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Heydar Gaybaliyev

Abstract

Water-Based Enhanced Oil recovery (EOR) by injecting "Smart Water" in Carbonate Reservoirs have shown promising results. The success of EOR-process waterflooding by “Smart Water” is dictated by the initial wetting condition of the rock and the potential of EOR methods related to wettability alteration. It is also found that adsorption of polar organic components has the largest effect on the wettability alteration in carbonates.

The main objective of this paper is to show adsorption of polar organic components towards water wet chalks surface with different initial water saturation (0%, 10%, and 100%). Three cores with 0%, 10%, and 100% initial water saturation were flooded 15 pore volumes (PV) of crude oil with fix Acid Number (AN=0.35 mgKOH/g) and Base Number (BN=0.20 mgKOH/g) at 50° C. The core without initial water saturation adsorbed most polar components in comparison with other cores. Wettability of the cores was analyzed by spontaneous, forced imbibition and chromatographic wettability tests. Based on oil recovery and chromatographic wetting index, the experimental results showed that the core initially saturated with 100% water behaved more water-wet core than other two cores.

The observations were in the followings: 1) The wetting condition of chalks is strongly linked to the acidic oil components. 2) As adsorption of polar components on the rock surface increases, it continuously causes decrease of water wetness.3) Initial water saturation has a strong influence on the wetting condition, as increasing water saturation can be seen to provide a more water wet condition because of reducing the amount of appropriate cites for adsorption in the core.

Nomenclature

σ	Interfacial Tension [mN/m]
θ	Contact Angle [°]
AN	Acid Number (mgKOH/g Oil)
BN	Base Number (mgKOH/g Oil)
EOR	Enhanced Oil Recovery
FI	Forced imbibition
I_w	Water wetting index
I_o	Oil wetting index
I_{AH}	Amott-Harvey index
OOIP	Original Oil In Place [%]
RES40-0.4	Oil sample used to saturate the core
RF	Recovery Factor
SPI	Spontaneous Imbibition
SK	Stevns Klint
SW	Synthetic seawater
Swi	Initial water saturation [%]
Swr	Residual water saturation [%]
SW0NaCl	Modified Synthetic seawater with reduced NaCl
SW0T	Synthetic seawater without SO4^{2-}
SW1/2T	Synthetic seawater in which the concentrations of SCN^- and SO_4^2 is 12mM respectively
SW4S0NaCl	Modified synthetic seawater with reduced NaCl and with 4 times the concentration of sulfate
USBM	United States Bureau of Mining
VB0S	Synthetic Valhall formation water, without sulphate

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1.Introduction

It is true that "recovery is at the heart of oil production from underground reservoirs" [1]. Accordingly, Green and Willhite state that "the development of enhanced-oil-recovery (EOR) processes has been ongoing since the end of World War II, when operators who owned reservoirs with declining reserves recognized that significant quantities of oil remained in their reservoirs after primary and secondary recovery" [2]. Over the years, intense interest commenced in EOR and this in its turn impacted on accretion in oil reserves and production. In this regard, some oil fields were discovered in North Slope of Alaska, the North Sea and other regions to add the number of oil to the world market. Whilst large volumes of oil stayed in solid reservoirs, if there is no competition economically with conventional sources, the oil will not be produced in large quantities by EOR processes [2]. Historically, they point out that three phases of "oil recovery operations" are in the followings: "primary, secondary and tertiary". On average, oil recovery factor is jagged in the mid-30 percent range around the world. Consequently, for enhanced oil recovery (EOR), it needs to be disclosed novel methods by now engineers to use the reservoir in a better way and cost effective modes properly [1]. Figure 1.1 shows the discoveries and production of oil since 1930."

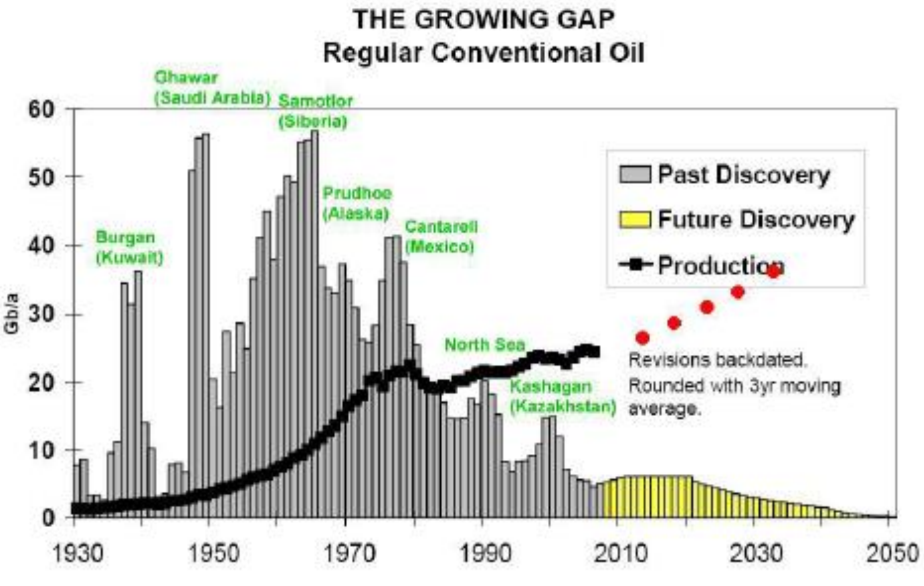


Figure 1.1: Discoveries and production of oil since 1930 [1].

