flow	>4000

Laminar flow is characterized by the smooth flow of the fluid in layers that do not mix, while **Turbulent flow** is characterized by eddies and swirls that mix layers of fluid together. **Intermediate flow** as the appellation betrays, is referred to an intermediate condition between the initial two flow conditions.

3.1.3 Hydrostatic Pressure

Let's assume a reservoir rock saturated with oil and brine. Gravity forces have an impact on the oil droplets, which are mainly determined by the density difference. In case the density difference between the two immiscible fluids is large, the gravity forces need to be taken under consideration in a multiphase flow system as the depth of burial is increased. According to Pascal's Law, the gravity pressure is given by the equation:

$$G = \Delta\rho gh \quad [3.1.3.1]$$

Where,

- G: gravity pressure [kg/(m*s²)]
- $\Delta\rho$: density difference [kg/m³]
- g: local acceleration due to gravity (9.81m/s²)
- h: height of the fluid column [m]

3.2 Permeability

The fluid flow inside a reservoir rock is carried out through the pores of the rock. Permeability of a rock is a measure of its ability to transmit fluid through it. The greater the permeability of the porous medium, the easier the fluid flows. ^[5]

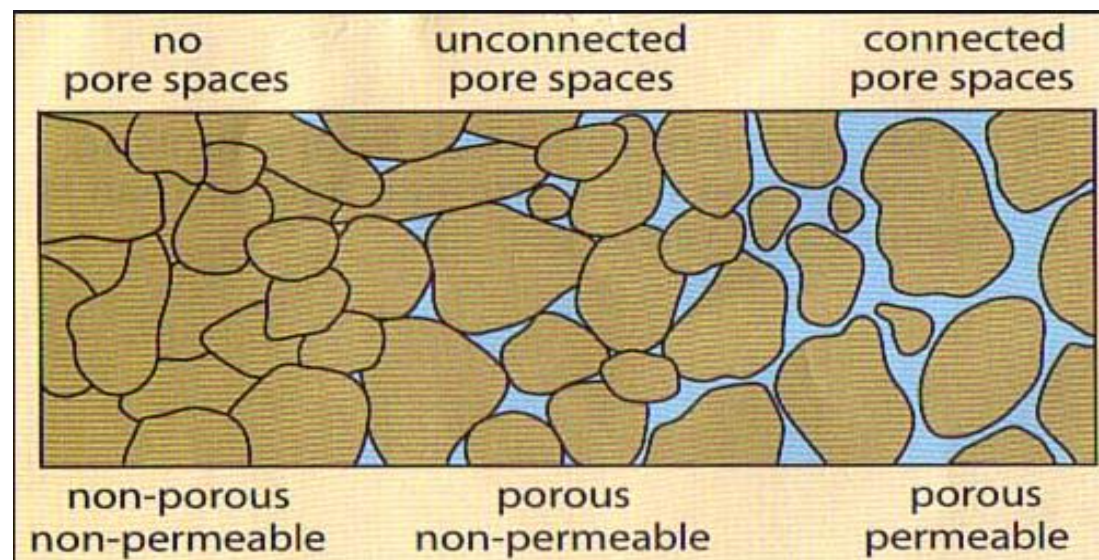


Figure 3.33: Porous medium and permeability

Permeability is related to the porosity, the shape of the pores and the level of their connectivity and tortuosity. Figure 3.3 illustrates the relation between connected and non-connected porous mediums. The more connected the porous are, the higher the permeability. Generally, permeability is defined with respect to the direction that it is examined (vertically, horizontally or at a random angle).

Permeability is also classified into: Effective permeability and relative permeability.

Absolute permeability (k) is the permeability of a porous medium saturated with a single fluid. It can be calculated from the steady-state flow Darcy's Law for linear incompressible fluid flow:

$$k = \frac{Q \cdot \mu \cdot \Delta P}{A \cdot L} \quad [3.2.3.1]$$

Where,

k: permeability (D)

Q: flow rate (ml/sec)

ΔP : pressure differential (atm)

A: area (cm²)

L: length (cm)

μ : absolute viscosity (cP)

In order for Darcy's Law to be applicable, four (4) conditions must apply:

- There is no chemical interaction between the fluid and the porous medium.
- The fluid inside the porous medium does not change phase.
- The flow must be laminar.
- The pores are considered connected.

However, usually oil reservoirs contain two or three different fluids. For that reason, effective and relative permeability must be taken under consideration.

Effective permeability (k_n) is a measure of the conductance of a porous medium for a given fluid phase, when the medium is saturated with more than one fluid. It is calculated from the equation:

$$q_n = \frac{k_n A \Delta \Phi_n}{\rho_n \mu_n L} \quad [3.2.3.2]$$

Where,

- q_n : volumetric flow rate for a specific phase, n [m³/min]
- A: flow area [m²]
- $\Delta \Phi_n$: flow potential drop for phase, n.
- ρ_n : density of a specific phase [kg/m³]
- μ_n : fluid viscosity for phase, n. [N*s/m²]
- L: flow length [m]

The different phases that might exist in general in a reservoir are: oil (o), gas (g) and water (w) and the effective permeability of each phase is symbolized as: k_o , k_g , k_w respectively.

Relative permeability (k_{rn}) is the ratio of the effective permeability of a fluid at a given saturation, to some base permeability. Usually, the base is either the absolute permeability (k) or the permeability of oil at connate water saturation:

$$k_{rn} = \frac{k_n}{k} \quad [3.2.3.3]$$

Where,

- k_{rn} : relative permeability of phase n [D].
- k_n : efficient permeability of phase n [D].
- k : absolute permeability [D].

Similarly, the relative permeability of each phase that exists in a reservoir is: k_{ro} , k_{rg} and k_{rw} for oil, gas and water respectively.

3.3 Waterflooding

As it has already been mentioned (Chapter 2.3: Oil Recovery Methods), waterflooding is applied in the field, in order to maintain reservoir pressure and produce oil through oil displacement. Often waterflooding is conducted experimentally in the laboratory in order to examine the potential oil production from a rock under specific conditions.

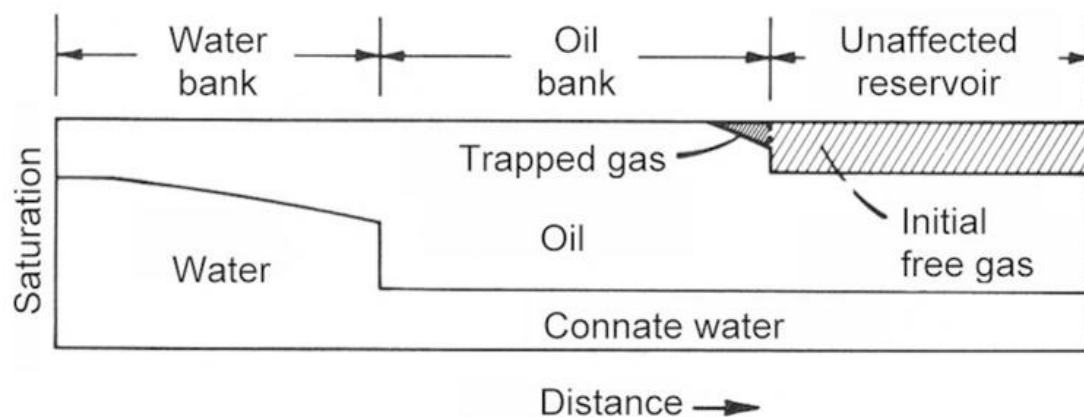


Figure 3.4: Saturation profile during waterflooding ^[5]

In Figure 3.4, the linear waterflooding process inside a reservoir is depicted. Initially, water flows through the porous medium where part of the oil is being displaced and part is being trapped in dead-ends or by capillary forces.

The efficiency of waterflooding depends on a variety of properties, such as: oil and brine viscosities, pores geometry, permeability, etc. These factors regulate the time water breakthrough will occur and consequently the amount of oil produced.

Water breakthrough is a term used to determine the time that the water injected for improving oil recovery, arrives at the production wells. ^[6]After water break-through, oil production rates are reduced.

Probably the most simplified and widely used method that estimated the oil recovery from water injection is the Buckley-Leverett theory (1942). This theory makes the assumptions: ^[8]

- Flow is linear and horizontal
- Water is injected into an oil reservoir
- Oil and water are both incompressible
- Gravity and capillary pressure effects are negligible

Inside a hydrocarbon reservoir three different flow zones can be defined as waterflooding takes place:

- **Water zone ($S_w \approx 100\%$):** Only water will be produced from a well completed in this zone.
- **Oil zone ($S_o = S_{or}$):** There is connate water which is essentially immobile and only oil will be produced from this zone.
- **Transition zone:** Both oil and water will be produced, and at each point the fraction of the flowrate that is water (water fraction) will depend on the oil and water saturations at that point.

Flow through a small volume element, with length (Δx) and cross-sectional area (A) can be expressed as:

$$q_t = q_w + q_o \quad [3.3.1]$$

$$q_w = q_t * f_w \quad [3.3.2]$$

$$q_o = q_t * f_o \quad [3.3.3]$$

Where,

- q_t : total flow rate
- q_w : water flow rate
- q_o : oil flow rate
- f_w : water fraction (water-cut)
- f_o : oil fraction

The water and oil fractional flows are given by the equations 3.3.4 and 3.3.5 respectively:

$$f_w = \frac{q_w}{q} \quad [3.3.4]$$

$$f_o = \frac{q_o}{q} \quad [3.3.5]$$

$$f_w + f_o = 1 \quad [3.3.6]$$

Where,

- q_w : volumetric water production rate [bbl/day]
- q_o : volumetric oil production rate [bbl/day]
- q : total production ($q = q_w + q_o$) [bbl/day]

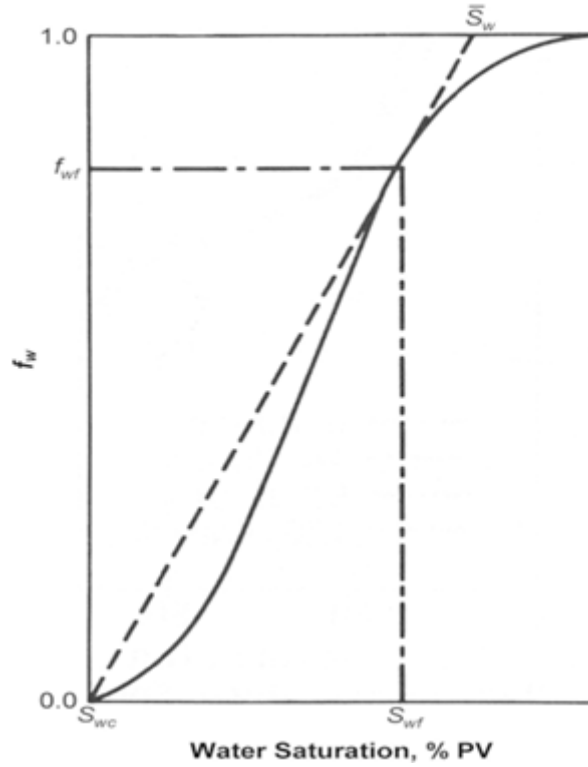


Figure 3.5: Fraction of water flowing with respect to water saturation [7]

The tangent shown in Figure 3.5 originates at the initial water saturation. The average water saturation (\bar{S}_w) behind the fluid front is determined by the intersection between the tangent line and $f_w=1$. The S_{wf} determines the water saturation at the front.

The slope of the fractional flow curve at conditions of the front is equal to:

$$\left(\frac{df_w}{dS_w}\right)_{S_{fw}} = \frac{1}{\bar{S}_w - S_{wi}} \quad [3.3.7]$$

In order the equation 3.3.7 to be valid the tangent to the fractional flow curve, from the point $S_w = S_{wc}$, where $f_w = 0$, must have a point of tangency with co-ordinates $(S_w = S_{wf}, f_w = f_{wf})$, and extrapolated tangent must intercept the line $f_w = 1$ at the point $(S_w = S_{wbt}, f_w = 1)$. Additionally, this equation ignores the effect of the capillary pressure gradient, $\partial P_c / \partial x$.

The water accumulation per unit time $\Delta S_w / \Delta t$ is given by the formula: [8]

$$\frac{\Delta S_w}{\Delta t} = - \frac{q_t \cdot \Delta f_w}{A \cdot \phi \cdot \Delta x} \quad [3.3.8]$$

Where,

- ϕ : porosity

3.3.1 Properties affecting waterflooding

Oil/Water Viscosity ratio (μ_o/μ_w) on waterflooding

The water/oil viscosity ratio has an impact on relative permeability curves. More specifically, at high water/oil viscosity ratio the relative permeability curve and the water breakthrough resembles the preferentially water-wet system. In contrast, if the ratio is low, then water break-through occurs rapidly and the system appears as having an oil-wet preference. This behavior is described by the *fractional flow equation*:

$$f_{w(S_w)} = \frac{1}{1 + (k_{ro}/k_{rw})(\mu_w/\mu_o)} \quad [3.3.1.1]$$

Or,

$$(k_{ro}/k_{rw})_{(S_w)} = (\mu_o/\mu_w)(f_w/(1 - f_w)) \quad [3.3.1.2]$$

Where,

- k_{ro}/k_{rw} : oil/water relative permeability ratio
- μ_o/μ_w : oil/water viscosity ratio
- f_w : fraction of water flowing

The overall mobility m , is defined as: ^[9]

$$m = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_{wo}} \quad [3.3.1.3]$$

Before water breakthrough, production is regulated by both the viscosity and the relative permeability ratio. The oil/water viscosity ratio is inversely proportional to the oil/water relative permeability ratio, as it is shown above, interpreting the connection between viscosity ratio and wettability.

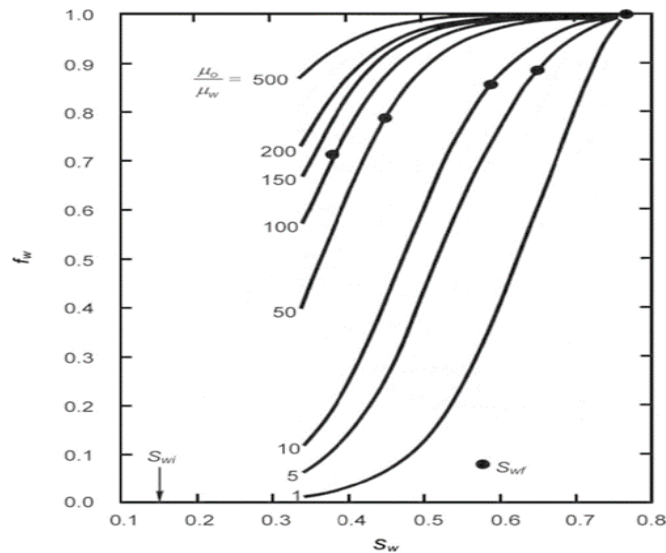


Figure 3.6: Effect of viscosity ratio on fractional flow (f_w) [7]

Figure 3.6 illustrates the effect that the oil/water viscosity ratio has on fractional flow. The higher the difference between oil and water viscosities, the less efficient the oil recovery is.

With respect to the experimental procedures, it should be noted that since viscosity is often sensitive to temperature, experimental tests conducted to evaluate the behavior of a specific oilfield, must be performed at reservoir T, P conditions. [1]

Porous medium geometry

As it has already been mentioned, the shape of the pores and their interconnectivity, affect the fluid flow inside the porous medium.

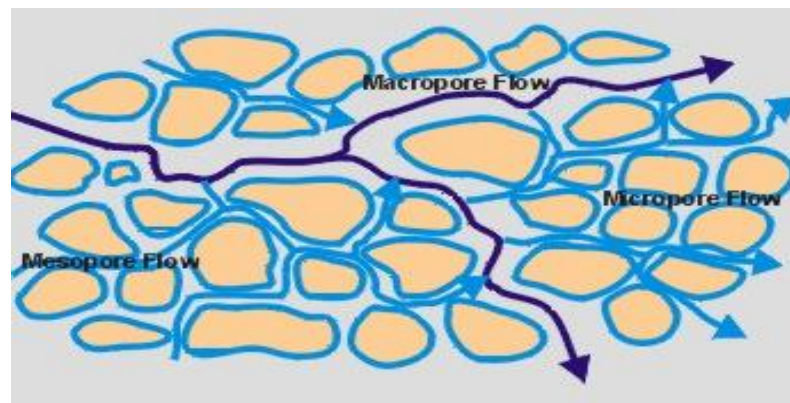


Figure 3.7: Flow paths in porous medium

Depending on the openings existing between the pores, the flow is characterized as:

1. **Macropore flow:** when the flow among the pores occurs relatively easily.
2. **Mesopore flow:** is defined as the flow through pores that stand closer to each other and for flow to happen, a higher pressure needs to be applied.
3. **Micropore flow:** where flow occurs more difficult with respect to the previous ones, due to the size of the pores.

The homogeneity or heterogeneity of the porous medium is an important rock characteristic, since the more homogeneous the rock is, the more pores are connected and the easier the flow occurs.

Relative Permeability

Relative permeability affects waterflooding, since the higher the relative water permeability in comparison to the relative oil permeability, the easier the water flows through the porous medium.

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4. Wettability

Throughout millions of years of geological changes, an equilibrium between the rock, the oil and the brine has been established. From a chemical and thermodynamic point of view, the oil and the brine interact with the rock in order to create the most stable system (principle of lower energy). It is well known that initially and before the hydrocarbons' migration has taken place, the rock is saturated with brine. When the oil escapes from the source rock and accumulates inside the reservoir, it displaces part of the brine. The amount of brine which will be displaced out of the rock depends on the wettability, the temperature, the pressure, the oil and the brine composition.

Wettability is the relative adhesion of two fluids to a solid surface. ^[1]The immiscible fluids can either spread or adhere onto the rocks' surface. The preference the rock shows, depends on different properties, which will be analyzed in detail below.

Let's assume a rock/oil/brine system (Figure 4.1), the preference of the rock to be wetted by one of the phases, depends on the contact angle that is created between the oil/water/rock/system.

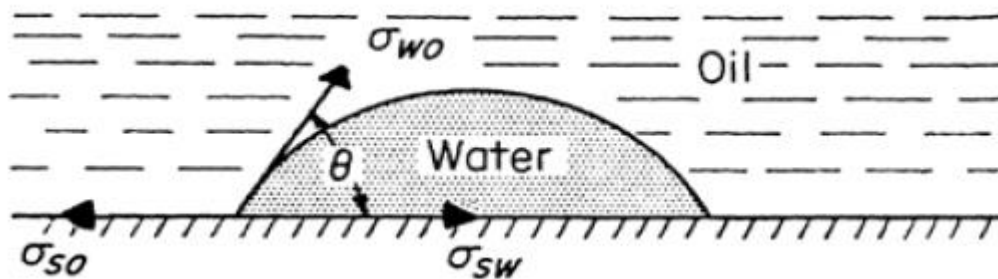


Figure 4.1: Rock/Oil/Water system (petroleum exploitation notes N. Varotsis)

The contact angle is calculated according to the equation:

$$\cos(\theta) = \frac{\sigma_{so} - \sigma_{sw}}{\sigma_{wo}} \quad [4.1]$$

Where,

- θ : water/rock contact angle
- σ_{so} : solid-oil surface tension
- σ_{sw} : solid-water surface tension
- σ_{wo} : water-oil surface tension

As it has already been mentioned (Chapter 3.1), surface tension is caused by the unbalanced forces between the hydrocarbons, the brine and the minerals at the rock surface. Depending on the value of the calculated contact angle, the wettability is classified as shown in the Table 1:

Table 1: Wettability classification based on contact angles (Source: Iglauder et al. (2015)^[2])

Wettability state	Contact angle (degrees)
Complete wetting or spreading of water	0
Strongly water-wet	0-50
Weakly water-wet	50-70
Neutrally wet	70-110
Weakly non-wetting to water	110-130
Strongly non-wetting to water	130-180
Completely non-wetting to water	180

4.1 Wettability Classification

The main reservoir porous media wetting states are: water-wet, oil-wet, mixed wet and fractionally wet. These conditions are described below:

4.1.1 Water-wet

Water-wet is considered the porous media that leads to a condition, where in a rock/oil/brine system more than 50% of its surface is covered with brine (water). Water fills the smaller pores and the “dead-ends” and exists as a film coating the larger pores. Oil exists as droplets in the larger pores and may cover surfaces where preferentially oil-wet minerals exist. It should be noted that the highest the water saturation the more discontinuous the non-wetting phase is. Water exists as continuous phase in case the water saturation is equal or greater to the initial water saturation (S_{wi}). Additionally, in case a water-wet rock is saturated with oil, water will spontaneously imbibe into the rock, displacing the oil, until a static equilibrium is accomplished, between the capillary forces and surface energy forces of the fluids and the rock surfaces. ^[1]

4.1.2 Oil-wet

In case of a preferentially oil-wet system, the condition is reversed. Since the rock is initially wet with water, when oil accumulates inside the porous medium, it spontaneously imbibes into the surface. Oil occupies the smaller porous and displaces the brine. When water exists in the larger pores, it is usually in the centre, on the film of oil. Consequently, oil is present as a continuous wetting phase in the porous medium, as long as the oil saturation is equal or greater to the residual oil saturation (S_{or}). ^[1]

4.1.3 Mixed-wet

The term mixed-wet is used to describe the state where “the small pores in the rock are water-wet and filled with water, whereas the larger pores are oil-wet and filled with oil, in contact with the pore walls that form a continuous path through the length of the rock”. ^[4.1] Salatheil (1973) supported that this condition occurs when the oil that accumulates inside the reservoir is composed by surface-active compounds, which would gradually displace the remaining films of water on the pore surface. Due to the strong capillary forces in the smaller pores, the water displacement pressure is too high for oil to enter. ^[1]

In Figure 4.2, the different rock wetting conditions are presented. The film layer of the wetting phase can be noticeable in the two extreme conditions.

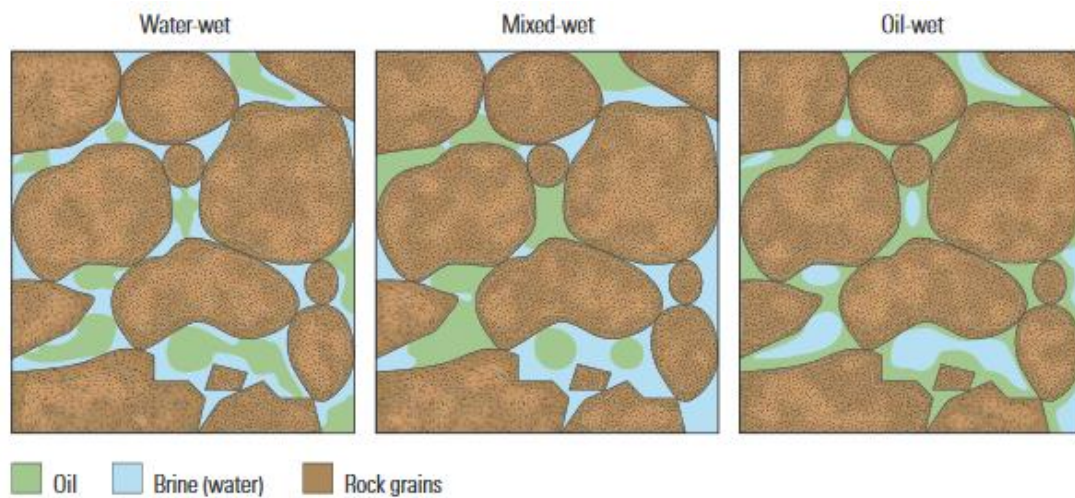


Figure 4.2: Wettability conditions (source: “fundamentals of wettability” www.slb.com)

4.1.4 Fractionally wet

This term is used to “characterize heterogeneous wetting, of the pore surfaces where the preferential wetting is randomly distributed throughout the rock” ^[1](Brown and Fatt, 1956). Usually, this kind of state occurs in heterogeneous rocks, where minerals are randomly distributed and there is no continuous oil networks through the rock.

It should be noted that both mixed-wet and fractionally-wet are referred as “neutral wet”.

4.2 Properties and Conditions that Affect Wettability

Wettability is a result of the contribution of many different properties and conditions. In order to study and measure wettability it is important to refer to the parameters that it is depended on. These parameters are: oil polar components, brine composition, mineralogy, surface reactivity, temperature and pressure. Additionally, the effect that ageing has on the wettability stabilization is discussed.

4.2.1 Oil polar compounds

Polar components play a key role in oil recovery mainly because they regulate the pH conditions of the system. It is well known that pH indicates the concentration of $[H_3O]^+$ present in a solution and pOH, the concentration of $[OH]^-$ in the solution, expressed in [mol/L].

For equilibrium to be established, oil polar components attach to the surface. Depending on the different chemical bond, some of them attach strongly and other weakly. The stronger the oil polar compounds are attached to the surface, the more oil wet the rock is, since, more energy is required to break the bonds.

The properties that indicate the amount of surface active negatively charged (acidic) and surface active positively charged (basic) polar components are called Acid Number (AN) and Base Number (BN) respectively. Both are expressed in [mg KOH/g oil]. The Acid Number indicates the mg of KOH needed to neutralize the acids components in 1g of oil. On the other hand, the Base Number indicates the amount of mg KOH needed to neutralize the amount of acids that is needed to neutralize the bases in 1g of oil. The higher the Base Number, the higher the number of acidic components (e.g. R-COO⁻) that are present in the oil, whereas a high Base Number indicates high amount of basic compounds (e.g. basic N-compounds)

More specifically,

$$AN = \frac{(v-b)*N*56.1}{w} \quad [4.2.1.1]$$

Where,

v: Volume of titration solvent (ml)

b: Volume of blank solution (ml)

N: Normality of the KOH solution

w: Weight of the sample (g)

And,

$$BN = \frac{C_{titrant} * (V_{titrant} - V_{blank})}{n_{e^{-} titrant} * m_{sample}} * M_{KOH}^{[15]} \quad [4.2.1.2]$$

Where,

- BN: Base Number [mg KOH/g oil]
- C_{titrant}: Concentration of titrant [eq/L]
- V_{titrant}: Volume of titrant [ml]
- V_{blank}: Volume of blank solution [ml]
- n_{e⁻ titrant}: Number of e⁻ in the titrant solution
- m_{sample}: Mass of sample [g]
- M_{KOH}: Molar mass of KOH solution [g/mol]

Normality is a measure of the concentration of a liquid solution expressed in molar equivalents [meq] of a chemical compound or an ion, diluted in one (1) litre solution.

Molarity is a measure of the concentration of a liquid solution expressed in grams of a chemical compound, diluted in one (1) litre solution.

There are several methods that estimate those properties (e.g. photometric determination, thermometric determination, conductometric determination, spectrometric determination)^[14]. The one that will be used in this study is called **potentiometric titration**. It

is based on Nernst's equation (1889), through which for the first time, the ion concentration of a solution was related to voltage. Nernst's equation is applied for any electrochemical reaction. Since an electrochemical reaction is defined as any process either caused or accompanied by the passage of an electric current and in most cases exchange of electrons occurs.^[28] Such reactions are the reduction-oxidation (redox) reactions.

The Nernst's equation is expressed as:

$$E = E_o - \frac{RT}{nF} \ln(Q) \quad [4.2.1.3]$$

Where:

E: Reduction potential in anion-equilibrium condition.

E_o: Standard reduction potential in steady state conditions.

R: Gas constant (8.314 J/(mol*K)).

n: Number of e⁻ that are being exchanged.

F: Faraday's constant (96,485.3415 C/mol).

Q: reaction's indicator when the system is on a non- steady state condition.

$$Q = \frac{\text{Ionic products (reduction)}}{\text{Ionic reactors (oxidation)}} \quad [4.2.1.4]$$

Note: At equilibrium:

- Q=K (reaction's constant) and
- E=0 (no ionic exchange)

The method is similar to direct titration of neutralization reactions, but in this case, no chemical indicator is used and instead, the potential across the analyte is measured. More specifically, the electrode used for the potentiometric titration is calibrated by using buffer solutions of pH=4, pH=7 and pH=10. A blank solution is an acid or base that is added to increase the acid or base content for better resolution. The content of the blank is subtracted from the sample measurement, in order to get the result of the acid or base content of the actual sample. The current of the blank solution which is measured by an electrode, is used as an indicator for the sample measurements. The Acid and Base number in both blank and sample measurements, is indicated by using a titrant solution which is added automatically by the potentiometric titration device until the solution is neutralized. The solution of the titrant and all the chemical used for the potentiometric titrations are shown in Tables 1 and 2.



Figure 4.3: Compact Potentiometric Titrator G20 Mettler-Toledo International Inc .^[29]

The parts that the potentiometric titration device consists of are:

1: One litre bottle which contains Titrant solution.

2: Removable plastic container.

3: Stirrer.

4.a: Electrode – Reception for the electrode to come in contact with the solution needed to be measured.

4.b: Electrode – Reception for the electrodes to be placed after the measurement has finished. Contain liquid KCl [3M] for the electrode not to be dried.

5: Pumps

Table 2: Solutions used in potentiometric titration for Acid and Base Number measurements

Solution	Chemicals for AN measurements	Chemicals for BN measurements
Titrant	KOH, 2-propanol	Perchloric acid, Acetic Anydrite, Acetic Acid
Titration Solvent	DI water, 2-propanol, Toluene	Methyl-isobutyl ketone (MIBK)
Spiking Solution	Stearic Acid, Titration solvent	Quinoline, Decane
Electrode/Electrolyte	KCl	Sodium perchlorate, 2-propanol

The potentiometric titration device is connected to a personal computer and the signals of the electrode are recorded and visualized through a software. The software depicts graphically the current measured through the electrode in millivolts [mV] in relation with the volume (ml) of titrant added in order to neutralize the solution measured.

The endpoint of the titration is designated by the software by calculating the first and the second integral of the curve. In Figure 4.4, a typical potentiometric titration curve is depicted and the main features of the curve are described below.

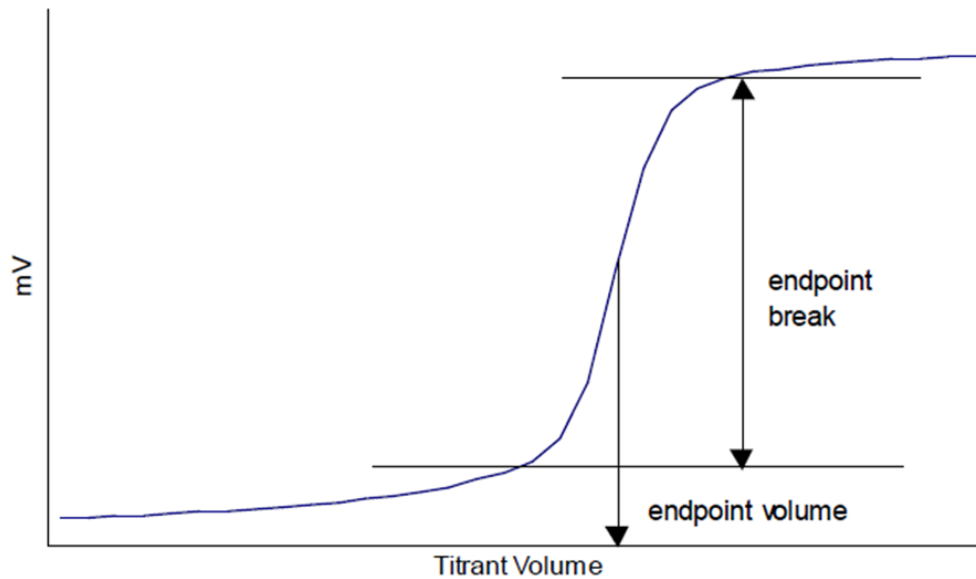


Figure 4.44: Typical Potentiometric titration curve^[16]

Features of the titration curve ^[4.17]

- The wave-like **shape** occurs because of the rapid change in voltage around the endpoint of the reaction.
- The **endpoint break** is the large change in voltage after the endpoint.
- The **endpoint break** should be as large as possible to improve accuracy of detection: this is done by choosing the titrant volume carefully.
- The **endpoint volume** is defined as the volume half-way up the endpoint break.
- The **voltage values before** the endpoint are due to the analyte.
- The **voltage values after** the endpoint are due to the titrant.

4.2.2 Brine composition

The formation water affects the initial wetting condition of the reservoir rocks, since the polar components of the brine react first with the surface. It has been experimentally verified that the interaction between Magnesium (Mg^{2+}), Calcium (Ca^{2+}) and Sulphate (SO_4^{2-}) play a key role on limestone water-wetness.^[4.22] From previous experimental studies, it has been observed that the higher the concentration of these ions, the more water-wet the limestone appears to be.

4.2.3 Surface reactivity

Another property that determines wettability is the relative magnitude of the forces of interaction between the two liquid phases and the rock surface.^[4.23, 4.24] These interactions are classified into non-polar (Lifshitz–van der Waals interactions) and polar (acid–base interactions) ones. The surface reactivity is determined by the acid-base interactions. More

specifically, it is the interaction between the polar components, which makes ion-bridge like charges that regulate the wetting condition^[4,18].

It is noted that the larger polar compounds do not exhibit high interactivity. In contrast it has been noticed that these compounds reduce surface reactivity. As a result, it is the smaller polar components that regulate the surface reactivity. This phenomenon is attributed to the kinetic energy that the smaller molecules (or ions) have, which leads to greater reactivity.

Another way for polar compounds to be adsorbed onto the surface is through surface precipitation. For chalk rocks, sulfate precipitates on the surface and is being “consumed”. No strong bonding has been experimentally recorded though, since the sulfate adsorption can be removed by flooding approximately three pore volumes (3PV) of DI water through the core. However, Sulphate precipitation plays a key role on improving oil recovery on Chalk rocks and it is considered one of the main factors affecting the wetting state of the rock.

4.2.4 Mineralogy

Each type of reservoir rock contains a variety of minerals that interact with the oil and brine differently. For instance, clay is the main wetting mineral in Sandstones, which makes their surface negatively charged. As a result, positively charged oil polar compounds (e.g. amine group, $R-NH_4^+$) mostly interact with the surface. In contrast, Carbonates attract negatively charged oil compounds (e.g. carboxylic acid, $R-COO^-$). Carbonates develop stronger bonds with oil polar compounds which makes their surface usually more oil-wet, compared to sandstones.

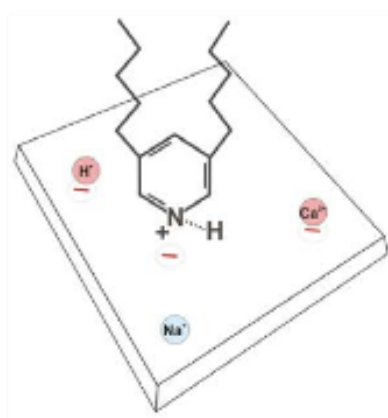


Figure 4.5: Charged Sandstone surface (UiS wettability presentation)

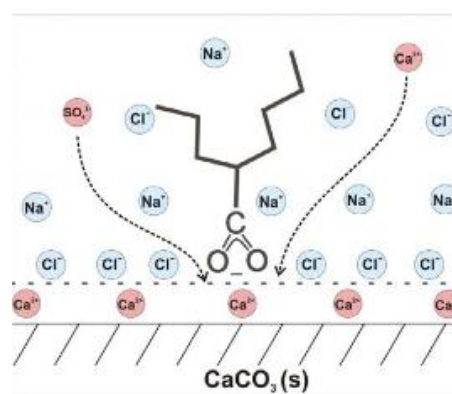


Figure 4.6: Charged Carbonate surface (UiS wettability presentation)

However, there are field observations that show that the existence of Anhydrite ($CaSO_3$) in Carbonate reservoir rocks, tends to make the surface more water wet. It is considered that sulphate precipitation is responsible for the water preference of the Carbonate rocks.

4.2.5 Temperature and pressure

The effect of temperature and pressure on wettability has been experimentally investigated. It has been found that as temperature and pressure increase in a sandstone/oil/brine system, the contact angle increases.^[4.25] As a result, the system tends to be more oil-wet. The opposite occurs for carbonates. As the temperature and the pressure increase, the contact angle decreases, which means that the system becomes more water-wet.^[4.25] However, more research needs to be done with respect to the reservoir conditions.

4.3 Methods to measure wettability

Measuring wettability is not an easy task. Several techniques have been developed and proposed, for this purpose. It is important to express wettability as a number (or percentage), in order to relate it to different properties (e.g. surface tension, capillary forces etc). In addition, rocks with similar wettability, appear alike in behavior. As a result, being able to quantify wettability numerically, makes the comparison between different rocks straightforward. The four most well-known methods to measure wettability are presented below.

4.3.1 Contact angle measurement

In order to measure the contact angle, many different devices and techniques can be used. Some of them are: static sessile drop method (goniometer)^[4.3], pendant drop method^[4.4], dynamic sessile drop method^[4.5], dynamic Wilhelmy method^[4.6], single-fiber Wilhelmy method^[4.7] and others^[4.8]. It is not considered necessary to describe each method separately.

4.3.2 Core Oil Recovery tests

In order to measure the wettability of a rock, oil recovery tests can experimentally be conducted. More specifically, two procedures are used: Spontaneous Imbibition (SI) and Forced Displacement, either separately or one as a succession of the other. Wettability is expressed as a percentage of the oil displaced, according to the equation:

$$\%OOIP = \frac{V_{oil\ produced}}{PV} * 100 \quad (\%) \quad [4.3.2.1]$$

Where:

- %OOIP: percent of original oil in place
- $V_{oil\ produced}$: Oil produced through the test
- PV: pore volume

4.3.2.a Spontaneous Imbibition Process (SI)

Spontaneous imbibition process is used as a macroscopic method to measure wettability. This experimental procedure is the most widely used, by the oil industry. The rocks that imbibe water spontaneously are at least partially water-wet.^[4.10] According to that technique, the core is placed inside the spontaneous imbibition cell made of glass, which has

a volumetric tube on top, where the oil is collected and measured. A spontaneous imbibition fluid, usually formation water, is used in order to fill the cell and imbibe onto the surface. In order to examine the capillary forces, the fluid is ought not to react chemically with the rock surface, since a chemical interaction would result to a wettability alteration. This procedure occurs at the same temperature conditions that the oil saturation or oil flooding took place. Typical temperature values: ambient conditions (20°C), 50°C, 70°C, 120°C. Higher temperatures are usually used in order to decrease oil viscosity and acquire better oil saturation.

The volume of the oil recovered depends on the capillary forces and the time that the core has been left inside the cell. Assuming a water wet system then:

- The stronger the capillary forces, the higher the oil recovery.
- The more time the core is left inside the cell, the greater the oil recovery.

4.3.2.b Forced Displacement

Forced Displacement (or Viscous Flooding) is a technique usually applied after the Spontaneous Imbibition, in order to maximize oil recovery and study the interaction between the capillary and the viscous forces. Viscous forces refer to the force applied by pumping the fluid through the core. During this process, a flooding set-up is used, where the core is placed inside a rubber holder. A forced displacement fluid is pumped through the core in order to displace the oil. This procedure takes place at the same temperature (50°C) and the same displacement fluid is used (VBOS) as in the Spontaneous Imbibition process.

The oil production through the Forced Displacement process depends onto the capillary and viscous forces that develop inside the porous medium during the oil displacement, on the homogeneity of the core, the flow rate, the confining pressure, the temperature and the permeability.

In Forced Imbibition, strong capillary forces or high water wetness can lead to snap-off and a lot of oil can be bypassed. As long as the force that drives the oil out of the core (viscous force) is greater than the capillary force, oil production will be observed, regardless of the wetting state of the core. In case a core is at least partially water-wet, the capillary forces can act in addition to the viscous forces and oil can be displaced from the smaller pores. This occurs only in the case that the microscopic sweep is larger than the snap-off, since snap-off is also taking place at water-wet conditions.



Figure 4.7: Two different Stevns Klint Chalk cores after oil flooding cut in half (UiS)5

The more **homogeneous** the core is, the more oil is displaced, since the pores are connected and the forced displacement fluid covers higher percentage of the porous medium (Figure 4.7).

The application of **confining pressure** ensures that the core is sufficiently hold by the rubber sleeve and the fluid is passing through the core only. Furthermore, it simulates the overburden pressure which is applied on the formation. It is not ought to exceed a specific value (typical value: 20bar), for the core not to be damaged.

The **temperature** acts complementary to the oil production, since the higher the temperature, the easier the oil flows, since viscosity of the decreases (lower relative oil permeability). It is noted that the higher the **permeability**, the faster the oil recovery occurs.

4.3.3 Amott Index

The Amott index is the most widely used index by the oil industry, to define wettability. It is based on two spontaneous imbibitions and two forced displacements. ^[4.12] (Anderson 1986b, Morrow 1990):

The initial condition is at point X (view Figure 4.8) where the core is saturated with oil (S_{or}). Spontaneous imbibition takes place and the amount of oil displaced by the brine (V_{wsp}) is noted (point B). Until that point, the brine imbibes naturally onto the surface. Afterwards, viscous flooding (or centrifugation) is applied until no more oil can be displaced (point Y). Then the Water Index is calculated as:

$$Water\ Index = \frac{V_{wsp}}{S_{wt}} \quad [4.3.3.1]$$

Where,

- V_{wsp} : volume of oil displaced by spontaneous imbibition (SI)
- S_{wt} : amount of oil displaced (by SI and forced displacement)

On diagram (Figure 4.8) these values are referred as:

$$Water\ Index = \frac{AB}{AC} \quad [4.3.3.2]$$

Where,

- AB: space on Amott index diagram which refers to the spontaneous water imbibition area.
- AC: space on Amott index diagram which refers to the total water imbibition area.

The same procedure is followed in order to calculate the oil index, but this time instead of using brine as spontaneous imbibition fluid on an oil saturated core, the core is saturated with brine (S_{wi}) and oil is used in order to displace the brine. Initially, spontaneous imbibition with oil is performed until point D, where no more oil can naturally imbibe into the rock (V_{osp}). Afterwards, forced displacement (or centrifugation) with oil until the X point is applied (V_{wt}). Oil displaces brine, until equilibrium is established. The Oil Index is calculated through the equation:

$$Oil\ Index = \frac{V_{osp}}{Total\ Oil\ Imbibition} \quad [4.3.3.3]$$

Where,

- V_{osp} : amount of water displaced by water imbibition
- V_{wt} : total amount of oil displaced (by water imbibition and forced displacement)

On diagram (Figure 4.8) these values are referred as:

$$Oil\ Index = \frac{CD}{AC} \quad [4.3.3.4]$$

Where,

- CD: space on Amott index diagram which refers to the amount of water displaced by the imbibition.
- AC: space on Amott index diagram which refers to the total water imbibition area.

The wettability Amott index W is then calculated as the difference:

$$W = \text{Water Index} - \text{Oil Index} \quad [4.3.3.5]$$

The wettability Amott index can take values from zero (0) to one (1). The more oil wet the system is, the closer the value of Wettability Index (W) is to 0. The opposite occurs for water wet cores. As it can be shown in Figure 4.9, the Amott index can also be expressed as Amott ternary diagram, in order to better interpret the wetting condition.

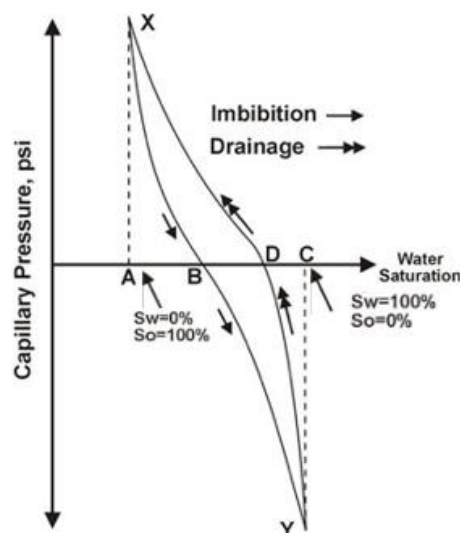


Figure 4.8: Amott Wettability Index Calculation [13]6

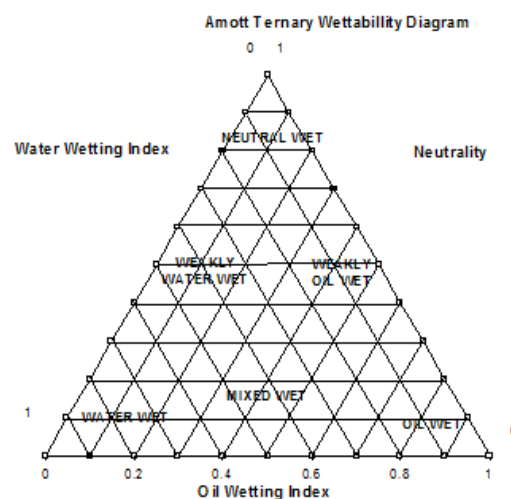


Figure 4.9: Amott Wettability Index Ternary Diagram [13]

4.3.4 Chromatographic wettability test

The chromatographic wettability test for carbonates was proposed by Strand et al. (2006). The operating principle of Ion Chromatography is the same as of the liquid or gas chromatography. It is based on the delay time for each ion to be detected by the ion chromatograph. That way, the concentrations of the desired ions of each effluent are measured.