1.1 Oil Recovery steps

Oil recovery divides into 3 steps such as primary recovery, secondary recovery and tertiary recovery as shown in figure 1.2.

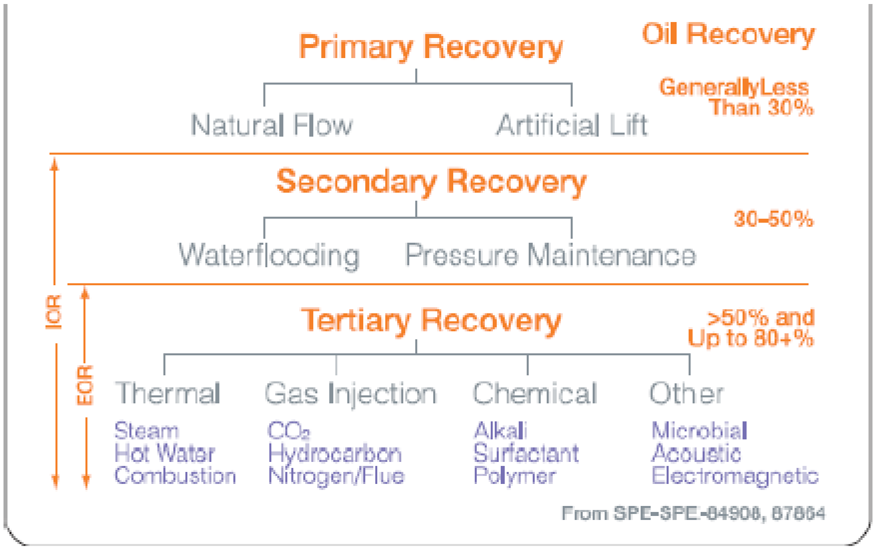
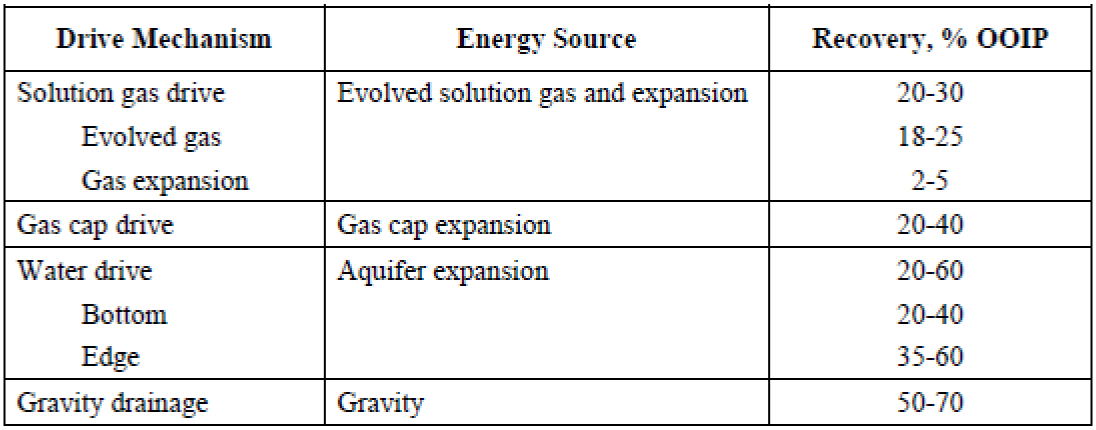


Figure 1.2: Definitions of Oil Recovery [1].

1.1.1 Primary Recovery

Natural energy impacts on the work of primary recovery in a reservoir, and the necessity of primary recovery is displayed in this process as an essential source for displace oil to produce wells. “Solution-gas drives, gas-cap drive, natural water drive, fluid as well as rock expansion and gravity drainage” include in natural energy sources [2].Table 1.1 illustrates the recovery ranges for each drive mechanism.

Table 1.1: Recovery ranges for each drive mechanism [3]



Drive Mechanism	Energy Source	Recovery, % OOIP
Solution gas drive	Evolved solution gas and expansion	20-30
Evolved gas		18-25
Gas expansion		2-5
Gas cap drive	Gas cap expansion	20-40
Water drive	Aquifer expansion	20-60
Bottom		20-40
Edge		35-60
Gravity drainage	Gravity	50-70

1.1.2 Secondary Recovery

If there is no sufficient natural energy to sustain reservoir pressure, in this case secondary recovery requires additional energy to inject water or gas. This stage enables to enhance recovery by injecting fluids, maintaining reservoir pressure and displacing oil to produce well [4]. Water flooding is utilized more in secondary recovery method in comparison with other ones [2].