The brines flooded during the chromatographic wettability test is Sea Water without tracer nor sulfate and Sea Water enriched with a specific amount of tracer (SCN^-) and sulfate. The first one is used in order to displace brines flooded from previous tests (e.g. VBOS during the forced displacement) and remove ions, like sulphate (SO_4^{2-}) that could affect the test. The

tracer present in the SW¹/₂T is used as a calibrator, since it does not adsorb onto the surface at all, whereas Sulfate adsorb onto the water-wet calcite surfaces and the delay time that it takes for sulfate to be detected is proportional to the water-wetness of the core. (Figure 4.9)

The chromatographic wettability test is ought to be conducted at ambient conditions for the results to be representative, since higher temperature can cause wettability alteration and turn the core into more water-wet. During flooding, effluent samples of the brine which contains tracer (SCN⁻) are collected in order to be analyzed by the Dionex ICS-3000 Ion Chromatograph device. More specifically, the relative concentrations of the tracer (SCN⁻) and the sulphate (SO₄²⁻) measured by the Ion Chromatograph are plotted with respect to the pore volumes flooded. The **relative concentration** of each ion (SCN⁻, SO₄²⁻) is calculated as:

$$C_{relative} = \frac{C_{effluent}}{C_{initial}} \quad [4.3.4.1]$$

Where,

- C_{effluent}: the concentration of SCN⁻ or SO₄²⁻ of the effluent sample
- C_{initial}: the initial concentration of SCN⁻ or SO₄²⁻ of the brine flooded.

The effluent samples are collected in glass containers that have a capacity of approximately seven milliliters (7ml). The weight of these containers is measured before and after the flooding. The weight difference is the mass of the brine collected. The mass can be converted into volume using the density of the brine. That way, the **pore volumes** flooded can be calculated.

$$PV_{flooded} = \frac{m_{initial} - m_{final}}{d_{brine}} \quad [4.3.4.2]$$

Where,

- m_{initial}: the initial weight of the container [g].
- m_{final}: the final weight of the container [g].
- d_{brine}: the density of the brine flooded [g/ml].

As it was mentioned above, the tracer does not adsorb onto the surface of the rock, whereas the amount of sulphate that is being adsorbed by the rock is related to its water-wetness. The longer it takes for sulphate to flood through the core, the more water-wet the core is. ^[4.9] It is noted that the chromatographic brines (SWOT and SW¹/₂T) both have approximately the same density and viscosity.

In Figure 4.10 the relative concentrations of sulfate (SO₄²⁻) and the tracer (SCN⁻) are plotted with respect to the pore volumes flooded. Since separation between the tracer curve and the sulphate curve is exhibited, the core shows a degree of water-wetness. Both lines follow a logistic Sigmoid curve (S-shaped curve). ^[4.32]

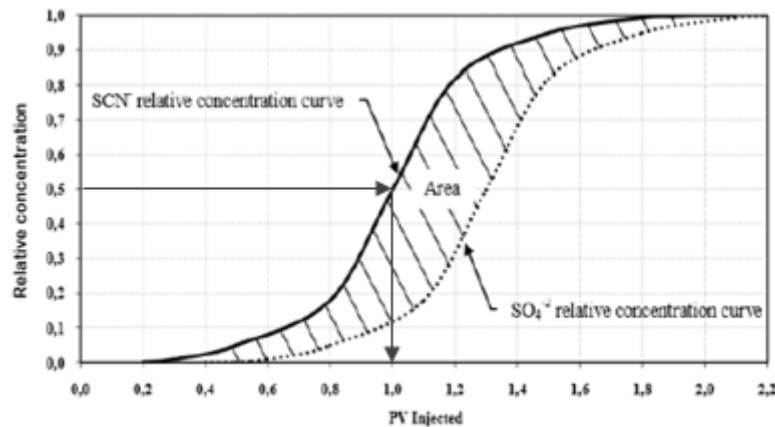


Figure 4.10: Schematic illustration of the chromatographic wettability test separation (Aksulu 2010)

The wettability index (I_{CW}) proposed by Strand et al. (2006) is given by the ratio:

$$I_{CW} = \frac{A_{wet}}{A_{WW}} \quad [4.3.4.3]$$

Where,

- A_{wet} : area defined by the sulphate curve and the tracer curve (hatched area).
- A_{WW} : area defined by the sulphate curve and the tracer curve in a completely water-wet system (reference area)

The core used in order to define the reference area, is as mentioned, a completely water-wet core ($S_{wi}=1$ as it, has not been flooded with oil) and is called reference core. The area defined between the sulphate curve and the tracer curve (as the hatched one in Figure 4.10) for that core, will be bigger compared to any other mixed-wet or oil-wet case, since there is a larger surface for sulfate (SO_4^{2-}) to be adsorbed onto.

That means that when I_{CW} is equal to 1 (100%), the surface is completely water wet, when it is equal to 0.5 (50%), the surface is neutral wet, whereas if it is equal to 0 (0%) the surface is completely oil wet. ^[4.21] This test in general exhibits good repeatability and it is considered reliable for reservoir cores and more specifically for cores that appear to be homogeneous. However, it is limited to carbonate cores and material that contain low amounts of anhydrite ($CaSO_4$), because sulphate adsorbs onto carbonates due to its positively charged surface. ^[4.9, 4.21] This method has not been developed for other reservoir rocks, yet.

4.4 Properties affected by Wettability

The wetting state of the rock has an impact on relative permeabilities (k) and water flooding behavior, since wettability regulates, the flow and the fluid distribution in the rock. Other parameters that are being affected by wettability is the initial oil saturation and the oil recovery.

Wettability affects the **relative permeabilities**, since it controls the distribution of the immiscible fluids on the rock surface. This occurs due to the capillary forces, which

preferentially restrain either oil or water onto the surface and detain its flow. In Figure 4.11, an oil/water relative permeability curve is depicted. The rock is preferentially water wet and for that reason, the relative water permeability (k_{rw}) is lower compared to the relative oil permeability (k_{ro}).^[4.30, 4.31]

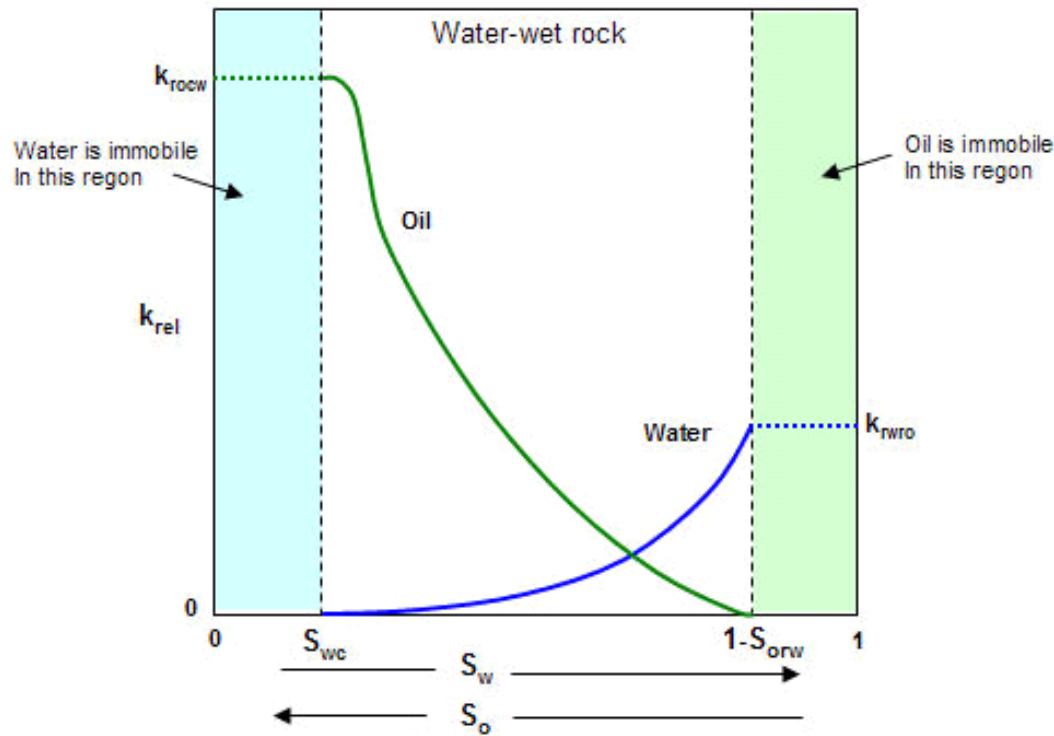


Figure 4.11: Schematic Relative Permeability curve of a water wet rock^[4.26]

The points that belong to the $[0, S_{wc}]$ and $[(1-S_{orw}), 1]$ ranges are depicted with a non-continuous line, because although these points have been experimentally measured, they do not correspond to real relative permeability values. The points at S_{wc} and $(1-S_{orw})$ are called end points relative permeabilities.^[4.19]

It is noted that the **connate water saturation (S_{wc})** refers to the lowest possible water saturation. It is also called irreducible water saturation.^[4.19]

With respect to **initial oil saturation (S_{oi})** of a reservoir rock, it is obvious that the more oil wet the rock is, the higher amount of brine will be displaced during oil migration. Due to capillary forces, the oil will imbibe onto the surface, by the time it enters inside the porous medium, creating a layer of oil and displacing the formation water.

Another observation is the fact that the more water wet a rock is, the faster **water breakthrough** occurs. That can be explained due to the fact that water exists as a film layer onto the rocks surface. As a result, snap-off can take place and a big volume of oil is possible to be by-passed. Additionally, in this case (water-wet condition), the oil recovery is abruptly reduced after the water breakthrough occurs.

On the other hand, assuming an oil-wet reservoir rock, water breakthrough will be delayed, because of the larger volume of oil that needs to be displaced and the higher amount of energy needed to be applied. However, it has been experimentally found that with respect

to **oil production**, neutrally wet cores exhibit the higher oil recovery. This phenomenon is attributed to the negligible capillary forces between water, oil and the rock. Both oil and water flow through the porous medium facing a relatively similar resistance.

5. Objective of the thesis

As it has been discussed in the previous Chapters, formation water's composition plays an important role on the initial wettability of a petroleum reservoir rock/fluids system. It was decided to use Stevns Klint Chalk cores as porous media and to study the effect that the presence of sulfate anion (SO_4^{2-}) and magnesium cation (Mg^{2+}) in the formation water has on the initial wettability of a petroleum reservoir rock/fluids system and to the overall oil recovery.

From previous studies, it has been observed that in case the formation water contains Mg^{2+} , the oil recovery by spontaneous imbibition is increased. Increased oil recovery has also been confirmed if SO_4^{2-} is present in the formation water. However, it is not known which one of these two ions has the greatest impact on oil recovery.

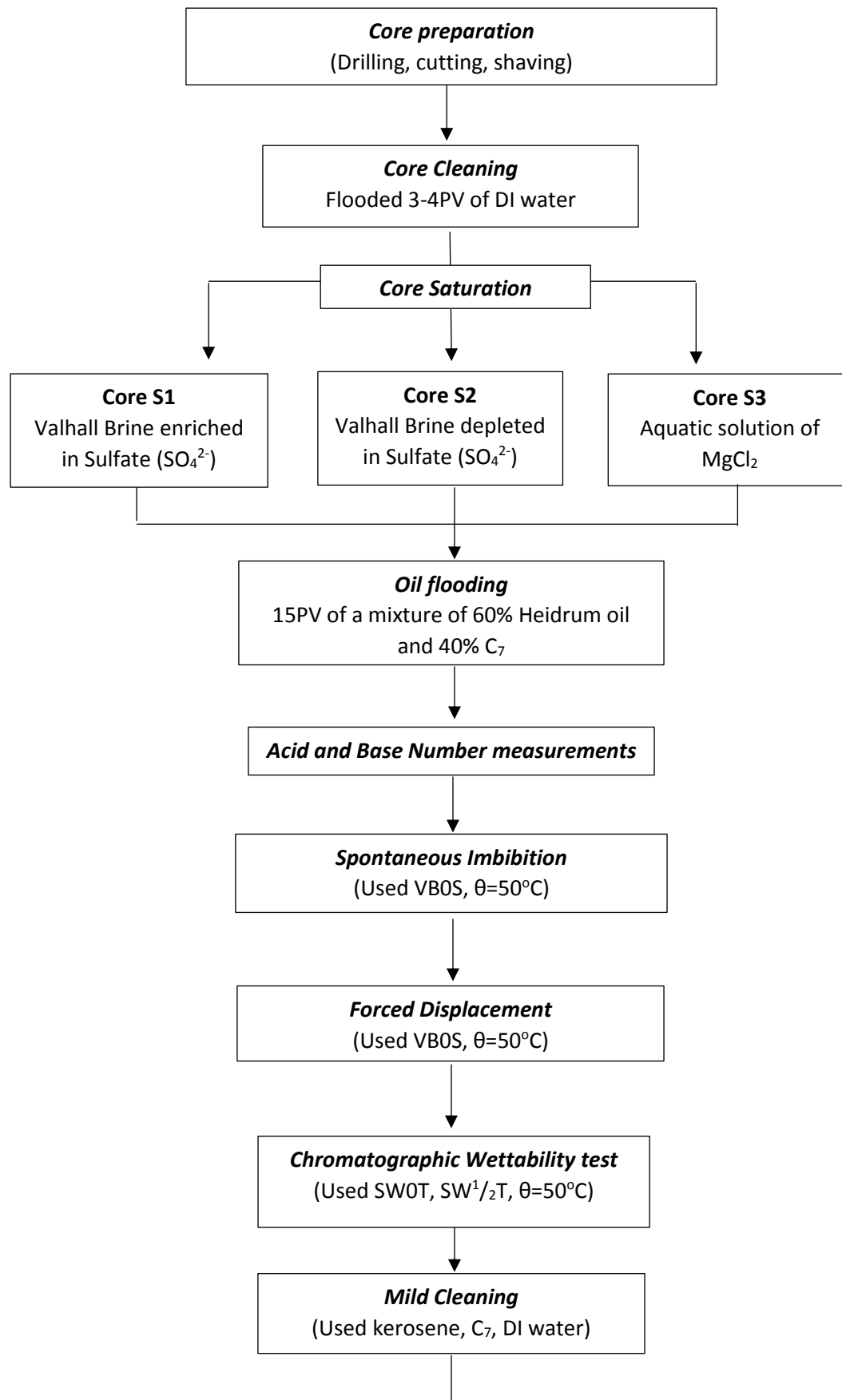
Through experimental work, the adsorption of active polar compounds onto the surface of the cores was examined and measured, by using a potentiometric titration device. The wetting state was determined through oil recovery and Chromatographic Wettability tests. The resulting wetting states are discussed with respect to the polar compounds adsorption. Afterwards, the initial wetting state of the cores was restored by Mild Cleaning procedure, through which the oil flooded was removed. Additional spontaneous imbibition and chromatographic wettability tests took place, in order to determine the wettability of the cores after Mild Cleaning and compare the results from the Wettability tests conducted after the oil flooding.

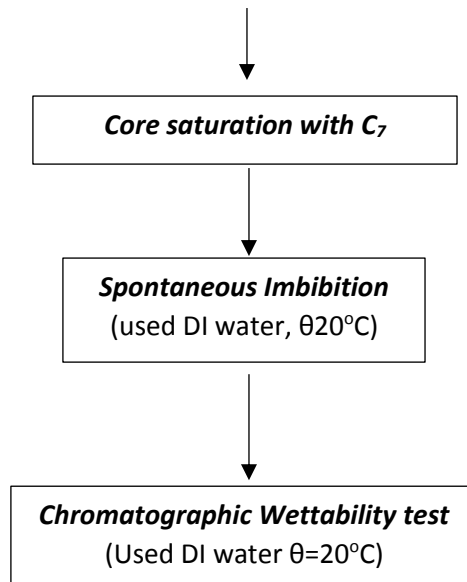
The results of this study are intended to contribute to the better understanding of the mechanism with which these ions interact with the polar compounds and alter the wetting state.

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6. Experimental Procedures

The experimental procedures that were followed are shown at the flow chart below:





Each procedure is described in detail in the Chapters that follow (6.1 - 6.14).

6.1 Cores' Preparation

The type of rock which was used during the course of this study originates from the Chalk Stevns Klint formation. It is located in Denmark, it consists of approximately 98% pure biogenic CaCO_3 and resembles the North Sea Chalk reservoirs. ^[5] (Chapter 1.3)

Three cores were drilled from the same block sampled in the quarry, to ensure that the three samples will exhibit to a great extend similar properties. avoid possible uncertainties and variations, by using a core drilling machine (Fig. 6.1).



Figure 6.1: Core drilling machine



Figure 6.2: Core shaving machine



Figure 6.3: Core cutting machine

The drilled cores were left in the oven at 90°C for at least 24 hours to dry. Afterwards they were cut and shaved in specific length and diameter. The dimensions of the 3 cores are showed in Table 1.

Table 1: Dimensions of the drilled cores

Core	Diameter (mm)	Length (cm)
S1	37.55	6.95
S2	37.60	6.73
S3	37.63	7.07

6.2 Cleaning Procedure

The cores were cleaned with Di-ionized Water (DI water) to remove easily dissolved solids (procedure set by Puntervold et. al. 2007). Each core was placed inside a rubber holder, which was placed inside the cleaning set-up, showed in Figure 6.4. The confining pressure that was used, was 20bar. Approximately 4 to 5PV of DI water were flooded, at two different flow rates: 0.1ml/min and 0.075ml/min. The inlet pressures were noted by pressor sensors, in order to calculate the permeability of the cores, using Darcy's Law, with both flow rates in order to acquire higher accuracy.

For Darcy's Law to be applied, the core should be considered homogeneous and no turbulent flow should be developed.

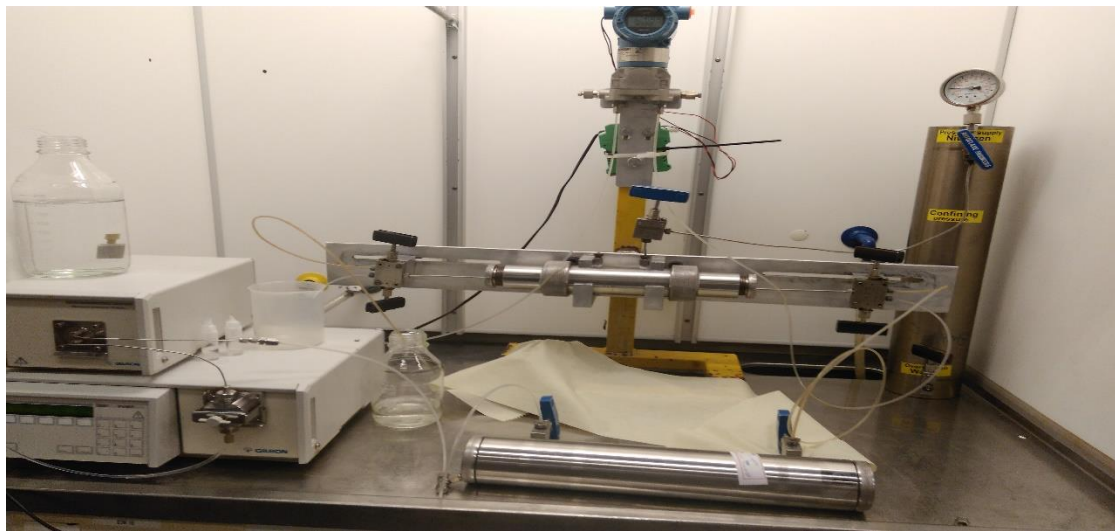


Figure 6.4: Cleaning set-up

The set-up used consists of:

- Water-pump (flow rate: [0.001, 10] ml/min).
- Cylinder filled with distilled water (DI water)
- Cylinder filled with Nitrogen at 20bar (used for confining pressure)
- Pressure sensor

According to Darcy's Law:

$$k = \frac{Q \cdot \mu \cdot \Delta P}{A \cdot L} \quad [6.1.1]$$

Where,

k: permeability (D)

Q: flow rate (ml/sec)

ΔP : pressure differential (atm)

A: area (cm²)

L: length (cm)

μ : viscosity of the fluid (cP)

The cleaning procedure took place at ambient conditions (20°C) and for that reason the viscosity of water was taken as 1.00cP. The results of the permeability calculations are shown in Table 2:

Table 2: Permeability results of each core

Core	Area (cm ²)	ΔP_1 (atm)	ΔP_2 (atm)	L (cm)	k ₁ (D)	k ₂ (D)	k _{avg} (D)	k _{ang} (mD)
S1	11.07	0.550	0.328	6.95	0,001903	0,002391	0,002147	2,147
S2	11.10	0.458	0.270	6.73	0,002203	0,002801	0,002502	2,502
S3	11.12	0.294	0.216	7.07	0,003609	0,003682	0,003645	3,645

ΔP_1 refers to the 0.1ml/min flow rate and ΔP_2 to the 0.075ml/min one.

The weight of the cores after cleaning and filled with DI water, was noted (m_{wet}). The cores were left in the oven at 90°C, for at least 24 hours to dry and their weight (m_{dry}) was noted. Hence, we were able to calculate the porosity of the cores (equation 6.1.2)

It is well known that the porosity is calculated by the ratio:

$$\emptyset = \frac{Pore\ Volume}{Bulk\ Volume} \quad [6.1.2]$$

Assuming that the cores are cylindrical, the bulk volume is calculated as:

$$BV = \pi r^2 L \quad [6.1.3]$$

Where,

r: radius

L: length

and,

$$PV = \frac{m_{wet} - m_{dry}}{d_{DI}} \quad [6.1.4]$$

Where,

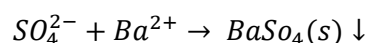
d_{DI} : density of DI water (1g/cc at 20°C)

The results of the porosity calculations are shown in Table 3:

Table 3: Porosities of the cores calculated

Core	m_{wet} (g)	m_{dry} (g)	Bulk Volume (cm ³)	Pore Volume (cm ³)	Porosity %
S1	143.29	108.77	76.965	34.52	44.85
S2	137.72	102.49	74.728	35.23	47.14
S3	144.33	107.32	78.628	37.01	47.07

To ensure that no sulfate was present inside the cores after the cleaning procedure, the last 4ml of effluent were collected and reacted with solid Barium (Ba). It is well known that when Sulphate reacts with Barium, precipitation takes place, according to the chemical equation:



Barium Sulfate (Barite), is a white crystalline solid. So, when it is formed, precipitation and colour change is observed. In this case, no precipitation or colour change occurred.



Figure 6.5: samples checked for sulphate

6.3 Brines' Preparation

Three different brines, with the same salinity, were prepared. For the core S1 the Valhall Brine six times enriched in Sulfate (VB6S), compared to the normal Sulfate concentration that the Valhall brine presents, was used in order to saturate the core afterwards. For the core S2 the Valhall Brine depleted in Sulfate (VB0S) was used and for the core S3 an aqueous solution of Magnesium Chloride. The compositions of the three brines are showed in Table 4.

Table 4: Chemical composition of brines used:

Brine/Salts (g/L)	VB6S	VB0S	MgCl ₂
NaCl	56.8505	57.7007	-
Na ₂ SO ₄	0.8531	-	-
NaHCO ₃	0.7810	0.7810	-
KCl	0.3950	0.3957	-
MgCl ₂ *6H ₂ O	1.5806	1.5821	134.1275
CaCl ₂ *2H ₂ O	4.2603	4.2610	-
TDS	64.7205	64.7205	64.7706

Where,

VB6S: Valhall Brine with 6mM of Sulfate

VB0S: Valhall Brine depleted in Sulfate

For $MgCl_2$ solution preparation $MgCl_2 \cdot 6H_2O$ was used. For that reason the additional mass due to H_2O , needed to be subtracted in order to calculate the Total Dissolved Solids (TDS):

Atomic weights:

- Mg: 24.3
- Cl: 35.5
- H: 1
- O: 16

As shown in Table 4, the total mass added was $m_{tot} = 134.1275g$. Which means that the total moles in the solution are:

$$n_{tot} = \frac{m_{tot}}{Mr_{(MgCl_2 \cdot 6H_2O)}}$$
$$n_{tot} = \frac{m_{tot}}{Ar_{Mg} + 2 * Ar_{Cl} + 2 * Ar_H + Ar_O}$$
$$n_{tot} = \frac{134.1275}{24.3 + 2 * 35.5 + 2 * 1 + 16}$$
$$n_{tot} = 0.6976mol$$

The Molecular weight of Magnesium Chloride is:

$$Mr_{MgCl_2} = Ar_{Mg} + 2 * Ar_{Cl}$$
$$Mr_{MgCl_2} = 24.3 + 2 * 35.5$$
$$Mr_{MgCl_2} = 95.3$$

As a result the mass of Magnesium Chloride in the solution is:

$$m_{MgCl_2} = n_{tot} * Mr_{MgCl_2}$$
$$m_{MgCl_2} = 0.6976 * 95.3$$
$$m_{MgCl_2} = 64.7706g$$

This mass found corresponds to the Total Dissolved Solids (TDS) of the solution.

It is noted that:

- Ar: molar mass of an element.
- Mr: molecular weight of a component.

where, Mr is equal to the sum of the molar masses of each element multiplied by the number of these elements present in the component.

In order to prepare the brines a high accuracy scale was used, to measure the mass of the solids shown in Table 5. To achieve better mixture across the solution, Chlorides were diluted in 200ml of DI water. Then, carbonates were diluted in 200ml of DI water and added in the initial solution. Finally, if there were sulfates in the brine composition, they were diluted in 100ml of DI water and added in the solution. Afterwards, additional 500ml or 600ml of DI water were added in the solution for the volume to become 1L.

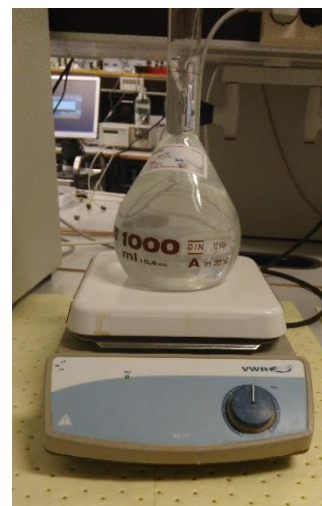


Figure 6.6: Brine mixing on a Magnetic stirrer

The brines were agitated using magnetic stirrers (Figure 6.6) for at least two or three days, until no or few undissolved solids were detected.

To remove any undissolved solids, dust, or other unwanted particles and to obtain a homogenous and stable brine, a filtration process was carried out. For that reason, a 0.22 μ m filter (Figure 6.7) was used.

To make sure that the brines were stable, two samples of approximately 4ml from each brine were left at room temperature and on 50°C. After 24h and 48h, the samples were checked and no precipitation was detected.

Afterwards, the brines were diluted by 10%. More specifically, 100ml of the initial brine were diluted in 900ml of DI water, in order to prepare 1L of 10% diluted brine.

In addition, the density and the specific weight (SG) of the brines were measured at 20.0°C. The results are shown in Table 5:

Table 5: Brines' density and specific gravity

Brines	Density (g/cc)	SG
VB6S	1,03425	1,0343
VB0S	1,04261	1,0806
MgCl ₂	1,04952	1,0876
10% VB6S	1,00443	1,0044
10% VB0S	1,00463	1,0426
10% MgCl ₂	1,00522	1,0432

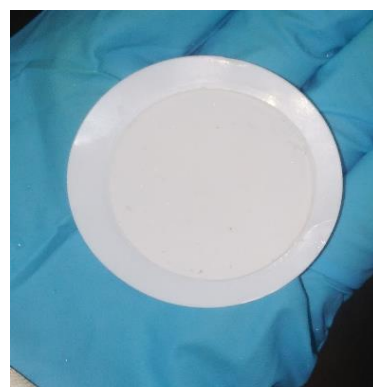


Figure 6.7: 0,22 μ m filter after the brine filtration

6.4 Brine Saturation Procedure

Two different core saturation procedures were applied. The cores S2 and S3 were saturated in a vacuum cell (Figure 6.8). According to that procedure the core is placed in a plastic container, with spherical marbles on the bottom. The marbles are needed for brine to flow through every direction (Figure 6.9). The plastic container is placed in the middle of the vacuum cell.

A pump is used to create vacuum pressure of approximately 0.04mbar. Afterwards, the brine inserts into the system, by opening the flow valve (Figure 6.8 Number 6), with great care and the cores were left under vacuum for at least 30min, until equilibrium is established.

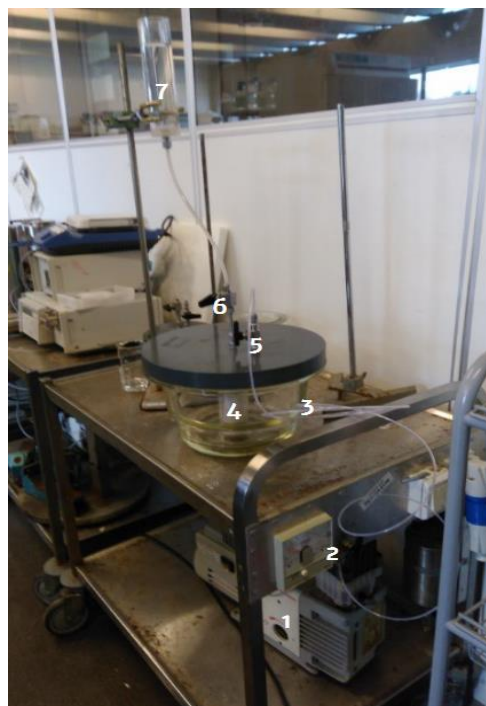


Figure 6.8: Core saturation system

Core saturation system description:

- 1: pump
- 2: Vacuum pressure sensor
- 3: Vacuum cell
- 4: Plastic container with the core
- 5: Air passage and vacuum valve
- 6: Brine passage and flow valve
- 7: Brine container

Vacuum Cell description:

- 1: Vacuum cell
- 2: Plastic container
- 3: Core
- 4: Spherical marbles

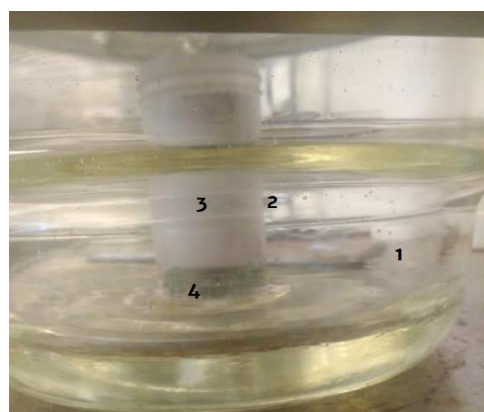


Figure 6.9: Vacuum Cell

The saturated weight of the cores (m_{sat}) was measured afterwards. To accomplish 10% brine saturation, the cores were left inside a desiccator (Figure 6.10) with solid silica (SiO_2) to evaporate. Depending on the amount of silica present in the desiccator the brine was

evaporating faster or slower (big amount, faster evaporation). It is noted that the solid silica needed to be changed every one hour in the beginning, due to the high amount of brine that it was adsorbed onto its surface. As the desired weight, which was calculated by equation 7.3.1 was about to be reached the weight of the core was checked more frequently and the amount of solid silica used was less. By the time that the desired weight was reached, the cores were placed in a secured plastic containers for at least 24h, to acquire homogeneous brine distribution through the core. The results are shown in Table 5.

The 10% saturated weight is calculated as:

$$m_{10\%sat} = m_{dry} + (10\% * PV * d_{brine}) \quad [7.3.1]$$

Where,

$$PV = \frac{m_{sat} - m_{dry}}{d_{brine}} \quad [7.3.2]$$

Equation [7.3.1] is valid only in case the core is intact. If pieces have broken down, correction is needed to be done, by taken under consideration the saturated weight and the dry weight of the pieces ($m_{(pieces, sat)}$ and $m_{(pieces, dry)}$ respectively). In that case, the 10% saturated weight is calculated as:

$$m_{10\%sat, fr} = \left[m_{10\%sat[7.3.2]} - \left(1 - \frac{m_{pieces, sat}}{m_{sat} + m_{pieces, sat}} \right) * m_{pieces, sat} \right] \quad [7.3.3]$$



Figure 6.10: Core desiccator cell

It is noted that slightly higher Pore Volumes were found through the saturated weights compared to the ones found by the cleaning process, probably because through this process bigger percent of pores were saturated. For that reason, the PV calculated by the cleaning process were not used, for these calculations

For core S1, which was saturated with Valhall Brine with 6mmol of Sulfate (VB6S), a different procedure was used. The core was flooded with the brine using the same set-up used for cleaning. More specifically, 10PV of VB6S were flooded, at a flow rate of 0.01ml/min, with a confining pressure of approximately 20bar, at ambient conditions. For every one pore volume (1PV), approximately 2ml of effluent were collected in order to be examined at the ion chromatographic (IC) device.

The reason why a different procedure was used for core S1 was to observe the distribution of sulfate through the core during the saturation process and examine the sulfate adsorption onto the surface of the core.

After brine flooding, the saturated weight of the core was noted and 10% saturated weight was reached with the same process as for the cores S2 and S3.

Table 6: Cores weight and pore volume as calculated by core saturation

Core	Brine used	m_{sat} (g)	$m_{pieces, sat}$ (g)	PV through sat measurements	Weight of 10% Saturated (g)
S1	VB6S	145.02	0	36.09	112.50
S2	VB0S	139.31	0.03	36.68	106.28
S3	MgCl2	145.07	1.28	38.83	110.13

6.5 Oil Preparation

The crude oil used, originates from the Heidrun Oil Field. This oil field is located in the Norwegian sector of the North Sea. It is characterized as being naphthenic, with 25.0 API (0.9043 g/cm^3), 0.52% sulfur, and a high Total Acid Number (TAN) of 2.90. In total four litres of oil were prepared by mixing 60% of crude oil with 40% Heptane, in order the oil to become less viscous. Each litre was placed in a 2L flask and it was stirred to mix. In order to decrease the Acid Number of the mixture powder Silica (SiO_2) was used, while the oil was stirred. Silica has the ability to adsorb the active polar compounds, onto its surface and it does not dissolve in crude oil. The amount of silica added was 10% of the weight of the oil, every three days. More specifically, since each flask was filled with 1L and assuming the oil density to be approximately 0.9 g/cm^3 , 90g of SiO_2 were added. In two out of the four flasks the amount of silica added was equal to 40% of the oil weight (360g of SiO_2 , 12 days). In one flask 30% of the oil in weight was added (270g of SiO_2 , 9 days) and in another flask only 10% of the oil in weight was added (90g of SiO_2 , 3 days).



Figure 6.1 1: Centrifuge on the inside

To remove the powder silica from the oil, the mixture was initially centrifuged. The centrifuged machine used has four holders, where specific 1L plastic containers fit. For the machine to work properly, all the containers need to weight approximately the same. For that reason, the weight of the containers filled with oil, was measured before placing them in the machine. Each centrifugation lasted approximately 30 minutes.

Afterwards, the oil was gradually filtered through 8 μ m, 5 μ m and 3 μ m filters, to remove any silica powder left. As shown in Figure 6.12, a pump was used to create vacuum in the container where oil was collected. The oil was gradually added in the upper part and passed through the filter.



Figure 6.12: Oil filtration system

The Acid Number of each container was measured. It was found that the flasks where powder Silica of 30% and 40% of oil weight were added, had zero Acid Number (no active negatively charged polar compound in the oil). The flask in which only the 10% of the oil in weight, was added had approximately 0.17AN. It is noted that a mixture of 60% crude oil and 40% of C₇ was prepared also, in which no powder Silica was added. The Acid Number was found equal to 1.85mg KOH/g oil.

The Acid Number that needed to be acquired was 0.34. For that reason the amount of oil of each flask needed was calculated through geometric mean of the volume of each oil added with respect to the AN of the that oil:

$$AN_{0,34} = \sum_{i=1}^n \frac{AN_i * V_i}{V_i} \quad [7.4.1]$$

The oil was stirred for at least 30min to ensure homogeneous distribution, and then stored.

It is noted that the 0.34AN (± 0.01) has been established from the academic community as a suggested AN for oil flooding, in order for the cores to be mixed-wet.

Table 7: Final Oil characteristics

Density [g/cc]	0.8063
Acid Number [mg KOH/g oil]	0.34
Base Number [mg KOH/g oil]	0.22
Volume [L]	2

6.6 Oil Flooding

To ensure equal oil distribution through the entire cores, approximately fifteen Pore Volumes (PV) of oil were flooded through each core, at 0.1ml/min flow rate. Effluents were collected every $\frac{1}{4}$ PV and the Acid and Base Number of specific samples were measured (see Chapter 8. Experimental Results). The flooding took place at 50°C, for oil to exhibit low viscosity.



Figure 6.13: Flooding set-up

The flooding set-up is shown in Figure 6.13. It consists of:

1. Oven, which can reach temperatures up to 500°C
2. Core holder
3. Cylinder filled with DI water, for confining pressure (20bar)
4. Cylinder filled with Nitrogen, for back-up pressure (10bar).
5. Cylinder filled with flooding fluids (e.g. oil, brines)
6. Valves
7. Pressure sensors (pressure transducer sensor [bar] on the right and differential pressure transducer [mbar] on the left).
8. Temperature sensor [°C]
9. Pump [ml/min]

It is noted that back pressure was applied by a diaphragm back pressure regulator (Figure 6.14). This component is connected to the outlet line of the set-up and has a membrane on the inside, which depending on the pressure provided by the cylinder filled with Nitrogen, does not let the fluid exit from system, unless the pressure is higher than the one selected. It was used in order for the pressure inside the flooding set-up to be approximately 10bar or slightly higher.



Figure 6.14: Example of Diaphragm back pressure

6.7 Ageing

After the oil flooding was completed, the cores were taken out of the flooding set-up, were wrapped with Teflon tape, to avoid further, adsorption of polar components onto the rock's surface and then each one was placed into an ageing cell (Paul Andrew Hopkins et.al.2017). The cell was filled with the oil used for the flooding in the oven at 50°C for two (2) weeks, in order for equilibrium to be established.

6.8 Spontaneous Imbibition Process

Each core was placed in a glass cell for the spontaneous imbibition process to take place. Valhall Brine depleted in Sulfate (VBOS) was used for all the cores as a spontaneous imbibition fluid. This brine does not contain sulfate anion, subsequently it does not cause any wettability alteration and reflects the initial wetting of the cores.

The spontaneous imbibition cell consists of:

- Marbles on the bottom
- Upper and lower glass part
- Plastic valves
- Volumetric scale on the upper part [ml]

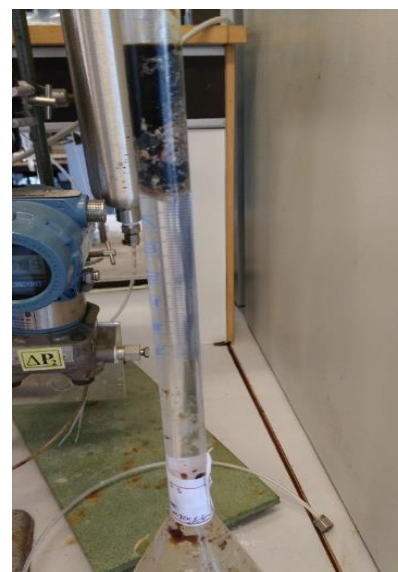


Figure 6.15: Upper part of the Spontaneous Imbibition Cell



Figure 6.16: Lower part of Spontaneous Imbibition cell

The spontaneous imbibition process took place at the same conditions as the oil flooding. For that reason the spontaneous imbibition cell was placed in an oven at 50°C. initially, measurement was taken every 10min to 15min. In order to take a measurement the cell was taken out of the oven and it was gently shaken. Especially in the beginning the oil was sticking onto the glass, making it difficult to make a measurement approximation.

The oil recovery in millilitres (ml) of oil recovered was then noted. The procedure lasted on average from nine to ten days. The results of oil recovery were plotted as %OOIP with respect to time.

6.9 Forced Displacement

After the oil recovery from the spontaneous imbibition was terminated, viscous flooding (or forced Imbibition) followed. The cores were placed inside the flooding set-up and approximately two to three PV of Valhall Brine depleted in Sulfate (VBOS), were flooded in two or three different flow rates, (Table 8) in order to recover as much oil as possible.

Condition under which the flooding took place:

- Temperature: 50°C
- Overburden Pressure: ≈20bar
- Back Pressure: ≈10bar

Table 8: Flow rates used for Forced Displacement

Core/rate	[ml/min]	[PV/day]	[ml/min]	[PV/day]	[ml/min]	[PV/day]
S1	0.025	1	0.050	2	0.100	4
S2	0.030	1	0.060	2	0.120	4
S3	0.080	3	0.160	6	-	

It should be noted that because of a mistake in the calculation, the flow rates used for the third core (S3) were in fact much higher than what they should have been. The effect that this mistake had on the recovery will be discussed in Chapter 8 (Experimental Results).

The 0.03ml/min, 0.06ml/min and 0.12ml/min flow rates correspond to 1PV/day, 2PV/day and 4PV/day respectively.

6.10 Chromatographic Wettability Test at 50°C

The Chromatographic test took place under the same conditions as the viscous flooding. Two different brines were prepared:

- Non-containing Tracer Sea Water (SW0T)
- Containing Tracer Sea Water (SW¹/₂T)

Table 9: Chemical composition of the Chromatographic wettability test fluids

Substance/ mass (g)	SW0T	SW ¹ / ₂ T
NaCl	26.7905	23.4100
KCl	0.7503	0.7501
MgCl ₂ x2H ₂ O	9.0504	9.0501
CaCl ₂ x6H ₂ O	1.9100	1.9104
NaHCO ₃	0.1699	0.1700
LiCl	-	0.5098
KSCN	-	1.1700
Na ₂ SO ₄	-	1.7100
TDS	38.6711	38.6804

The flow rate used in this process is 0.1ml/min. Initially, SW0T is flooded for at least 24 hours (approximately 3-4 PV), to displace the Valhall Brine without Sulphate (VB0S) which was used for the viscous flooding procedure. Afterwards, Sea Water with Tracer was flooded for additional 24 hours, at the same rate. The effluent was collected and analyzed at the Ion Chromatographic device.

It is noted that the SW¹/₂T is named this way because it contains half the concentration of Tracer and SO₄²⁻, which was initially used when the test was established (SWT: Sea Water with Tracer). It was observed that if lower concentration is used, the results

will exhibit higher accuracy, because it takes longer time to reach the plateau. That way, the relative Areas were larger by using $SW^{1/2}T$ compared to the relative Areas measured with SWT. (Chapter 4.3.4. Chromatographic Wettability Test).

6.11 Mild Cleaning

After the Chromatographic Wettability Test, core restoration took place in order to restore the initial wetting state of the cores. This procedure is called mild cleaning (Paul Andrew Hopkins et.al 2017). The cores were flooded with kerosene, to remove the oil. Then heptane (C_7) was flooded, in order to remove kerosene. And finally DI water was flooded, to remove C_7 . The Volumes of each fluid used for this process are shown in Table 10:

Table 10: Volumes flooded for Mild Cleaning procedure

Core:		Core S1		Core S2		Core S3	
Substance	PV needed to be flooded	Volume flooded (ml)	Time (h)	Volume flooded (ml)	Time (h)	Volume flooded (ml)	Time (h)
Kerosene	4PV	144	24.1	147	24.5	155	25.9
C_7	2PV	72	12.0	74	12.2	78	13.0
DI water	3PV	108	18.1	110	18.4	117	19.5

After the mild cleaning procedure was completed, the weight of each core was measured and they were left inside the oven (at 90°C) for at least 24h, to dry.

6.12 Saturation with C_7

In order to measure the wettability of the cores after the mild cleaning, the former were saturated with Heptane. For that reason the vacuum cell described in Chapter 7.3 “Brine Saturation Procedure”, was used. During this procedure, the cores were left saturated with C_7 , under 0.04mbar vacuum pressure for approximately one hour, to ensure homogeneous C_7 distribution through the cores. It is noted that C_7 was chosen as an oil phase to saturate the core because it does not contain any polar compounds. As a result, the wetting state of the cores is defined by the polar compounds existing in the core.

6.13 Spontaneous imbibition with DI water

After the cores were saturated with heptane, they were placed in spontaneous imbibition cells (Figure 6.17). The spontaneous imbibition fluid used was DI water and the process took place at room temperature. The recovery was completed much faster compared to the initial spontaneous imbibition with oil and VBOS (Chapter 7.7 Spontaneous Imbibition Process). The cores were left in the spontaneous imbibition cell on an average of six to seven days.



Figure 6.17: Spontaneous Imbibition with DI water

6.14 Chromatographic Wettability at 20°C

After the Spontaneous Imbibition with DI water was completed, the cores were left in the oven at 90°C, for approximately 24 hours and a chromatographic wettability test took place afterwards. The reason that the cores were dried before the chromatographic test was for Sea Water not to intermingle with heptane. In order to analyze the effluents in the Ion Chromatograph, no hydrocarbons must be present. The same procedure described in Chapter 7.9 “Chromatographic Wettability Test” was followed.