1.1.3 Tertiary Recovery

Retrieving sufficient oil is the aim of Tertiary recovery/EOR in the comparison with primary and secondary ones, since on average, primary and secondary recovery consist of 1/3 of oil, but then, the statistics show that the goal of tertiary recovery discovers it holds 2/3 of original oil. Yet, tertiary recovery methods just obtain 3.5 of oil production and in its turn lead to take three million kegs of oil for each day. Thermal methods, the most prominent mode, make 2 million barrel of heavy oil production chiefly in Canada, California, Venezuela and so.on.CO_2^- EOR considers as the second largest EOR method, which chases the hydrocarbon gas injection as well as chemical EOR modes [1].

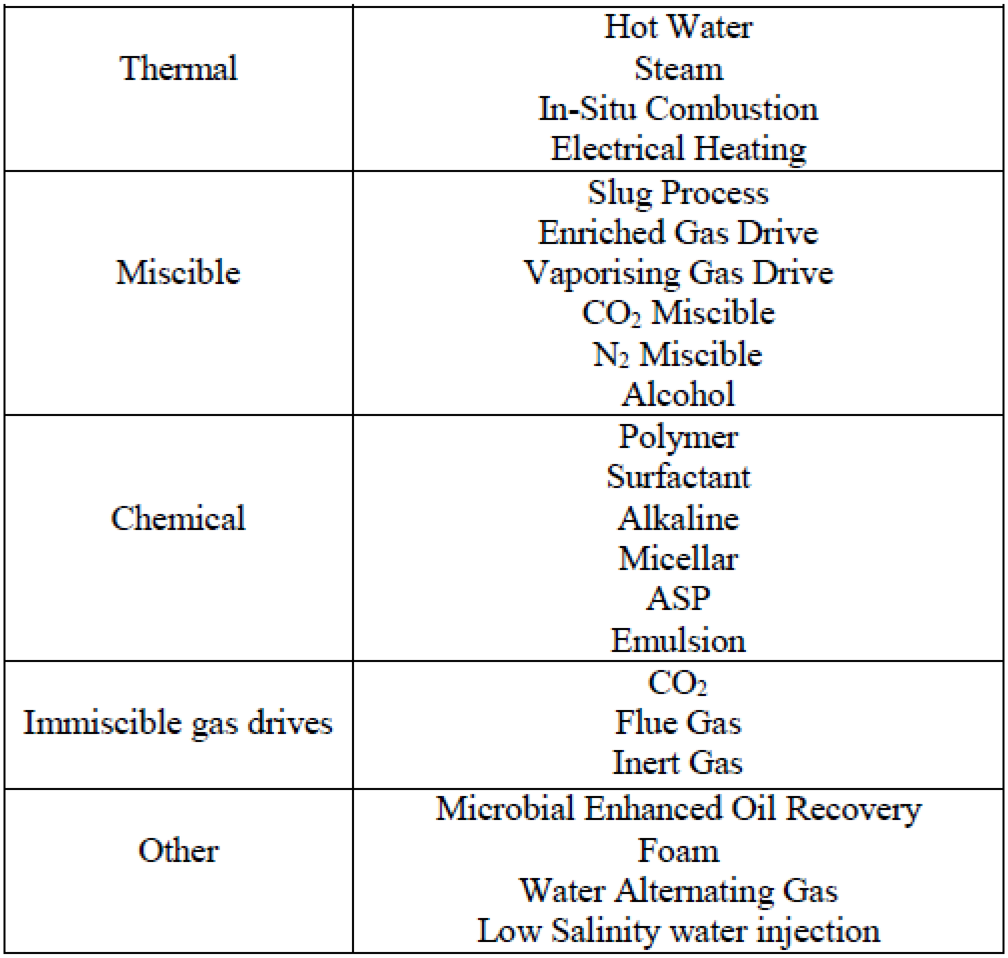
Decreasing of oil "viscosity", modifying of “capillary as well as viscous forces” among “the injected fluid, the rock surface and the oil", also utilizing “solvent” to pull out oil are the main reasons of EOR methods [1].

Overall displacement efficiency for any EOR process can be guessed as the result of Macroscopic (E_V) and Microscopic (E_D) forces;

$$E = E_V E_D \tag{1.1}$$

Microscopic and Macroscopic displacement efficiency is related to the displacement of oil at the pore scale and the displacing fluid in the reservoir respectively. Macroscopic displacement efficiency results from vertical and horizontal sweep efficiencies. These processes can be separated into 5 groups such as “mobility control processes, chemical processes, miscible processes, thermal processes and microbial EOR” [2] as shown table 1.2.

Table 1.2: Classification of EOR Processes [5, 6].



Thermal	Hot Water Steam In-Situ Combustion Electrical Heating
Miscible	Slug Process Enriched Gas Drive Vaporising Gas Drive CO_2 Miscible N_2 Miscible Alcohol
Chemical	Polymer Surfactant Alkaline Micellar ASP Emulsion
Immiscible gas drives	CO_2 Flue Gas Inert Gas
Other	Microbial Enhanced Oil Recovery Foam Water Alternating Gas Low Salinity water injection

Recently, a new EOR method has been proposed; Wettability alteration, which increases capillary forces and improves microscopic sweep efficiency which is shown in table 1.3

Table 1.3: Proposed EOR processes by water based wettability alteration

Wettability Alteration	Smart Water Low Salinity (in Sandstone) Seawater/modified Seawater (in Carbonates)

The main purpose water based enhanced oil recovery (EOR) is to adjust and optimize ion composition of the injected brine by changing in the equilibrium of the crude/brine/rock-system to alter the wetting properties of the reservoir. Consequently, more oil can be displaced from porous media. The procedure is cheap, environmentally friendly and no expensive chemicals are added for injection.