7. Experimental Results

7.1 Core saturation with VB6S analysis

As it has already been mentioned, an ion-chromatographic (IC) device was used in order to acquire a clear picture of the S1 core saturation process. The results of the analysis are shown in Table 1:

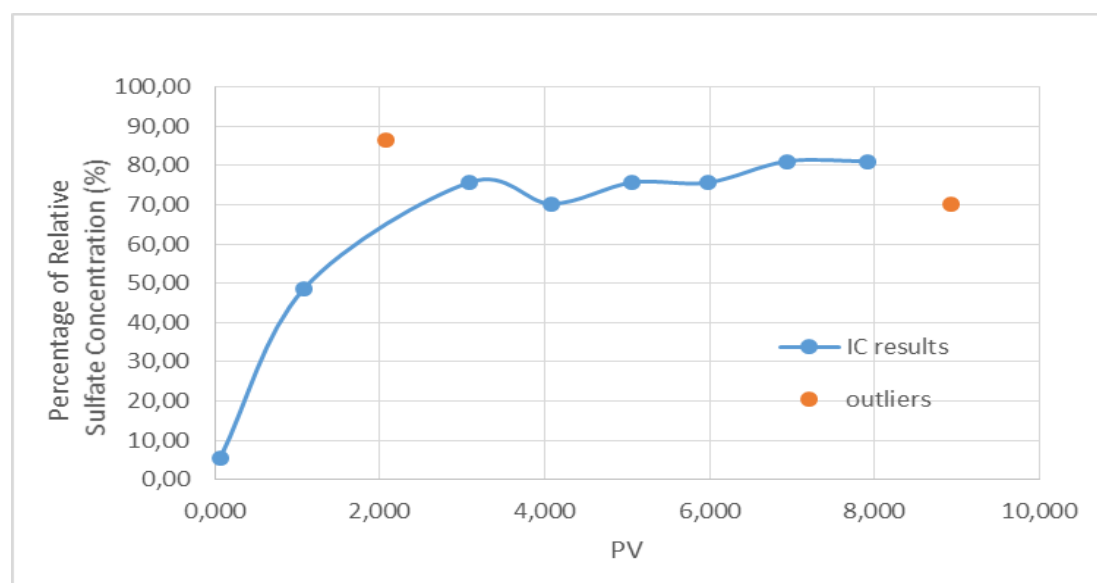
Table 1: IC Sulfate concentration results (core S1 saturation)

sample	PV injected	SO ₄ ²⁻ concentration [mmol/L]	Relative Concentration of SO ₄ ²⁻ (%)
1	0.06	0.0001	5.41
2	1.08	0.0009	48.65
3	2.08	0.0016	86.49
4	3.08	0.0014	75.68
5	4.08	0.0013	70.27
6	5.06	0.0014	75.68
7	5.98	0.0014	75.68
8	6.94	0.0015	81.08
9	7.92	0.0015	81.08
10	8.92	0.0013	70.27
11	9.82	-	-

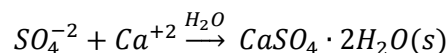
Approximately 10PV of Valhall Brine 6 times enriched in Sulfate (VB6S) were flooded through the core. The eleventh (11th) effluent sample, Shown in Table 1, was not analyzed, because it reacted with Barium, in order to observe and estimate the amount of BaSO₄ precipitation (see Chapter 6.2)

The sulfate concentration of the 10% diluted brine which was flooded was: 0.00185mmol/L.

Diagram 1 Sulfate concentration – Pore Volumes flooded (core S1 saturation)



It is noted that the concentration of sulfate inside the core started to stabilize after the third PV of brine was injected, but the final concentration of the effluents did not reached the value of the initial brine concentration. This observation is attributed to precipitation on the rock surface. More specifically, sulfate (SO_4^{2-}) adsorbed onto the surface by reacting with calcium cation (Ca^{2+}) and producing $CaSO_4$ (gypsum), according to the chemical equation:



As a result, the sulfate was “consumed” through probably both surface precipitation and adsorption onto the rock, being unable to attain in the effluent the initial brine concentration. It is noted that experimentally it has been observed that the sulfate can be removed from the core by flooding approximately 3PV to 4PV of DI water.

It is noted that the samples are diluted 500 times before they are placed in the Ion chromatographic device. It is possible that either because of human mistake or random error the samples 3 and 10 were considered as outliers, since they did not follow the normal concentration distribution.

7.2 Oil flooding

7.2.1 Acid Number Measurements

A potentiometric titration device was used in order to measure the Acid Number of the oil injected and of the effluent samples. The results of each core are shown in Tables 2, 3 and 4. In Diagram 2 the Acid Number of the samples was plotted with respect to the PV injected.

Table 2: Core S1 AN measurements

Sample	AN [mg KOH/g oil]	PV injected
2	0.00	1.07
4	0.02	1.31
8	0.05	1.79
12	0.14	2.27
16	0.19	2.76
20	0.22	3.23
28	0.26	4.20
32	0.3	4.68
48	0.34	6.64
116	0.34	13.92

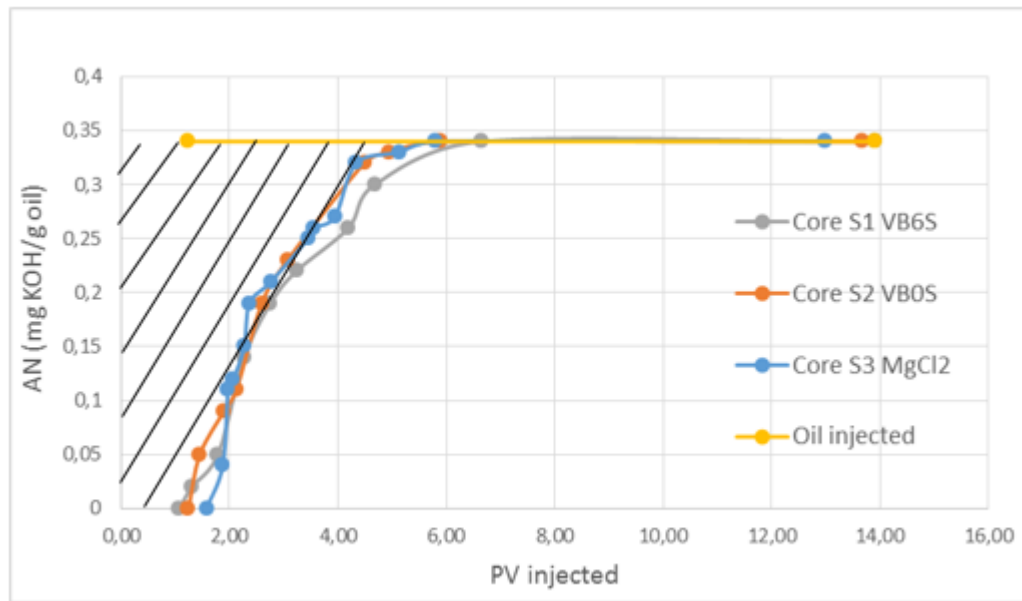
Table3: Core S2 AN measurements

sample	AN [mg KOH/g oil]	PV injected
4	0.00	1.24
6	0.05	1.45
10	0.09	1.90
12	0.11	2.13
16	0.19	2.60
20	0.23	3.07
32	0.32	4.49
36	0.33	4.96
44	0.34	5.88
114	0.34	13.67

Table 4: Core S3 AN measurements

Sample	AN [mg KOH/g oil]	PV injected
8	0,00	1,58
11	0,04	1,88
12	0,11	1,97
13	0,12	2,07
15	0,15	2,27
16	0,19	2,37
20	0,21	2,76
27	0,25	3,45
28	0,26	3,55
32	0,27	3,94
36	0,32	4,34
44	0,33	5,14
51	0,34	5,80
132	0,34	12,99

Diagram 2: Acid Number- PV flooded



The hatched area is equal to the amount of negatively charged polar compounds adsorbed onto the cores' surface. It is noticed that all cores appeared to adsorb almost the same amount of negatively charged polar compounds, since the areas are really close to each other.

To calculate this area, the integral of each graph and the total area were calculated. The adsorption was equal to the subtraction of these two areas:

$$adsorption = total\ area - \int_{x_{initial}}^{x_{final}} f(x)$$

Where,

$$total\ area = x_{final} * y_{final}$$

And

$$\int_{x_{initial}}^{x_{final}} f(x) = \sum_{i=1}^n \left[\frac{y_i + y_{i+1}}{2} * (x_{i+1} - x_i) \right]$$

Where, (x,y) the PV injected and the AN respectively (values shown in Tables 2,3 and 4).

As a result, the adsorption of each core are in Table 5:

Table 53: Total adsorption of negatively charged polar components of each core

Core	Integral [mg KOH/g oil]*PV injected	Total Area [mg KOH/g oil]*PV injected	Adsorption [mg KOH/g oil]*PV injected
S1 (VB6S)	3.7110	4.7624	1.0514
S2 (VB0S)	3.7293	4.6772	0.9479
S3 (MgCl₂)	3.4770	4.4160	0.9390

7.2.2 Base Number measurements

The same procedure was followed for the base number measurements. In table 6, 7 and 8 the Base Number measurements are presented with respect to the PV injected. Additionally, in Diagram 3, the results are plotted.

Table 6: Core S1 BN measurements

sample	Base Number [mg KOH/g oil]	PV injected
3	0.08	1.19
7	0.08	1.67
15	0.08	2.64
23	0.09	3.60
27	0.09	4.07
31	0.16	4.56
35	0.2	5.05
39	0.22	5.54
115	0.22	13.90

Table 7: Core S2 BN measurements

sample	Base Number [mg KOH/g oil]	PV injected
3	0.1	1.13
7	0.1	1.56
11	0.115	2.01
15	0.11	2.48
19	0.08	2.95
23	0.1	3.42
27	0.09	3.90
31	0.11	4.37
35	0.17	4.84
39	0.205	5.31
43	0.22	5.77
47	0.22	6.24
107	0.22	13.61

Table 8: Core S3 BN measurements

sample	Base Number [mg KOH/g oil]	PV injected
3	0.1	1.1
6	0.1	1.38
10	0.12	1.77
13	0.13	2.07
14	0.13	2.17
21	0.11	2.86
26	0.13	3.35
30	0.11	3.74
34	0.15	4.14
38	0.19	4.54
42	0.2	4.94
49	0.21	5.57
52	0.22	5.91
66	0.22	7.49
92	0.21	10.41
106	0.22	11.98
113	0.22	12.76

Diagram 3: Base Number-PV flooded

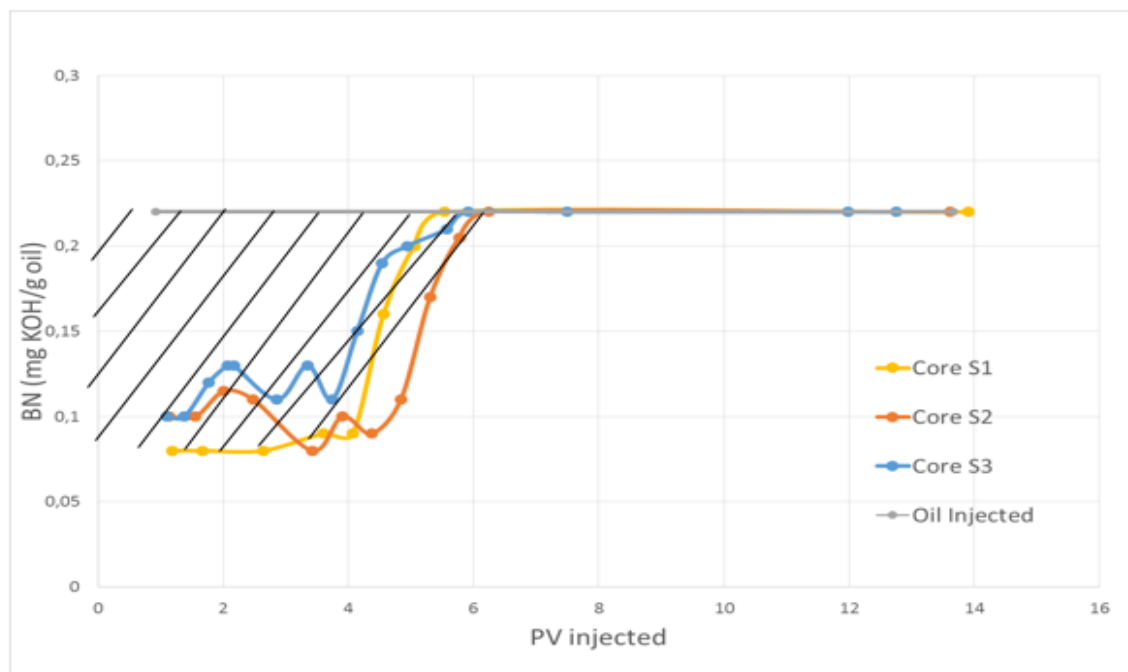


Table 9: Total adsorption of positively charged polar components

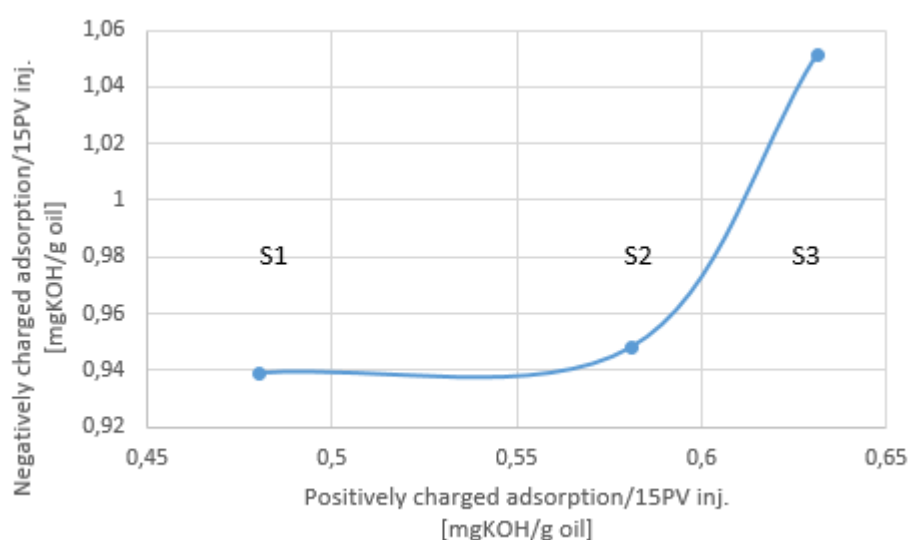
Core	Integral [mg KOH/g oil]*PV	Total Area [mg KOH/g oil]*PV	Adsorption [mg KOH/g oil]*PV
S1 (VB6S)	2.4267	3.0580	0.6314
S2 (VB0S)	2.4133	2.9942	0.5809
S3 (MgCl₂)	2.3271	2.8072	0.4802

Generally, it is not expected positively charged polar components to be attached onto the chalk's surface, since as it has already been mentioned, the carbonate surface is positively charged due to calcium cations (Ca^{2+}). By definition (Chapter 4.2.1) the amount of mg KOH/g oil is proportional to the polar compounds adsorbed onto the surface of the rock. By comparing the results shown in Tables 8 and 9, it is noticed that the adsorption of negatively charged polar compounds is greater than the positively charged one.

It is interesting to note from Diagrams 2 and 3 that positively charged adsorption takes place as long as the negative one does (approximately until the sixth PV injected). That could be attributed to a possible “synergy” between the negative and the positive polar compounds. Probably, chemical replacements occurred until equilibrium established.

In addition, a higher adsorption of both negatively and positively charged polar components is noted on the first core (S1), less on the second (S2) and the least adsorption on the third one (S3). The reason why these differences are exhibited is not known. It could be attributed to the different brines used to saturate the cores of even in small differences on the cores' characteristics (e.g. dimensions, permeability, porosity, pore volume etc). The important thing is to notice the analogy: high negative adsorption-high positive adsorption, which confirms the possible synergy mentioned above. In diagram 4 the positively charged adsorption is plotted with respect to the negatively charged:

Diagram 4: Relation between the adsorption of positively and negatively charged polar compounds



7.3 Spontaneous Imbibition process at 50°C

As it has already been mentioned, each core was left in a spontaneous imbibition cell for an average of nine (9) to ten (10) days and the volume of oil recovered, was noted. Each core was ten per cent (10%) saturated with brine, which means that the remaining ninety per cent (90%) of the porous media was filled with oil.

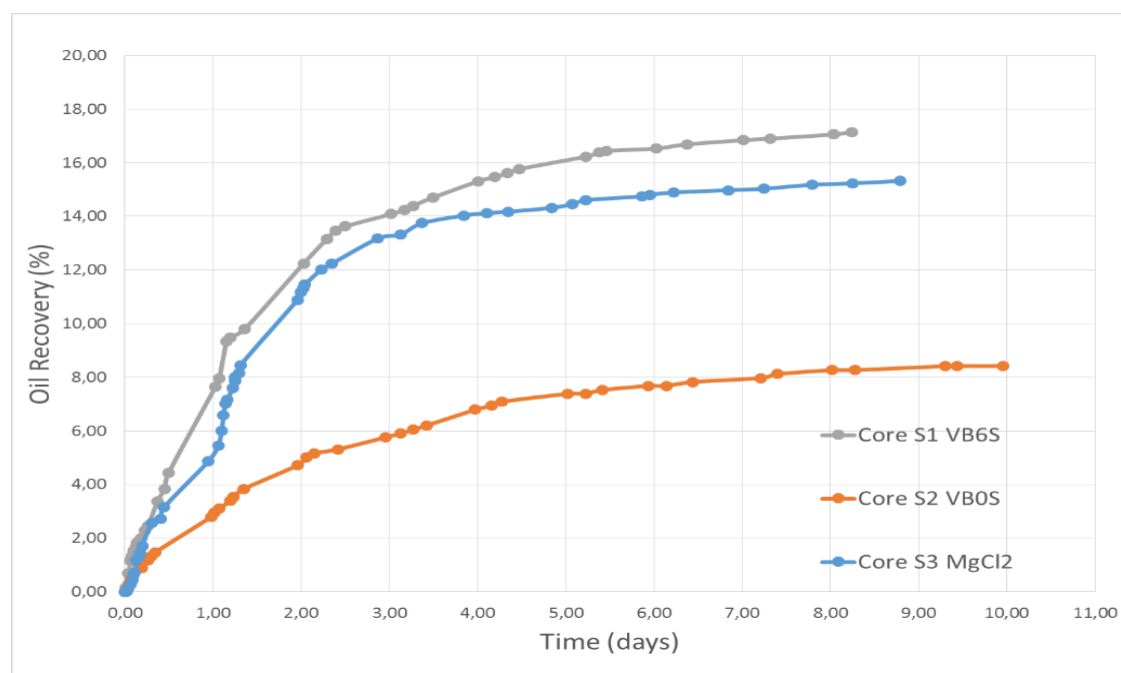
As a result, the relative oil recovery was calculated as the ratio of volume of oil recovered by the initial volume of oil (90%PV).

$$OOIP = \frac{\text{oil recovered (ml)}}{0.9 \cdot PV \text{ (ml)}} * 100\% \quad [7.2.1]$$

The data are shown in Tables 9, 10 and 11 (view Appendix) for cores S1, S2 and S3 respectively.

In diagram 5, the %OOIP recovery is plotted with respect to the time (in days) that the Spontaneous Imbibitions were conducted.

Diagram 5: Oil recovery from spontaneous imbibition (%OOIP of S1, S2, S3 cores)-Time



As it can be noted in Diagram 5, the core S1 that was saturated with brine enriched in sulfate (VB6S) seems to be the most water-wet core of all, since it appears to have given the highest oil recovery (17.15% OOIP). The core S3 that was saturated with brine enriched in Magnesium ($MgCl_2$), exhibited the second highest oil recovery (15.32% OOIP), even though the difference was not substantial with respect to the first one (S1). At last, the core S2 that was saturated with Valhall brine depleted in Sulfate (VB0S) is the least water-wet, since it exhibited the lowest oil recovery (8.42% OOIP).

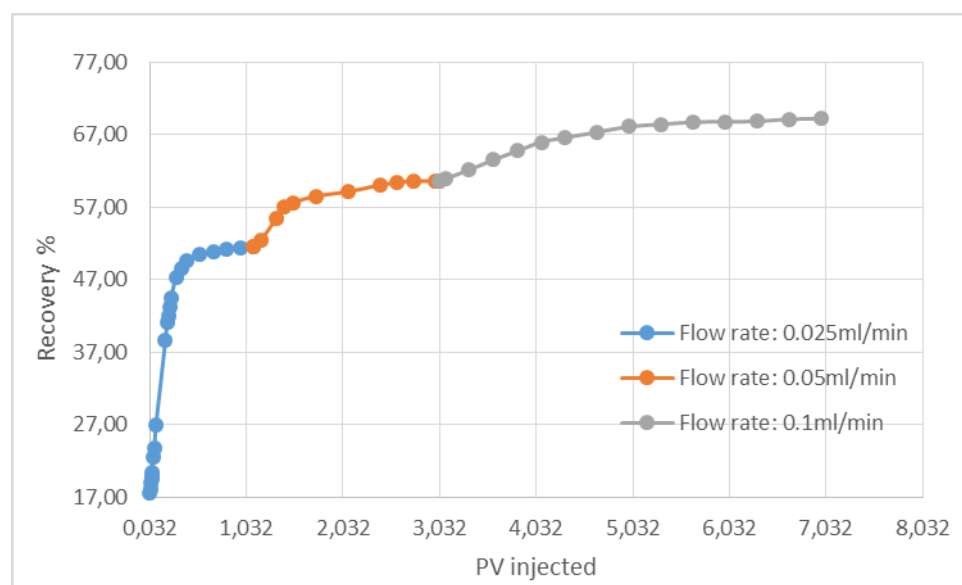
It is very interesting to observe the different wetting states of the cores. As it was mentioned above, all the cores seemed to adsorb almost the same amount of polar components, however the oil recovery was different. That is attributed to the fact that the capillary forces between each rock/oil/brine system was different. More specifically, the oil

adsorbed to the most water-wet core had the least strong attachment to the core, due to chemical bonds with the brine's active polar compounds. That can also be explained by the fact that there are many different polar components in the oil and not all of them adsorb with the same intensity onto the chalk core. It is well known that during oil flooding, the less strongly attached polar components are being replaced by the more strongly attached ones, for equilibrium to establish (Le Chatelier's Principle, Principle of lower energy).