1.2 Objectives

This project focus on optimized oil recovery in carbonate reservoirs by wettability alteration and adsorption of acidic and basic polar organic components onto chalk surfaces with different initial water saturation. The initial wetting of carbonate reservoirs is very important to the overall oil recovery. All chalk cores have been cleaned, flooded with crude oil and thereafter the wettability was evaluated by spontaneous, forced imbibition and chromatographic wettability tests. The topic of this thesis supports study to the Smart water project.

2. Basic Principles of EOR in Carbonate Reservoirs

2.1 Carbonate Reservoirs

The fact that there are carbonate rocks which form in shallow marine environments is inevitable. Tremendous small lime (CaO) such as secreting animals, plants and bacteria do not live in deep water but rather shallow. A number of carbonate rocks are formed by secretions and shells of small lime [7].

Lucia [8] reveals that sedimentation is the primal process to form carbonate reservoirs, and carbonate sediments are created "either by direct precipitation out of seawater or by biological extraction of calcium carbonate from seawater" to produce skeletal material.

Carbonate minerals are composed of CO_3^{2-}, also including one or many cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, which are shown in the table 2.1 [9].

Table 2.1: Mineralogy of the most common carbonate minerals

Carbonate sediments formed in normal marine environments consist of three main minerals;
Low-Mg calcite $CaCO_3$(<4% $MgCO_3$) (hexagonal)
High-Mg calcite (Ca, Mg) CO_3(>4% $MgCO_3$) (hexagonal)
Aragonite ($CaCO_3$) (orthorhombic)
Other common carbonate minerals are:
Siderite $FeCO_3$
Magnesite $MgCO_3$
Strontianite $SrCO_3$
Rhodochrosite $MnCO_3$
Smithsonite $ZnCO_3$
Ankerite Ca (Mg, Fe) $(CO_3)_2$
Dolomite Ca $Mg(CO_3)_2$

The main features of carbonate reservoirs are heterogeneous porosity and permeability [10]. The porosity of most carbonate reservoirs matches from 5% to 15% and it decreases with depth [11]. World oil and gas reserves holding in carbonates consist of more than 60 % and 40 % respectively and are basically focused in Middle East [12]. "The average recovery for all reservoirs is 35%. However, it is recognized that recovery factors are higher for sandstone reservoirs than for carbonates" [12]. Figure 2.1 describes the world distribution of carbonate reservoirs.

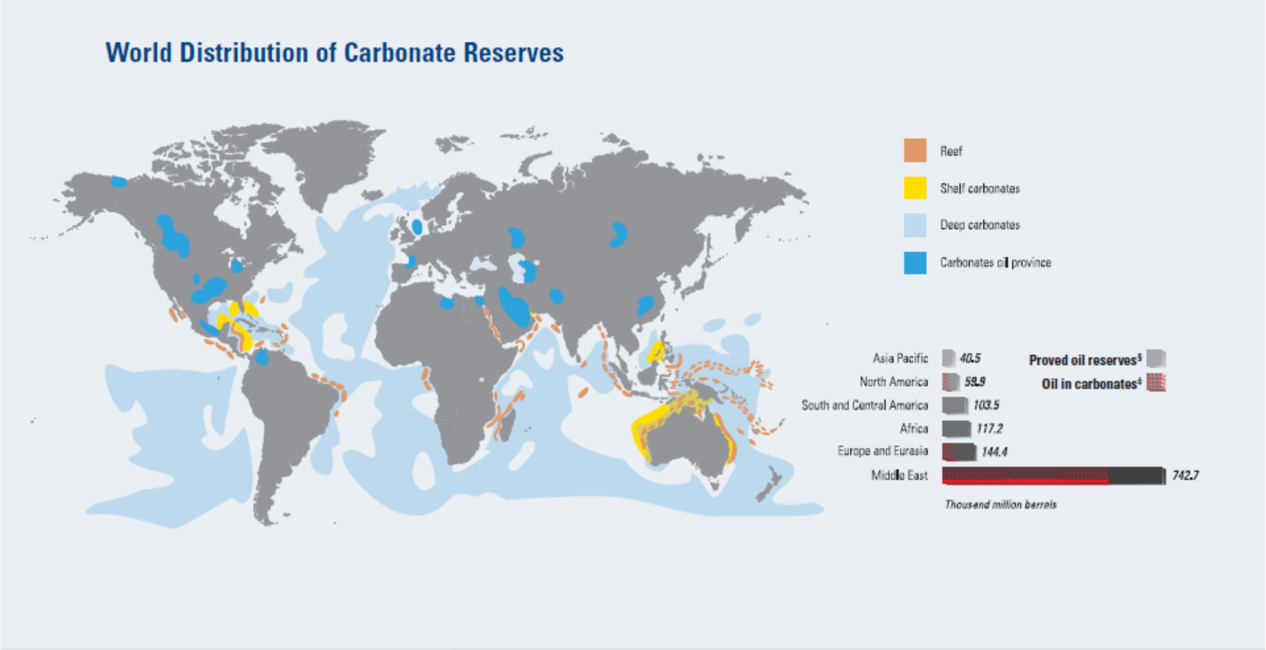


Figure 2.1: World Distributions of Carbonate Reserves [12]

2.2 Wettability

"Wettability is clarified as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids"[13].Wettability is generally considered as one of the substantial parameters influencing saturation, distribution and flow of fluids in porous media [14]. Wettability can be estimated by contact angle (θ), and it divides into three types. For example, water-wet (θ <90°), oil wet (θ>90°) and intermediate or mixed wet (θ=90°) [2]. Water wet condition, oil and water occupies large and small pores respectively , but oil wet condition, the position of oil and water are reversed. Oil remains small pores. Besides, for intermedia or mixed wettability is when some parts are water wet and some oil wet [15]. Figure 2.2 shows a range of different wetting conditions.

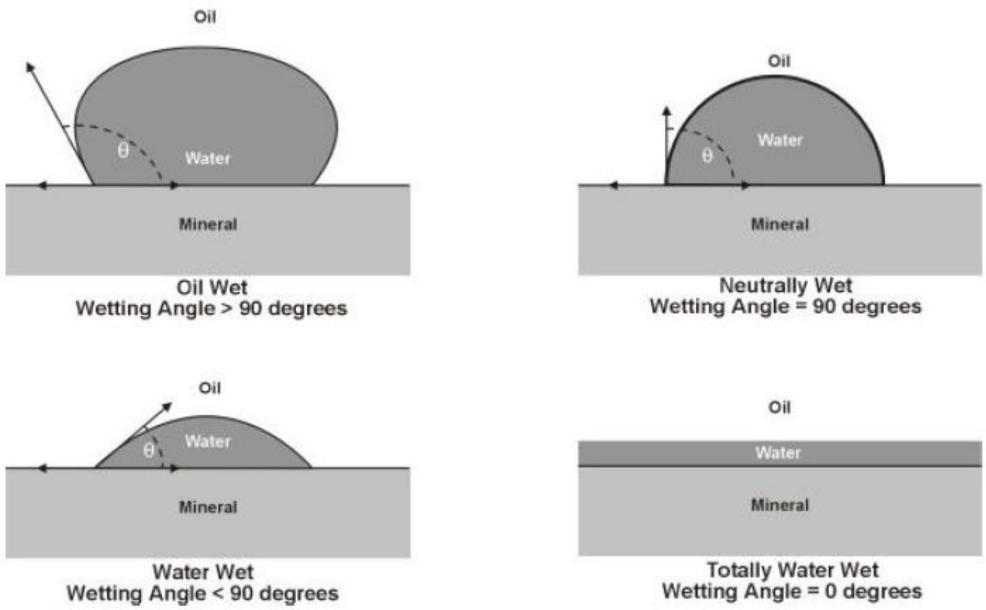


Figure 2.2: Wettability Classification [16]

If the contact angle is close to 0°, it demonstrates strongly water-wet and for strong oil- wet system, the contact angle reaches 180° [2]. Homogenous wettability can be included strongly water wet, oil wet systems and intermediate wettability [17, 18].Water wet and oil wet reservoirs are different during water flooding with regards to displacement process as shown in figure 2.3. Hereby, water wet system illustrates an imbibition process and oil wet shows drainage process [15]. In addition, based on studies, water wet system is the most favorable system during water flooding [19].

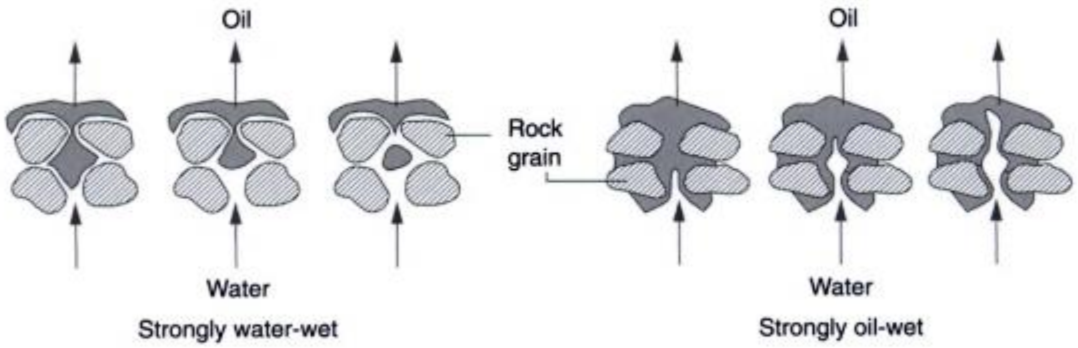


Figure 2.3: Oil displacement in water wet and oil wet reservoirs during water flooding [15].