7.4 Forced Displacement

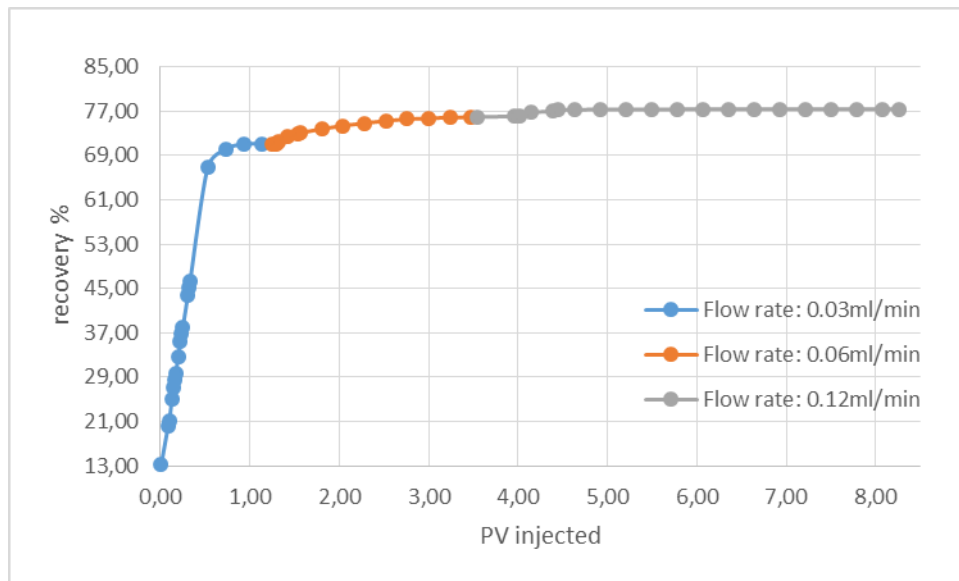
During forced displacement, each core was flooded with Valhall Brine depleted in Sulfate (VB0S) with low flow rates (1PV/day, 2PV/day, 3PV/day, 4PV/day, 6PV/day), as it has already been mentioned. A volumetric burette was used in order to collect and measure the oil recovered. During the night, samples were collected in 12ml volumetric glasses and the oil produced, was measured.

Diagram 6: Forced Displacement with VB6S core S1



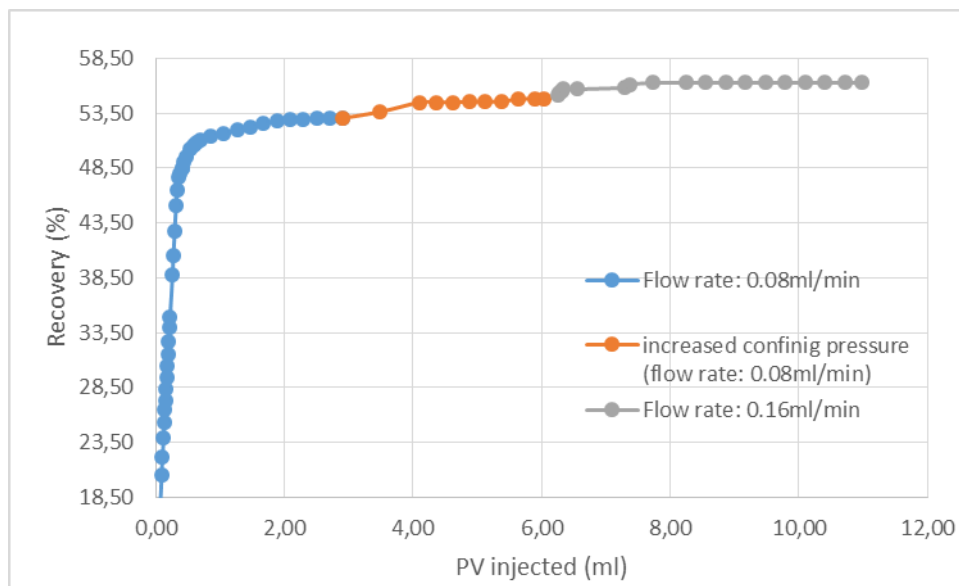
- Maximum oil recovery with 1PV/day: 51.53% OOIP.
- Maximum oil recovery with 2PV/day: 60.65% OOIP.
- Maximum oil recovery with 4PV/day: 69.21% OOIP.

Diagram 7: Forced displacement with VBOS core S2



- Maximum oil recovery with 1PV/day: 71.13% OOIP.
- Maximum oil recovery with 2PV/day: 75.93% OOIP.
- Maximum oil recovery with 4PV/day: 77.34% OOIP.

Diagram 8: Forced Displacement with $MgCl_2$ core S3



- Maximum oil recovery with 3PV/day: 53.04% OOIP.
- Maximum oil recovery with 3PV/day after confining pressure increase: 54.84% OOIP.
- Maximum oil recovery with 6PV/day: 56.29% OOIP.

Before drawing any conclusions it is important to keep in mind that the cores did not exhibit the same water saturation (S_w) after the spontaneous imbibition process. More specifically after this process the water saturation of each core were:

- Core S1: $S_w = (\text{initial water saturation}) + (\% \text{OOIP}) = 10\% + 17.15\% = \mathbf{27.15\%}$
- Core S2: $S_w = (\text{initial water saturation}) + (\% \text{OOIP}) = 10\% + 8.42\% = \mathbf{18.42\%}$
- Core S3: $S_w = (\text{initial water saturation}) + (\% \text{OOIP}) = 10\% + 15.32\% = \mathbf{25.32\%}$

The forced displacement flow used and the conditions under which the processes were conducted were the same for all cores. As a result, the overall oil recovery depended on the brine with which each core was initially saturated with and the water saturation attained after Spontaneous Imbibition.

It is noted that core S3 had approximately the same water saturation with the core S1. As a result, the different oil recoveries are attributed on the brine which each core was saturated with and the different flow rates used. More specifically, if judging by the Spontaneous Imbibition results, where cores S1 and S3 exhibited the highest oil (17.15%, 15.32% OOIP, respectively), core S3 exhibited lower oil recovery compared to the expected one. This could be attributed to the higher rate used on core S3 since capillary forces play a key role due to the low absolute permeability of the cores. By increasing the flow rate, the capillary forces are overruled and the time needed for the capillary forces to contribute to the overall recovery is not given. It is noted that due to a possible leak present during the forced displacement on core S3, the confining pressure had decreased from 19bar to approximately 18bar. During the process the pressure was increased to 20bar (Diagram 8: orange points). It can be easily understood that the leak affected also the overall recovery.

It is interesting to notice that core S2, which exhibited the lowest oil recovery through the spontaneous imbibition process, recovered more oil through forced displacement procedure. That core can only be compared with core S1, since the same flow rates were used. The core S1 seemed to be the only one which was affected by the flow rate increase, since higher oil recovery was noticed with respect to higher flow rate. That implies that viscous forces had an impact on the overall recovery, although usually the capillary forces are the ones that regulate oil recovery. For some reason which is not known, the capillary and viscous forces seem to act complementary for core S2, in contrast with core S1, for which a “competition” between these forces seems to have taken place. The forced displacement fluid used for all cores did not contain any sulfate or magnesium ions, so this result is not attributed to a possible wettability alteration.

7.5 Chromatographic Wettability Test at 50°C

During this test, approximately three to four Pore Volumes of Sea Water (SWOT), were flooded through each core, in order to displace the Valhall brine depleted in Sulfate, which was used for the viscous flooding. Afterwards, approximately other four Pore Volumes of Sea Water with half concentration of Tracer ($SW^{1/2}T$) were flooded through the core in order to carry out the Chromatographic test. The effluents were collected in vials, the weight of which was measured before and after, in order to calculate the exact volume of Sea water that was flooded. The PV injected were calculated as:

$$PV \text{ injected} = \frac{\sum(m_f - m_i)}{\rho_{SW^{1/2}T}} \quad [7.4.1]$$

Where,

- m_f : the mass of each vial after the flooding
- m_i : the mass of each vial before the flooding
- $\rho_{SW^{1/2}T}$: the density of the $SW^{1/2}T$ flooded

Afterwards, the samples were analyzed for cations and anions in the IC device. The results are shown in Tables 16, 17, 18 (view Appendix). The concentrations of sulfate and tracer measured by the Ion Chromatographic device, were plotted with respect to the PV injected (Diagrams 9, 10, 11). Additionally, the wet Area (A_{wet}) was calculated by the trapezoidal integrant:

$$A_{wet} = \sum \left(\frac{(PV_{i+1} - PV_i) * (C_{i+1} + C_i)}{2} \right)_{tracer} - \sum \left(\frac{(PV_{i+1} - PV_i) * (C_{i+1} + C_i)}{2} \right)_{SO_4^{2-}} \quad [7.4.2]$$

Diagram 9: Chromatographic Wettability test at 50oC. Core S1

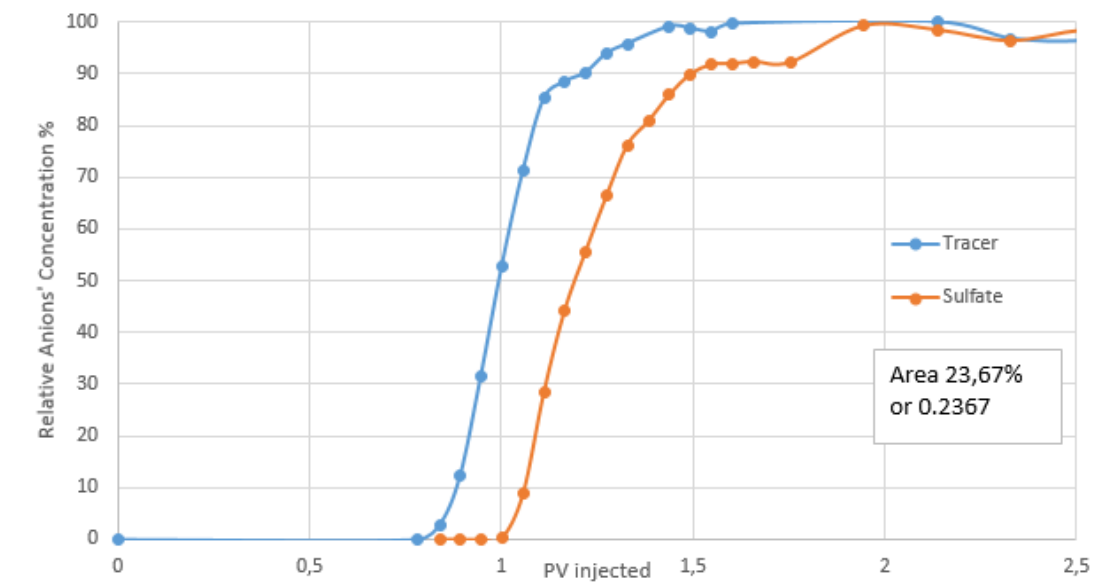


Diagram 10: Chromatographic Wettability test at 50oC. Core S2

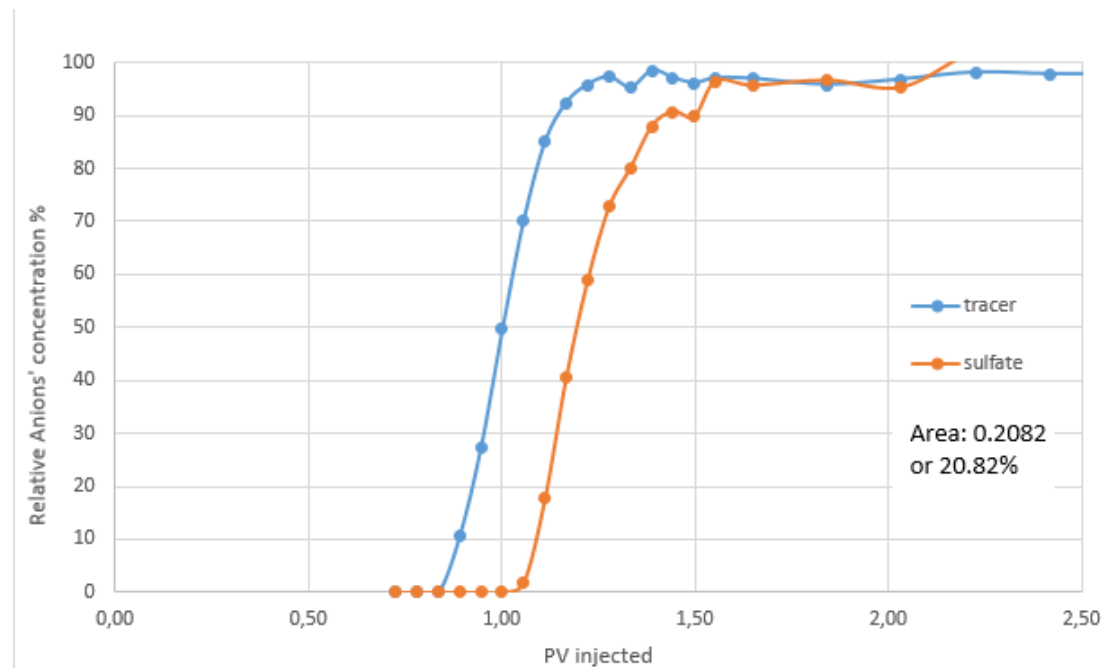
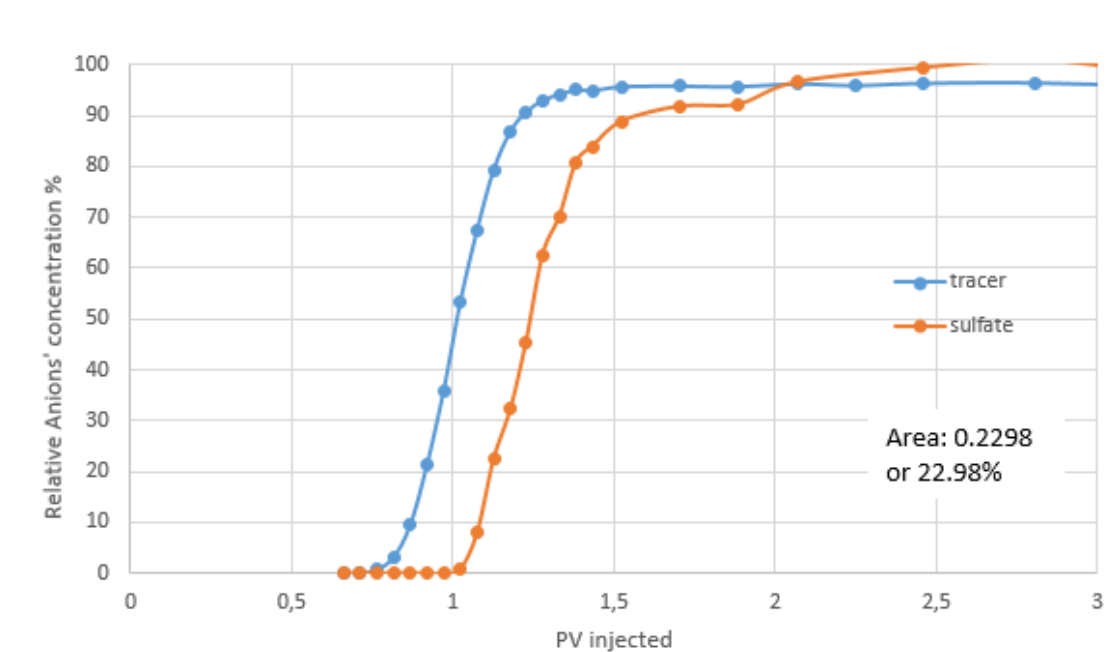


Diagram 114: Chromatographic Wettability test at 50oC. Core S3



As it has been mentioned (Chapter 4.3.4 Chromatographic Wettability test, equation 4.3.4.3.) in order to calculate the Wettability index, the corresponding area of a completely water wet core (A_{ww}), at 50°C is needed. For that reason bibliographic data were used:

Chromatographic wettability tests on completely water wet Stevns Klint Chalk cores had been conducted at 20°C, 40°C and 70°C. The corresponding areas are shown in Table 19.

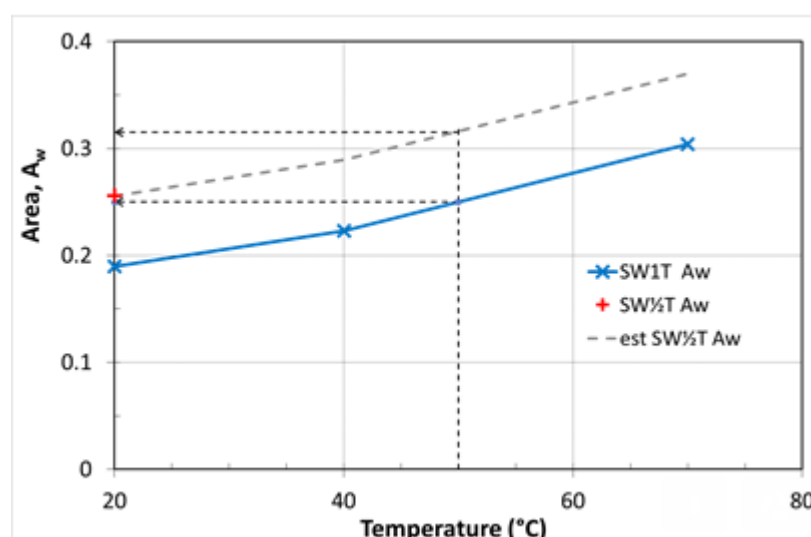
It is noted that the wet and water wet areas do not have units, since neither the x-axis (PV injected) nor the y-axis (Relative concentration) have.

Table 19: Chromatographic Wettability tests $f(A, T)$ (Ermis Proestakis, Uis, 2016)

a/a	Temperature (°C)	A_{ww} SW1T	A_{ww} $SW^{1/2}T$
1	20	0.1897	0.2560
2	40	0.2231	-
3	70	0.3040	-

As shown in Table 19, not all floodings were conducted with $SW^{1/2}T$. For that reason an estimation has been made in order to calculate the area of a completely water-wet core at 50°C, using $SW^{1/2}T$. More specifically the Areas A_{ww} by using SW1T are plotted with respect to temperature (Diagram 12):

Diagram 12: Wet Area at 50°C estimation by using $SW^{1/2}T$



It was assumed that the slope of the SW1T line was the same as for the $SW^{1/2}T$ one. The point that corresponds to the wet Area by using $SW^{1/2}T$ at 20°C was used as a starting point of the line. For temperature equal to 50°C, the wet Area was found to be approximately $A_{ww} = 0.315$ by using $SW^{1/2}T$.

Using the water wet area found, the Chromatographic Wettability index is calculated for each core (equation 4.3.4.3)

- Core S1: $I_{CW, S1} = 0.2367/0.315 = 0.7514$ or 75.14% water wet
- Core S2: $I_{CW, S2} = 0.2082/0.315 = 0.6609$ or 66.09% water wet
- Core S3: $I_{CW, S3} = 0.2298/0.315 = 0.7295$ or 72.95% water wet

As a result, core S1 (initially saturated with VB6S) appears to have the largest water wet area (75.14%) which makes it the most water wet core with respect the two others. Core S2 (initially saturated with VB0S) appears to be the least water wet, whereas core S3 (initially

saturated with MgCl_2) exhibits an intermediate wetting state compared to the other two cores.

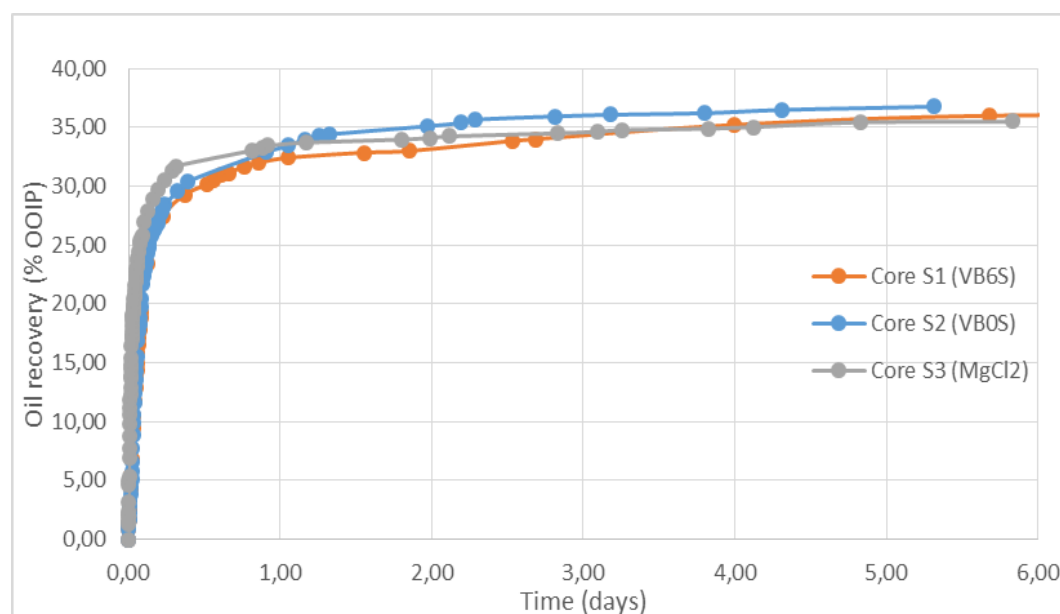
It is noted that the Chromatographic Wettability tests were not supposed to be conducted at 50°C ., due to a wrong assumption. However, since all the tests were conducted at this temperature, the results can be comparable. It is possible though that wettability alteration took place, due to the high temperature and turned the cores into more water-wet ones. As a result, the final Chromatographic Wettability indices might not respond to the real wetting state of the cores. The results would have been representative in case the test would have been conducted at ambient conditions.

7.6 Spontaneous imbibition with DI water

After the Mild Cleaning procedure, each core was saturated with heptane and to avoid possible evaporation, each one was placed rapidly in a spontaneous imbibition cell. The spontaneous imbibition fluid, used was de-ionized (DI) water. Measurements were taken every thirty to fifty seconds, due to the high rate the DI water was displacing the heptane.

The data of the measurement are shown in Tables 20, 21 (see Appendix). In Diagram 13 the oil recovery (%OOIP) is plotted with respect to the time that the Spontaneous imbibition process of each core was conducted:

Diagram 135: Spontaneous Imbibition with DI water



In general, the rapid rate with which the DI water imbibed onto the surface of each core, proves their water-preference. It is noticed that all cores exhibited approximately the same oil recovery, although **core S2** (initially saturated with VB0S) exhibited the highest recovery (36.77% OOIP), **core s1** (initially saturated with VB6S) exhibited the second higher

(36.00% OOIP) and **core s3** (initially saturated with MgCl_2) the least oil recovery (35.57% OOIP).

All cores are considered mixed-wet, however due to the accuracy of the spontaneous imbibition cell ($\pm 0.1\text{ml}$) and the small difference in OOIP of each core, it is not considered safe to rank the cores as more or less water-wet. Spontaneous imbibition is a process which depends mostly on the time needed for the capillary forces to act and the pore volume of the core. It was found that cores with higher pore volume, recovered oil at a higher rate compared with cores with a lower one. It is noted that core S1 broke in half after the mild cleaning procedure (Figure 7.1). Consequently, it would have been expected the oil recovery to be over-estimated, however no significant effect was noticed.



Figure 4.1: Core S1 placed in the spontaneous imbibition cell broke in half.

7.7 Chromatographic Wettability Test at 20°C

In order to investigate the wetting state of the cores, another Chromatographic Wettability test was conducted at ambient conditions. It is noted that due to a failure on the Ion Chromatographic device the Chromatographic Wettability test of the core S1 did not take place. The results found by the Ion Chromatographic device are shown in Tables 17 and 18. In Diagrams 14 and 15, the relative concentrations of sulfate and tracer are plotted with respect to PV injected:

Diagram 146: Chromatographic Wettability test at ambient conditions Core S2

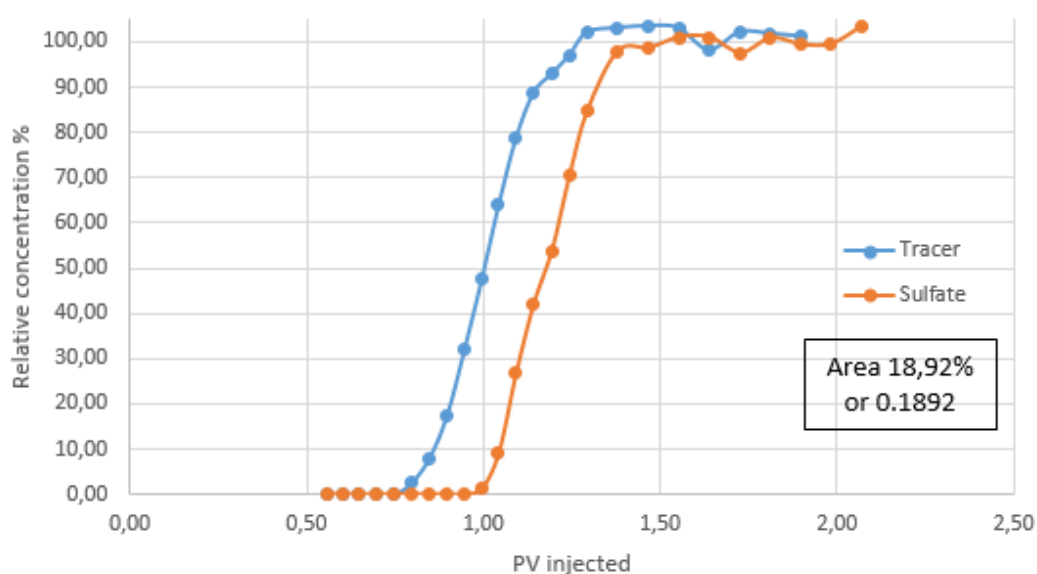
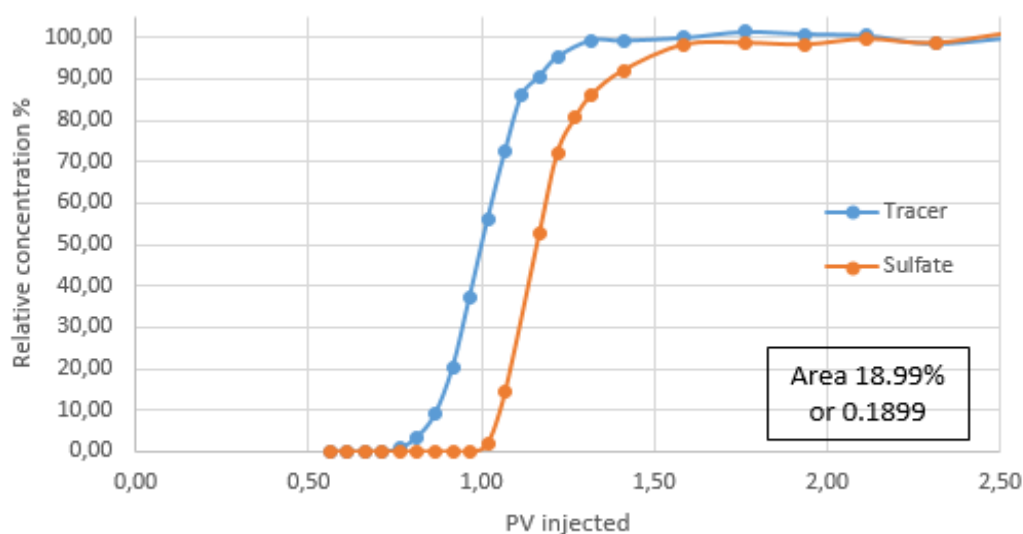


Diagram 157: Chromatographic Wettability test at ambient conditions Core S3



This time the completely water wet reference area (A_{ww}) is known and equal to 0.2560 (Chapter 7 Table 13). Subsequently, the Chromatographic Wettability indexes are calculated by equation 4.3.4.3:

- Core S2: $0.1892/0.2560 = 0.7391$ or 73.91% water wet
- Core S3: $0.1899/0.2560 = 0.7418$ or 74.18% water wet

It is noted that the wetting difference of the cores after the Mild Cleaning is not as great as after the oil flooding: 66.09% OOIP and 72.95% OOIP, for cores S2 and S3 respectively (Chapter 7.4). That could probably be attributed to the amount of polar compounds removed by Mild Cleaning. Core S3 (initially saturated with $MgCl_2$) seems to be slightly more water-wet compared to core S2 (initially saturated with VBOS).

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8. Conclusions and Discussion

In general, the overall results are considered satisfactory. It is considered important to note the negatively and positively charged polar compounds distribution in the cores after oil flooding. It is thought that a possible synergy between the negative and positive polar compounds is developed. Although no positive polar compounds were expected to adsorb onto the surface, it was found that there is adsorption only as long as negatively charged polar compounds are adsorbed. That indicates an interaction between the different polar compounds and it is considered possible that chemical replacements between the different polar compounds and the rock surface took place until an equilibrium was established.

Another very interesting observation is the fact that although all the cores had adsorbed approximately the same amount of positively and negatively charged polar compounds, the cores saturated with brines enriched in Sulfate (S1) and Magnesium (S3) were found to be more water-wet compared to the core in which these compounds were absent (S2). That observation is possible to indicate the different adhesion force developed between the polar compounds adsorbed and the surface of the rock.

It is noted that the initial Chromatographic Wettability tests were conducted at 50°C and not at ambient conditions, due to a mistake. As a result, wettability alteration took place, converting the cores into more water-wet. However, the results could still be comparable.

After the mild cleaning process, wettability test using spontaneous imbibition process and Chromatographic Wettability methods were conducted. The results from the first method did not fit with the initial observations, since the less water-wet core (S2) behaved as the most water-wet compared to the other two. However, the results from the Chromatographic Wettability tests, in ambient conditions, indicated that core S3 is slightly more water-wet compared to core S2. The most reliable results are considered the ones derived from the Chromatographic Wettability tests because Spontaneous Imbibition measurement is a process which depends on many parameters (time, core characteristics, etc) and it is not possible to estimate the oil recovery, in great accuracy ($\pm 0.1\text{ml}$). As a result, especially in cases where the wetting state of the cores have approximately the same value, the Spontaneous Imbibition process is not recommended. It is noted that a second Chromatographic Wettability test was not conducted for core S1 due to a mechanical failure on the Ion Chromatograph.

To sum up, the importance of the brine composition on the wetting state of Chalk rock and subsequently on oil recovery was verified. More specifically, the effect of polar compounds on the initial wetting condition has been observed, with Sulphate (SO_4^{2-}) to be responsible for enhancing water-wetness in comparison with the other polar compounds. The Magnesium (Mg^{2+}) exhibited the second greater impact on the water-wetting state, whereas Calcium (Ca^{2+}) had the least effect on the wetting behavior.

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9. Recommendations for future work

Additional research is suggested to take place to investigate the adhesion forces developed between polar compounds that are adsorbed on the surface of the rock and study the factors that control the adsorption. S.A.R.A fraction is proposed as a method to examine and classify the different polar compounds existing in the mixture of oil (60%v/v Heidrun field crude oil, 40%v/v heptane) used. (Chapter 7.2)

It is suggested that only 10%w/w powder Silica to be added for every 100g of oil during the oil preparation, since the Acid Number was found approximately equal to 0.18 mg KOH/g oil, which is low enough since the desired AN is 0.34 mg KOH/g oil. Additionally, time (3 days needed) and material (only 30g of solid SiO_2 is needed) are saved (Chapter 6.5)

Last but not least, a chromatographic wettability test on a completely water-wet Stevns Klint Chalk core at 50°C is recommended to be conducted, in order to check the chromatographic wettability indexes calculated in Chapter 7.5.

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Appendixes

Spontaneous Imbibition at 50°C

Table 10: Spontaneous Imbibition Records Core S1

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovered %OOIP
10/4/2017	0.00	0.00	0	0.00
	0.33	0.01	0.05	0.15
	1.03	0.04	0.225	0.69
	1.58	0.07	0.375	1.15
	1.78	0.07	0.4	1.22
	2.03	0.08	0.44	1.35
	2.53	0.11	0.5	1.53
	3.03	0.13	0.55	1.68
	3.37	0.14	0.6	1.84
	3.87	0.16	0.62	1.90
	4.37	0.18	0.65	1.99
	5.37	0.22	0.75	2.30
	6.37	0.27	0.8	2.45
	8.87	0.37	1.1	3.37
	10.78	0.45	1.25	3.83
	11.95	0.50	1.45	4.44
11/4/2017	24.70	1.03	2.5	7.65
	25.70	1.07	2.6	7.96
	27.70	1.15	3.05	9.34
	28.70	1.20	3.1	9.49
	32.62	1.36	3.2	9.80
12/4/2017	48.70	2.03	4	12.25
	55.03	2.29	4.3	13.17
	57.32	2.39	4.4	13.47
	59.90	2.50	4.45	13.63
13/4/2017	72.42	3.02	4.6	14.08
	76.20	3.18	4.65	14.24
	78.40	3.27	4.7	14.39
	83.78	3.49	4.8	14.70
14/4/2017	96.20	4.01	5	15.31
	100.70	4.20	5.05	15.46
	104.20	4.34	5.1	15.62
	107.43	4.48	5.15	15.77
15/4/2017	125.37	5.22	5.3	16.23
	129.12	5.38	5.35	16.38
	131.12	5.46	5.37	16.44
16/4/2017	144.67	6.03	5.4	16.53
	153.12	6.38	5.45	16.69

17/4/2017	168.32	7.01	5.5	16.84
	175.70	7.32	5.52	16.90
18/4/2017	192.95	8.04	5.57	17.05
	197.95	8.25	5.6	17.15

Table 11: Spontaneous Imbibition Records Core S2

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovered %OOIP
1/4/2017	0.00	0.00	0.00	0.00
	0.30	0.01	0.00	0.00
	0.50	0.02	0.03	0.07
	0.72	0.03	0.05	0.15
	1.15	0.05	0.10	0.30
	1.55	0.06	0.15	0.44
	4.52	0.19	0.30	0.89
	6.23	0.26	0.40	1.18
	7.17	0.30	0.45	1.33
	8.30	0.35	0.50	1.48
2/4/2017	23.62	0.98	0.95	2.81
	24.47	1.02	1.00	2.95
	25.68	1.07	1.05	3.10
	28.68	1.20	1.15	3.40
	29.52	1.23	1.2	3.54
	32.40	1.35	1.3	3.84
3/4/2017	47.07	1.96	1.6	4.72
	49.40	2.06	1.7	5.02
	51.47	2.14	1.75	5.17
	57.95	2.41	1.8	5.32
4/4/2017	70.85	2.95	1.95	5.76
	75.07	3.13	2.00	5.91
	78.52	3.27	2.05	6.05
	82.07	3.42	2.1	6.20
5/4/2017	95.40	3.98	2.3	6.79
	99.73	4.16	2.35	6.94
	102.57	4.27	2.4	7.09
6/4/2017	120.57	5.02	2.5	7.38
	125.43	5.23	2.5	7.38
	130.07	5.42	2.55	7.53
7/4/2017	142.57	5.94	2.6	7.68
	147.4	6.14	2.6	7.68
	154.57	6.44	2.65	7.83

8/4/2017	173.15	7.21	2.7	7.97
	177.65	7.40	2.75	8.12
9/4/2017	192.48	8.02	2.8	8.27
	198.62	8.28	2.8	8.27
10/4/2017	223.23	9.30	2.85	8.42
	226.57	9.44	2.85	8.42
11/4/2017	239.07	9.96	2.85	8.42

Table 12: Spontaneous Imbibition Records Core S3

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovered %OOIP
27/3/2017	0.00	0.00	0	0
	0.60	0.03	0.01	0.03
	1.02	0.04	0.05	0.14
	1.55	0.06	0.10	0.29
	1.95	0.08	0.15	0.43
	2.27	0.09	0.20	0.57
	2.62	0.11	0.25	0.72
	3.08	0.13	0.41	1.17
	3.77	0.16	0.45	1.29
	4.18	0.17	0.50	1.43
	4.72	0.20	0.60	1.72
	7.42	0.31	0.90	2.58
	9.67	0.40	0.95	2.72
	10.67	0.44	1.10	3.15
28/3/2017	22.75	0.95	1.70	4.87
	25.42	1.06	1.90	5.44
	26.35	1.10	2.10	6.01
	26.88	1.12	2.30	6.59
	27.38	1.14	2.45	7.02
	27.88	1.16	2.50	7.16
	29.33	1.22	2.65	7.59
	30.03	1.25	2.75	7.88
	30.12	1.25	2.80	8.02
	31.00	1.29	2.85	8.16
	31.45	1.31	2.95	8.45
29/3/2017	46.95	1.96	3.80	10.88
	47.83	1.99	3.90	11.17
	48.60	2.03	3.95	11.31
	49.03	2.04	4.00	11.45
	53.53	2.23	4.20	12.03
	56.20	2.34	4.27	12.23

30/3/2017	68.83	2.87	4.60	13.17
	74.95	3.12	4.65	13.32
	80.95	3.37	4.80	13.75
31/3/2017	92.28	3.85	4.90	14.03
	98.43	4.10	4.93	14.12
	104.40	4.35	4.95	14.18
1/4/2017	116.13	4.84	5	14.32
	121.80	5.08	5.05	14.46
	125.50	5.23	5.1	14.60
2/4/2017	140.87	5.87	5.15	14.75
	142.82	5.95	5.17	14.81
2/4/2017	149.38	6.22	5.2	14.89
3/4/2017	164.27	6.84	5.23	14.98
	174.02	7.25	5.25	15.03
4/4/2017	187.00	7.79	5.3	15.18
	198.17	8.26	5.32	15.23
5/4/2017	210.92	8.79	5.35	15.32

Forced Displacement at 50°C

Table 13: Forced displacement data. Core S1.

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP	PV injected corrected
19/4/2017 Rate: 0.025ml/min	0.00	0	0	17.15	-0.088
	0.58	0.02	0	17.15	-0.064
	1.33	0.06	0	17.15	-0.033
	1.58	0.07	0	17.15	-0.023
	2.20	0.09	0	17.15	0.003
	2.92	0.12	0.15	17.61	0.032
	3.08	0.13	0.3	18.06	0.039
	3.20	0.13	0.6	18.98	0.044
	3.37	0.14	0.8	19.60	0.051
	3.47	0.14	0.9	19.90	0.055
	3.53	0.15	1.05	20.36	0.058
	3.78	0.16	1.75	22.50	0.068
	4.12	0.17	2.2	23.88	0.082
	4.45	0.19	3.19	26.91	0.096
	6.83	0.28	7.04	38.70	0.194
	7.25	0.30	7.84	41.15	0.211
	7.58	0.32	8.14	42.07	0.225
	7.83	0.33	8.54	43.29	0.236

	8.17	0.34	8.94	44.52	0.249
	9.50	0.40	9.84	47.27	0.304
	10.83	0.45	10.24	48.50	0.360
	12.17	0.51	10.64	49.72	0.415
	15.50	0.65	10.89	50.49	0.552
	18.83	0.78	11.04	50.95	0.690
	22.17	0.92	11.14	51.25	0.828
	25.50	1.06	11.22	51.50	0.966
	28.70	1.20	11.23	51.53	1.098
Rate: 0.05ml/min	28.72	1.20	11.23	51.53	1.099
	29.68	1.24	11.53	52.45	1.179
	31.68	1.32	12.53	55.51	1.345
	32.68	1.36	13.03	57.04	1.427
	33.68	1.40	13.23	57.65	1.510
	36.68	1.53	13.53	58.57	1.758
	40.68	1.70	13.73	59.19	2.089
	44.68	1.86	14.03	60.10	2.419
	46.68	1.95	14.13	60.41	2.585
	48.77	2.03	14.205	60.64	2.757
	51.6	2.15	14.21	60.65	2.991
Rate: 0.1ml/min	52.02	2.17	14.21	60.65	3.026
	52.42	2.18	14.31	60.96	3.092
	53.92		14.71	62.19	3.340
	55.42		15.16	63.56	3.588
	56.92		15.56	64.79	3.836
	58.42		15.96	66.01	4.084
	59.92		16.16	66.63	4.332
	61.92		16.41	67.39	4.662
	63.92		16.66	68.16	4.993
	65.92		16.76	68.46	5.324
	67.92		16.86	68.77	5.654
	69.92		16.885	68.85	5.985
	71.92		16.895	68.88	6.316
	73.92		16.995	69.18	6.646
	75.92		17.005	69.21	6.977

Table 14: Forced displacement data. Core S2.

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP	PV injected corrected
12/4/2017 Rate:0.03ml/min	0	0	0	0	-0.09
	0.50	0.00	0.00	0.00	-0.06

	1.95	0.08	0.00	13.17	0.01
	3.62	0.15	2.40	20.25	0.09
	3.83	0.16	2.65	20.99	0.10
	4.48	0.19	4.00	24.98	0.13
	4.88	0.20	4.70	27.04	0.15
	5.18	0.22	5.20	28.52	0.16
	5.40	0.23	5.60	29.70	0.17
	5.93	0.25	6.60	32.65	0.20
	6.47	0.27	7.55	35.46	0.22
	6.72	0.28	8.00	36.79	0.24
	7.02	0.29	8.4	37.97	0.25
	8.20	0.34	10.35	43.73	0.31
	8.47	0.35	10.85	45.20	0.32
	8.7	0.36	11.2	46.24	0.33
	12.87	0.54	18.2	66.91	0.53
	17.03	0.71	19.3	70.16	0.73
	21.20	0.88	19.6	71.04	0.93
	25.37	1.06	19.63	71.13	1.13
Rate: 0.06ml/min	26.62	1.11	19.63	71.13	1.25
	27.12	1.13	19.63	71.13	1.30
	27.23	1.13	19.68	71.28	1.31
	27.33	1.14	19.73	71.43	1.32
	28.50	1.19	20.03	72.31	1.43
	29.67	1.24	20.23	72.90	1.54
	29.92	1.25	20.28	73.05	1.56
	32.42	1.35	20.53	73.79	1.80
	34.92	1.45	20.73	74.38	2.04
	37.42	1.56	20.88	74.82	2.28
	39.92	1.66	21.03	75.26	2.52
	42.42	1.77	21.13	75.56	2.76
	44.92	1.87	21.18	75.71	3.00
	47.42	1.98	21.23	75.85	3.24
	49.92	2.08	21.255	75.93	3.48
Rate: 0.12ml/min	50.30	2.10	21.265	75.96	3.55
	52.42	2.18	21.305	76.08	3.96
	52.75	2.20	21.325	76.13	4.02
	53.42	2.23	21.525	76.73	4.15
	54.70	2.28	21.625	77.02	4.39
	55	2.29	21.675	77.17	4.45
	55.95	2.33	21.705	77.26	4.63
	57.45	2.39	21.725	77.32	4.92
	58.95	2.46	21.73	77.33	5.21
	60.45	2.52	21.7305	77.33	5.49
	61.95	2.58	21.731	77.33	5.78

	63.45	2.64	21.7311	77.33	6.07
	64.95	2.71	21.7316	77.34	6.35
	66.45	2.77	21.7317	77.34	6.64
	67.95	2.83	21.7322	77.34	6.93
	69.45	2.89	21.7323	77.34	7.21
	70.95	2.96	21.7323	77.34	7.50
	72.45	3.02	21.7328	77.34	7.79
	73.95	3.08	21.7333	77.34	8.08
	74.95	3.12	21.7333	77.34	8.27

Table 15: Forced displacement data. Core S3.

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP	PV injected corrected
6/4/2017 Rate: 0.08ml/min	210.92	8.788	-0.06	0.00	15.32
	211.85	8.827	0.06	0.80	17.61
	212.08	8.837	0.09	1.80	20.48
	212.20	8.842	0.10	2.40	22.19
	212.35	8.85	0.12	3.00	23.91
	212.45	8.85	0.13	3.50	25.34
	212.50	8.85	0.14	3.90	26.49
	212.58	8.86	0.15	4.20	27.35
	212.67	8.86	0.16	4.55	28.35
	212.75	8.86	0.17	4.90	29.35
	212.83	8.87	0.18	5.30	30.50
	212.92	8.87	0.19	5.65	31.50
	213.00	8.88	0.20	6.05	32.65
	213.08	8.88	0.21	6.50	33.93
	213.17	8.88	0.22	6.85	34.94
	213.47	8.89	0.26	8.20	38.80
	213.58	8.90	0.27	8.80	40.52
	213.75	8.91	0.29	9.60	42.81
	213.92	8.91	0.32	10.40	45.10
	214.05	8.92	0.33	10.90	46.53
	214.25	8.93	0.36	11.30	47.68
	214.50	8.94	0.38	11.40	47.97
	214.73	8.95	0.41	11.60	48.54
	214.83	8.95	0.42	11.6	48.54
	215.00	8.96	0.44	11.80	49.11
	215.33	8.97	0.48	11.95	49.54
	215.83	8.99	0.54	12.2	50.26

	216.57	9.02	0.59	12.3	50.54
	216.95	9.04	0.63	12.4	50.83
	217.35	9.06	0.68	12.5	51.12
	219.02	9.13	0.85	12.6	51.40
	220.68	9.20	1.06	12.7	51.69
	222.35	9.26	1.26	12.8	51.98
	224.02	9.33	1.47	12.9	52.26
	225.68	9.40	1.68	13	52.55
	227.35	9.47	1.88	13.1	52.84
	229.02	9.54	2.09	13.15	52.98
	230.68	9.61	2.29	13.151	52.98
	232.35	9.68	2.50	13.161	53.01
	234.02	9.75	2.71	13.171	53.04
	235.68	9.82	2.91	13.181	53.07
	240.38	10.02	3.49	13.381	53.64
	245.28	10.22	4.10	13.681	54.50
	247.37	10.31	4.36	13.686	54.51
	249.45	10.39	4.61	13.6865	54.51
	251.53	10.48	4.87	13.6965	54.54
	253.62	10.57	5.13	13.7065	54.57
	255.70	10.65	5.39	13.7165	54.60
	257.78	10.74	5.64	13.7865	54.80
	259.87	10.83	5.90	13.7965	54.83
	260.95	10.87	6.03	13.8015	54.84
Rate: 0.16ml/min	261.83	10.91	6.25	13.9015	55.13
	261.88	10.91	6.27	14.0015	55.42
	262.08	10.92	6.32	14.0515	55.56
	262.18	10.92	6.34	14.1015	55.70
	263.02	10.96	6.55	14.1015	55.70
	266.02	11.08	7.29	14.1515	55.85
	266.35	11.10	7.37	14.2515	56.13
	267.78	11.16	7.72	14.3015	56.28
	269.67	11.24	8.25	14.3015	56.28
	270.92	11.29	8.56	14.302	56.28
	272.17	11.34	8.87	14.3025	56.28
	273.42	11.39	9.17	14.303	56.28
	274.67	11.44	9.48	14.3035	56.28
	275.92	11.50	9.79	14.304	56.28
	277.17	11.55	10.10	14.3045	56.28
	278.42	11.60	10.41	14.305	56.29
	279.67	11.65	10.72	14.3055	56.29
	280.92	11.70	10.98	14.3056	56.29

Chromatographic Wettability test at 50°C

It is noted that the concentration of DI and Sea Waters flooded (SW0T, SW^{1/2}T) were analyzed. The numbers 5-40 indicate the number of samples analyzed.