2.2.1 Methods of Wettability Measurement

We utilize different methods in order to measure wettability, and these methods are classified into two categories such as qualitative and quantitative methods. Qualitative methods are called indirect measurement methods. In terms of qualitative methods, it can be included imbibition rates, microscope examination, flotation method, relative permeability methods, glass slide method, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, dye adsorption and nuclear magnetic [20].

Coming to the quantitative methods which are also considered as direct methods, contain contact angle measurement, imbibition and forced displacement (Amott) method and United States Bureau of Mining (USBM) wettability method. In addition, unlike qualitative methods, quantitative methods are frequently utilized [20].

2.2.2 Contact Angle Measurements

Contact Angle method measures wettability in a straightforward and common way [20].This measurement divides into several methods, containing the tilting plate method, sessile drops or bubbles, vertical rod method, tensiometric method, cylinder method and capillary rise method. Among them, sessile drop method is frequently utilized for determining wettability of rock surface and makes contact angle measurement in a direct way. The idea of this method is not thorough and a droplet of water is placed on a smooth surface and the contact angle is measured through the water phase as in figure 2.4. If contact angle is small, the surface is considered water wet but when contact angle is large solid is assumed oil wet condition [21].

The contact angle can be obtained from Young's equation: [20]

$$\sigma_{ow} \cos\theta = \sigma_{os} - \sigma_{ws}, \tag{2.1}$$

where

σ_{ow} = interfacial tension between the oil and water,
σ_{os} = interfacial tension between the oil and solid,
σ_{ws} = interfacial tension between the water and solid, and
(θ) = contact angle, the angle of the water/oil/solid contact line

The contact angle is suitable for smooth surface for determining wettability whereas it is not able to define wettability on porous rocks, because the reservoir rock is contained variety of minerals with different surface chemistry [22]. From the economic side, this method is suitable in comparison with other ones.

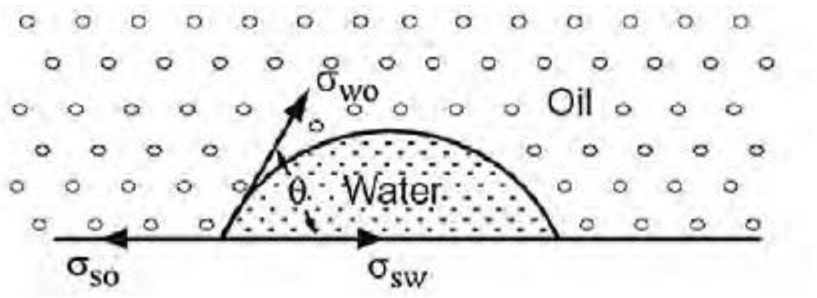


Figure 2.4: Force balance at the water oil rock interface, defining the contact angle [11, 20].

2.2.3 Amott Wettability measurement

The Amott method merges imbibition and forced displacement for determining the average wettability of a core. This method is grounded on the fact that wetting fluid will absorb spontaneously into the core and displace the non-wetting fluid [20]. This method may be very important relative permeability test methods for creating data to reservoir situation [16]. Generally, when rock samples are utilized in this experiment core plugs diameter fits between and 1.5 in and length matches from 2 to 3 in [21].The Amott wettability measurement contains four phases [16]; as presented in figure 2.5.

1. First phase is spontaneous imbibition phase, Amount of spontaneously imbibing water into core which is saturating oil is measured. (AB)

2. At the second step is Forced imbibition of water stage thus the volume of forcibly imbibing water in the core is determined, (BC)

3. Next stage is Spontaneous drainage of oil phase. At this stage, the volume of spontaneously imbibing of oil in core is measured. (CD)

4. Finally, Forced drainage is the last phase of oil. The volume of forcibly imbibing oil is determined. (DA)

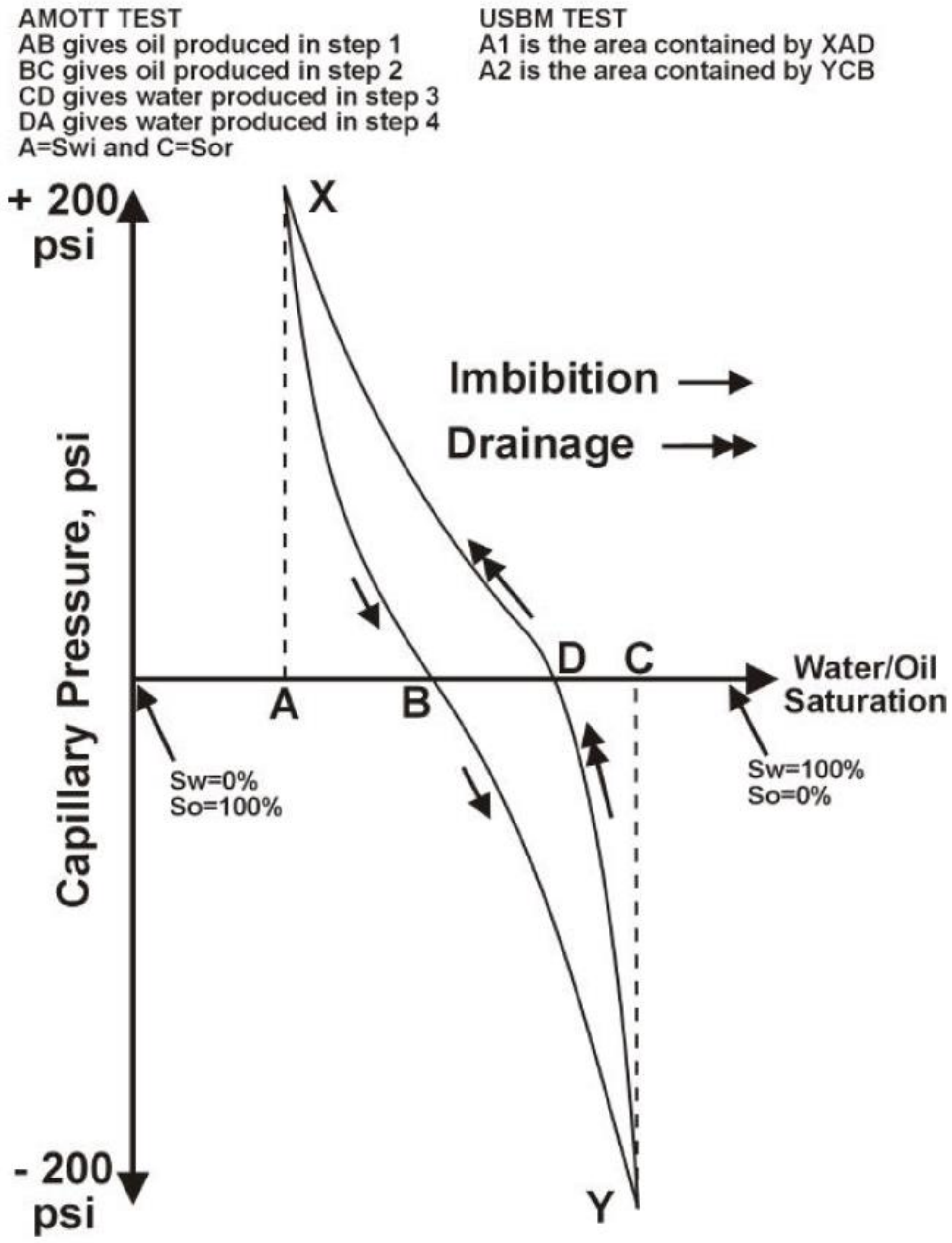


Figure 2.5: Amott and USBM measurements methods [16].

The experiment results express water wetting and oil wetting index by following equations;

Water wetting index $I_w = \frac{AB}{AC}$ (2.2)

Oil wetting index $I_o = \frac{CD}{CA}$ (2.3)

The difference between water wetting and oil wetting index provides the Amott-Harvey index, $I_{AH.}$ The value of I_{AH} matches from 1 to -1. If $I_{AH} = 1$ means that the core is a strongly water-wet otherwise $I_{AH} = -1$, the core is a strongly oil-wet.

$$I_{AH} = I_w - I_o \tag{2.4}$$

2.2.4 United States Bureau of Mining (USBM) Wettability Measurement

This measurement is very identical to the Amott method, however it demands to do imbibition [16].The main advantage of this method is very delicate close to neutral wettability in comparison with Amott method [20].

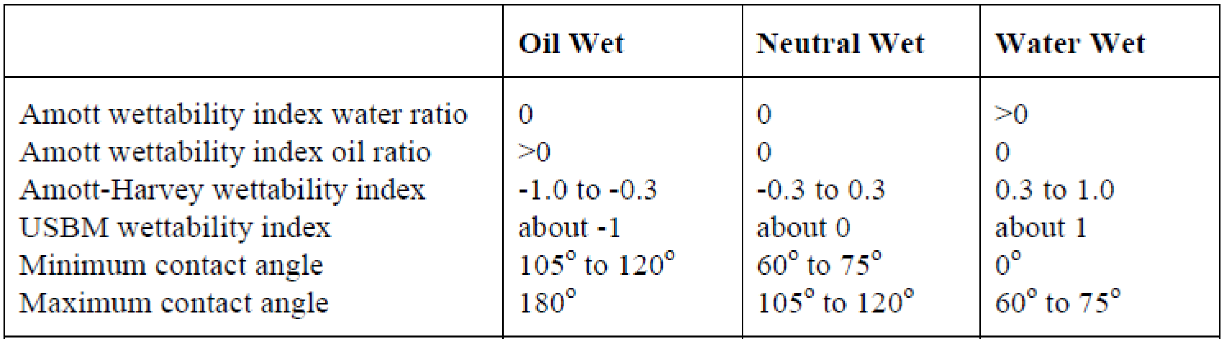
On the other hand, one the disadvantage of USMB method can only be done plug-size samples because the samples have to be rotated in a centrifuge [20]. The USBM wettability index (WI_{USBM}) defined from under capillary curves, WI_{USBM} is the logarithm of the ratio of the area under spontaneous drainage curve to the area over forcibly imbibition curve (Figure 2.5) [16] .

$$WI_{USBM} = \log\frac{A1}{A2} \tag{2.5}$$

A1 –Area spontaneous drainage curve
A2 –Area forcibly imbibition curve

Both the Amott and USBM method are widespread in the oil industry but the Amott method is very reliable and precise in the neutral wettability region. The comparison of both methods are introduced in Table 2.2 [16].