Table 16: Chromatographic Wettability test results core S1

Samples/ properties	Sulphate (SO ₄ ²⁻) [mmol/L]	% Sulphate	Tracer (SCN ⁻) [mmol/L]	%tracer	PV injected	PV corrected
DI	0		0		-	-
DI	0		0		-	-
SW0T	0		0	average	-	-
SW0T	0		0	0.0901	-	-
SW ^{1/2} T	0.0716	0.072	0.0902	0	-	0
SW ^{1/2} T	0.0724		0.0896	0	-	0.78
5	0	0.00	0.0025	2.77	0.82	0.84
6	0	0.00	0.011	12.21	0.87	0.89
7	0	0.00	0.0285	31.63	0.93	0.95
8	0.0002	0.28	0.0476	52.83	0.98	1.00
9	0.0063	8.75	0.0641	71.14	1.04	1.06
10	0.0205	28.47	0.0768	85.24	1.09	1.11
11	0.0319	44.31	0.0797	88.46	1.15	1.17
12	0.0401	55.69	0.0813	90.23	1.20	1.22
13	0.0479	66.53	0.0846	93.90	1.25	1.27
14	0.0549	76.25	0.0863	95.78	1.31	1.33
15	0.0582	80.83	0.0836	92.79	1.36	1.38
16	0.0619	85.97	0.0893	99.11	1.42	1.44
17	0.0647	89.86	0.089	98.78	1.47	1.49
18	0.0661	91.81	0.0884	98.11	1.53	1.55
19	0.0662	91.94	0.0898	99.67	1.58	1.60
20	0.0665	92.36	0.0858	95.23	1.64	1.66
21	0.0664	92.22	0.0843	93.56	1.73	1.75
23	0.0715	99.31	0.0888	98.56	1.93	1.95
25	0.0709	98.47	0.0901	100.00	2.12	2.14
27	0.0694	96.39	0.0872	96.78	2.31	2.33
29	0.0709	98.47	0.0868	96.34	2.50	2.52
31	0.0711	98.75	0.0885	98.22	2.72	2.74
34	0.0747	103.75	0.0898	99.67	3.09	3.11
37	0.0701	97.36	0.0849	94.23	3.45	3.47
40	0.0705	97.92	0.0894	99.22	3.82	3.84
SW0T	5.3429	-	0	-	-	-
SW0T	5.3827	-	0	-	-	-
SW ^{1/2} T	0.0706	-	0.0891	-	-	-
SW ^{1/2} T	0.073	-	0.0915	-	-	-
DI	0.0153	-	0	-	-	-
DI	0.0174	-	0	-	-	-

Table 17: Chromatographic Wettability test results core S2

Samples/ Properties	Tracer (SCN ⁻) [mmol/L]	% Tracer	Sulphate (SO ₄ ²⁻) [mmol/L]	% Sulphate	PV injected	PV corrected
DI	0	-	0.0233	-	-	-
DI	0	-	0.018	-	-	-
SW ¹ / ₂ T	0.0898	-	0.0774	-	-	-
SW ¹ / ₂ T	0.09	-	0.0789	-	-	-
SW ¹ / ₂ T	0.0898	-	0.0794	-	-	-
SW ¹ / ₂ T	0.0886	-	0.0816	-	-	-
SW0T	0	-	0	-	-	-
SW0T	0	-	0	-	-	-
5	0	0	0	0	0.82	0.73
6	0	0.00	0	0	0.87	0.78
7	0	0.00	0	0	0.93	0.83
8	0.0096	10.61	0	0	0.99	0.89
9	0.0248	27.40	0	0	1.04	0.95
10	0.0449	49.61	0	0	1.10	1.00
11	0.0636	70.28	0.0014	1.87	1.15	1.06
12	0.077	85.08	0.0133	17.81	1.21	1.11
13	0.0836	92.38	0.0302	40.44	1.26	1.17
14	0.0867	95.80	0.0439	58.79	1.32	1.22
15	0.088	97.24	0.0543	72.71	1.37	1.28
16	0.0862	95.25	0.0598	80.08	1.43	1.33
17	0.0891	98.45	0.0657	87.98	1.48	1.39
18	0.0878	97.02	0.0677	90.66	1.54	1.44
19	0.087	96.13	0.067	89.72	1.59	1.50
20	0.0878	97.02	0.072	96.42	1.65	1.55
21	0.0877	96.91	0.0714	95.61	1.74	1.65
23	0.0867	95.80	0.0721	96.55	1.94	1.84
25	0.0876	96.80	0.0711	95.21	2.13	2.03
27	0.0888	98.12	0.0763	102.18	2.32	2.23
29	0.0885	97.79	0.0784	104.99	2.51	2.42
31	0.0885	97.79	0.0754	100.97	2.73	2.64
34	0.0883	97.57	0.0748	100.17	3.11	3.01
37	0.0878	97.02	0.0746	99.90	3.48	3.38
40	0.0872	96.35	0.0741	99.23	3.85	3.75
43	0.0887	98.01	0.0752	100.70	4.22	4.12
SW ¹ / ₂ T	0.0905	-	0.0803	-	-	-
SW ¹ / ₂ T	0.0892	-	0.0794	-	-	-
SW ¹ / ₂ T	0.0877	-	0.0759	-	-	-
SW ¹ / ₂ T	0.0885	-	0.0769	-	-	-
SW0T	0	-	0	-	-	-
SW0T	0	-	0	-	-	-
DI	0	-	0.0204	-	-	-

DI	0	-	0.0187	-	-	-
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Table 18: Chromatographic Wettability test results core S3

Samples/ Properties	Tracer (SCN ⁻) [mmol/L]	% Tracer	Sulphate (SO ₄ ²⁻) [mmol/L]	% Sulphate	PV injected	PV corrected
DI	0	-	0.0149	-	-	-
DI	0	-	0.0168	-	-	-
SW ¹ / ₂ T	0.0893	-	0.0735	-	-	-
SW ¹ / ₂ T	0.0888	-	0.0708	-	-	-
SW ¹ / ₂ T	0.0891	-	0.0705	-	-	-
SW ¹ / ₂ T	0.0911	-	0.0713	-	-	-
SW0T	0.0888	-	0.0697	-	-	-
SW0T	0.0893	-	0.0705	-	-	-
5	0	0	0	0	0.78	0.66
6	0	0	0	0	0.83	0.71
7	0.0006	0.66	0	0	0.88	0.76
8	0.0029	3.17	0	0	0.94	0.82
9	0.0086	9.39	0	0	0.99	0.87
10	0.0194	21.18	0	0	1.04	0.92
11	0.0328	35.81	0	0	1.09	0.97
12	0.0487	53.17	0.0006	0.79	1.14	1.02
13	0.0617	67.36	0.006	7.93	1.20	1.08
14	0.0726	79.26	0.017	22.47	1.25	1.13
15	0.0795	86.79	0.0244	32.25	1.30	1.18
16	0.083	90.61	0.0344	45.47	1.35	1.23
17	0.0851	92.90	0.0473	62.52	1.40	1.28
18	0.0862	94.10	0.0531	70.19	1.45	1.33
19	0.087	94.98	0.0611	80.77	1.50	1.38
20	0.0869	94.87	0.0635	83.94	1.55	1.43
21	0.0876	95.63	0.0672	88.83	1.64	1.52
23	0.0877	95.74	0.0694	91.74	1.82	1.70
25	0.0876	95.63	0.0697	92.13	2.01	1.89
27	0.0881	96.18	0.073	96.50	2.19	2.07
29	0.0878	95.85	0.0802	106.01	2.37	2.25
31	0.0882	96.29	0.0751	99.27	2.58	2.46
34	0.0883	96.40	0.0763	100.86	2.93	2.81
37	0.0878	95.85	0.0747	98.74	3.28	3.16
40	0.088	96.07	0.0744	98.35	3.63	3.51
43	0.0878	95.85	0.0772	102.05	3.97	3.85
SW ¹ / ₂ T	0.0898	-	0.0835	-	-	-
SW ¹ / ₂ T	0.0895	-	0.0785	-	-	-
SW ¹ / ₂ T	0.0897	-	0.0774	-	-	-
SW ¹ / ₂ T	0.0916	-	0.0787	-	-	-

SW0T	0.0892	-	0.0791	-	-	-
SW0T	0.0891	-	0.0777	-	-	-
DI	0	-	0.0186	-	-	-
DI	0	-	0.0198	-	-	-

Spontaneous Imbibition at 20°C

Table 204: Spontaneous Imbibition 2 report Core S1

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP
28/4/2017	0.00	0.00	0	0.00
	0.03	0.00	0.3	0.86
	0.07	0.00	0.45	1.29
	0.13	0.01	0.6	1.71
	0.20	0.01	0.85	2.43
	0.35	0.01	1.5	4.29
	0.39	0.02	1.9	5.43
	0.53	0.02	2.4	6.86
	0.73	0.03	3.3	9.43
	0.87	0.04	3.65	10.43
	1.02	0.04	4.1	11.72
	1.14	0.05	4.5	12.86
	1.23	0.05	4.8	13.72
	1.32	0.06	5.05	14.43
	1.40	0.06	5.25	15.00
	1.51	0.06	5.55	15.86
	1.62	0.07	5.8	16.57
	1.72	0.07	6	17.14
	1.80	0.08	6.25	17.86
	1.88	0.08	6.45	18.43
	1.96	0.08	6.6	18.86
	2.03	0.08	6.75	19.29
	3.03	0.13	8.2	23.43
29/4/2017	5.53	0.23	9.6	27.43
	8.90	0.37	10.25	29.29
	12.35	0.51	10.55	30.15
	13.46	0.56	10.7	30.57
	14.66	0.61	10.85	31.00
	15.86	0.66	10.9	31.15
	18.41	0.77	11.1	31.72
	20.61	0.86	11.2	32.00
	25.28	1.05	11.35	32.43

30/4/2017	37.28	1.55	11.5	32.86
	44.43	1.85	11.55	33.00
1/5/2017	60.86	2.54	11.85	33.86
	64.38	2.68	11.9	34.00
4/5/2017		5.68	12.6	36.00

Table 215: Spontaneous Imbibition 2 report Core S2

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP
21/4/2017	0.00	0.0000	0	0.00
	0.02	0.0008	0.3	0.83
	0.09	0.0037	0.5	1.38
	0.13	0.0053	0.6	1.66
	0.18	0.0073	0.8	2.21
	0.23	0.0097	1	2.76
	0.29	0.0120	1.2	3.32
	0.35	0.0147	1.4	3.87
	0.43	0.0177	1.6	4.42
	0.50	0.0210	1.85	5.11
	0.56	0.0233	2.1	5.81
	0.63	0.0264	2.4	6.63
	0.70	0.0294	2.8	7.74
	0.78	0.0323	3.2	8.85
	0.83	0.0345	3.6	9.95
	0.87	0.0362	3.85	10.64
	0.95	0.0396	4.2	11.61
	1.03	0.0430	4.5	12.44
	1.10	0.0456	4.7	12.99
	1.18	0.0491	4.9	13.55
	1.26	0.0524	5.15	14.24
	1.31	0.0546	5.4	14.93
	1.37	0.0569	5.6	15.48
	1.51	0.0630	6.1	16.86
	1.65	0.0688	6.4	17.69
	1.75	0.0728	6.6	18.25
	1.89	0.0786	6.8	18.80
	2.00	0.0833	7.15	19.77
	2.09	0.0872	7.4	20.46
	2.33	0.0972	7.85	21.70
	2.52	0.1049	8.1	22.39
	2.70	0.1124	8.3	22.94

	2.84	0.1184	8.5	23.50
	3.06	0.1274	8.8	24.33
	3.20	0.1333	8.95	24.74
	3.36	0.1400	9.1	25.16
	3.54	0.1474	9.3	25.71
	3.67	0.1531	9.35	25.85
	3.89	0.1622	9.45	26.12
	4.10	0.1710	9.5	26.26
	4.28	0.1782	9.6	26.54
	4.59	0.1913	9.7	26.82
	4.72	0.1965	9.8	27.09
	5.17	0.2155	10	27.64
	5.36	0.2235	10.1	27.92
	5.60	0.2333	10.2	28.20
	5.79	0.2412	10.3	28.47
	7.79	0.3245	10.7	29.58
	9.37	0.3905	11	30.41
22/4/2017	21.79	0.9078	11.9	32.90
	25.29	1.0537	12.1	33.45
	27.90	1.1627	12.3	34.00
	30.12	1.2551	12.4	34.28
	31.79	1.3245	12.45	34.42
23/4/2017	47.37	1.9738	12.7	35.11
	52.62	2.1926	12.8	35.38
	54.79	2.2828	12.9	35.66
24/4/2017	67.59	2.8162	13	35.94
	76.32	3.1801	13.05	36.08
15/4/2017	91.29	3.8037	13.1	36.21
16/4/2017	103.54	4.3141	13.2	36.49
17/4/2017	127.54	5.3141	13.3	36.77

Table 6: Spontaneous Imbibition 2 report Core S3

Date	Time the process was conducted (h)	Time the process was conducted (days)	Volume of oil recovered (ml)	Oil recovery %OOIP
15/4/2017	0.00	0.00	0	0.00
	0.02	0.00	0.5	1.33
	0.02	0.00	0.6	1.59
	0.03	0.00	0.70	1.86
	0.03	0.00	0.8	2.12
	0.04	0.00	0.90	2.39
	0.05	0.00	1.2	3.19

	0.08	0.00	1.75	4.65
	0.09	0.00	1.9	5.04
	0.11	0.00	2.00	5.31
	0.13	0.01	2.60	6.90
	0.16	0.01	2.90	7.70
	0.19	0.01	3.3	8.76
	0.22	0.01	3.70	9.82
	0.25	0.01	4.00	10.62
	0.27	0.01	4.20	11.15
	0.30	0.01	4.45	11.81
	0.32	0.01	4.65	12.34
	0.34	0.01	4.85	12.87
	0.36	0.02	5.15	13.67
	0.39	0.02	5.25	13.94
	0.41	0.02	5.45	14.47
	0.43	0.02	5.60	14.86
	0.46	0.02	5.8	15.39
	0.49	0.02	6.2	16.46
	0.52	0.02	6.40	16.99
	0.54	0.02	6.50	17.25
	0.56	0.02	6.55	17.39
	0.59	0.02	6.65	17.65
	0.62	0.03	6.85	18.18
	0.65	0.03	7.00	18.58
	0.67	0.03	7.15	18.98
	0.70	0.03	7.20	19.11
	0.73	0.03	7.25	19.24
	0.76	0.03	7.30	19.38
	0.78	0.03	7.35	19.51
	0.82	0.03	7.45	19.77
	0.86	0.04	7.55	20.04
	0.90	0.04	7.70	20.44
	0.94	0.04	7.75	20.57
	0.98	0.04	7.85	20.84
	1.02	0.04	7.95	21.10
	1.06	0.04	8.15	21.63
	1.12	0.05	8.25	21.90
	1.17	0.05	8.35	22.16
	1.22	0.05	8.45	22.43
	1.25	0.05	8.55	22.69
	1.29	0.05	8.65	22.96
	1.34	0.06	8.75	23.23
	1.41	0.06	8.90	23.62
	1.51	0.06	9.00	23.89
	1.63	0.07	9.20	24.42

	1.80	0.08	9.45	25.08
	1.91	0.08	9.55	25.35
	2.04	0.08	9.65	25.61
	2.15	0.09	9.75	25.88
	2.41	0.10	10.15	26.94
	3.07	0.13	10.50	27.87
	3.87	0.16	10.90	28.93
	4.74	0.20	11.20	29.73
	5.74	0.24	11.50	30.52
	6.91	0.29	11.80	31.32
	7.49	0.31	11.95	31.72
16/4/2017	19.57	0.82	12.45	33.05
	21.17	0.88	12.55	33.31
	22.07	0.92	12.60	33.44
	28.24	1.18	12.70	33.71
17/4/2017	43.32	1.81	12.80	33.98
	47.74	1.99	12.85	34.11
	50.74	2.11	12.90	34.24
18/4/2017	67.99	2.83	13.00	34.51
	74.24	3.09	13.05	34.64
	78.24	3.26	13.10	34.77
19/4/2017	91.74	3.82	13.15	34.90
	98.99	4.12	13.20	35.04
20/4/2017	115.99	4.83	13.35	35.43
21/4/2017	139.99	5.83	13.375	35.50
	163.99	6.83	13.40	35.57

Chromatographic Wettability test at 20°C

Table 7: Chromatographic Wettability test 2 results. Core S2

Samples/ properties	Sulphate (SO ₄ ²⁻) [mmol/L]		Tracer (SCN ⁻) [mmol/L]				
DI	0	% Sulpha te	0	% Tracer	ml injected	PV injected	PV corrected
DI	0		0				
SW0T	0		0				
SW0T	0		0				
SW 1/2T	0.0676		0.0873				
SW 1/2T	0.0669		0.0858				
SW 1/2T	0.0661		0.0865				
SW 1/2T	0.0673		0.0866				
5	0	0.00	0	0.00	28.94	0.734	0.55
6	0	0.00	0	0.00	30.76	0.785	0.60
7	0	0.00	0	0.00	32.75	0.834	0.65
8	0	0.00	0	0.00	34.72	0.881	0.70

9	0	0.00	0	0.00	36.69	0.931	0.75
10	0	0.00	0.0024	2.72	38.49	0.982	0.80
11	0	0.00	0.0071	8.05	40.47	1.031	0.85
12	0	0.00	0.0154	17.45	42.43	1.081	0.90
13	0	0.00	0.0282	31.95	44.32	1.130	0.95
14	0.0009	1.32	0.0421	47.71	46.29	1.180	0.99
15	0.0063	9.22	0.0564	63.91	48.22	1.227	1.04
16	0.0183	26.79	0.0694	78.64	50.01	1.276	1.09
17	0.0288	42.17	0.0783	88.73	51.98	1.326	1.14
18	0.0368	53.88	0.082	92.92	53.96	1.377	1.19
19	0.0481	70.42	0.0856	97.00	55.91	1.427	1.24
20	0.0579	84.77	0.0897	101.64	57.71	1.477	1.29
21	0.0603	88.29	0.0861	97.56	61.19	1.563	1.38
23	0.0669	97.95	0.0901	102.10	67.85	1.652	1.47
25	0.0674	98.68	0.091	103.12	74.52	1.737	1.55
27	0.069	101.02	0.0914	103.57	81.23	1.823	1.64
29	0.069	101.02	0.091	103.12	87.95	1.910	1.73
31	0.0666	97.51	0.0867	98.24	95.68	1.996	1.81
34	0.0689	100.88	0.0902	102.21	108.65	2.082	1.90
37	0.0679	99.41	0.0899	101.87	121.64	2.167	1.98
40	0.068	99.56	0.0894	101.30	134.75	2.256	2.07
43	0.0707	103.51	0.0895	101.42	146.90	2.339	2.15
SW0T	0		0			2.451	
SW0T	0		0			2.561	
SW 1/2T	0.0702		0.0889			2.675	
SW 1/2T	0.068		0.0869			2.786	
SW 1/2T	0.0694		0.0898			2.896	
SW 1/2T	0.0656		0.0874			3.007	
DI	0		0			3.122	
DI	0		0			3.232	

Table 8: Chromatographic Wettability test 2 results. Core S3

Samples/ Properties	Sulphate Area	% Sulphate	Tracer Area	% Tracer	ml injected	PV injected	PV corrected
DI	0.0166		0				
DI	0.017		0				
SW0T	0		0				
SW0T	0		0				
SW 1/2T	0.0718		0.0907				
SW 1/2T	0.0724		0.0921				
5	0	0.00	0	0.00	28.94	0.76	0.56
6	0	0.00	0	0.00	30.76	0.81	0.61
7	0	0.00	0	0.00	32.75	0.86	0.66
8	0	0.00	0	0.00	34.72	0.91	0.71

9	0	0.00	0.0009	0.98	36.69	0.97	0.77
10	0	0.00	0.0032	3.50	38.49	1.01	0.81
11	0	0.00	0.0082	8.97	40.47	1.07	0.87
12	0	0.00	0.0185	20.24	42.43	1.12	0.92
13	0	0.00	0.0342	37.42	44.32	1.17	0.97
14	0.0013	1.80	0.0513	56.13	46.29	1.22	1.02
15	0.0103	14.29	0.0664	72.65	48.22	1.27	1.07
16	0.0296	41.05	0.0785	85.89	50.01	1.32	1.12
17	0.0379	52.57	0.0828	90.59	51.98	1.37	1.17
18	0.052	72.12	0.0871	95.30	53.96	1.42	1.22
19	0.0581	80.58	0.0873	95.51	55.91	1.47	1.27
20	0.0621	86.13	0.0908	99.34	57.71	1.52	1.32
21	0.0664	92.09	0.0907	99.23	61.19	1.61	1.41
23	0.0709	98.34	0.0913	99.89	67.85	1.79	1.59
25	0.0712	98.75	0.0926	101.31	74.52	1.96	1.76
27	0.0709	98.34	0.0921	100.77	81.23	2.14	1.94
29	0.0719	99.72	0.0918	100.44	87.95	2.31	2.11
31	0.0712	98.75	0.09	98.47	95.68	2.52	2.32
34	0.0734	101.80	0.0919	100.55	108.65	2.86	2.66
37	0.0691	95.84	0.0901	98.58	121.64	3.20	3.00
40	0.073	101.25	0.0927	101.42	134.75	3.55	3.35
43	0.0721	100.00	0.0921	100.77	146.90	3.87	3.67
SW 1/2T	0		0				
SW 1/2T	0		0				
SW 1/2T	0.0741		0.0921				
SW 1/2T	0.0736		0.0909				
SW0T	0.0194		0				
SW0T	0.0199		0				
DI							
DI							