Table 2.2: Comparison of the Amott and USBM Wettability Methods.



	Oil Wet	Neutral Wet	Water Wet
Amott wettability index water ratio	0	0	>0
Amott wettability index oil ratio	>0	0	0
Amott-Harvey wettability index	-1.0 to -0.3	-0.3 to 0.3	0.3 to 1.0
USBM wettability index	about -1	about 0	about 1
Minimum contact angle	105° to 120°	60° to 75°	0°
Maximum contact angle	180°	105° to 120°	60° to 75°

2.2.5 Method based on chromatographic wettability test.

Strand et. al [23] proposed a new method to measure water-wet of carbonate surface by chromatographic test which is based on a chromatographic separation between a non-adsorbing tracer, thiocyanate, SCN^-, and adsorbing sulphate, SO_4^{2-}. Sulphate has an affinity towards the water-wet areas of the carbonate surface, creating a delay in the effluent concentration during the water flooding process. The thiocyanate tracer has no affinity to the surface and passes through the core with no adsorption to the surface. As the separation only occurs at the water-wet sites, the range between these two effluent concentration curves is proportional the water-wet condition. The ratio between area of these two components and corresponding area for completely water-wet-core gives new wetting index (WI_{New}).

$$WI_{New} = \frac{A_{Wett}}{A_{Heptane}} \tag{2.6}$$

WI_{New} = new wettability index
A_{Wett} = The area between the thiocyanate and sulphate curves generated by flooding a core aged in crude oil
$A_{Heptane}$ = The reference area between the thiocyanate and sulphate curves generated by flooding a core assumed to be strongly water-wet (saturated with heptane).

Wettability index ranges between 0 and 1, represents completely oil-wet and completely water-wet conditions respectively. The chromatographic wettability test is a quick and very beneficial method to utilize close to neutral wettability (WI_{New} =0.5) [23]. Figure 2.6 shows a schematic illustration of the separation between the Sulphate and thiocyanate [24].

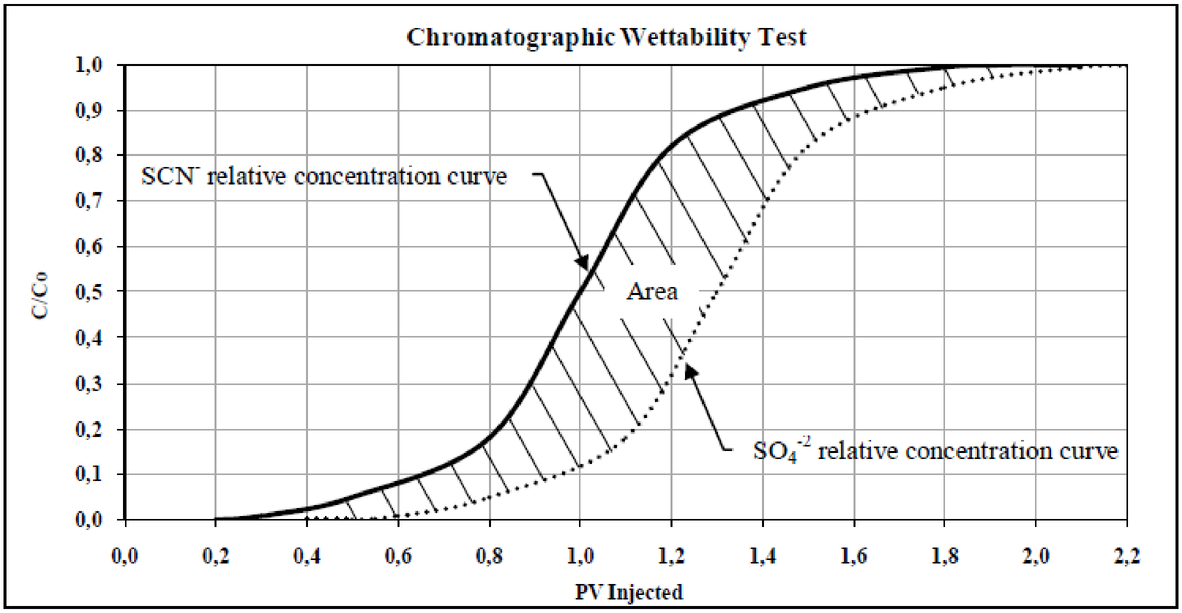


Figure 2.6: Schematic illustration of the chromatographic wettability test separation [24].

3.Water based EOR in Carbonates

3.1 EOR by “Smart Water” in carbonate rocks

EOR from carbonates has proven to be a great challenge due to the unfavorable wetting conditions of the rock. Imbibition of water becomes difficult because of wetting condition in many reservoirs containing carbonate and this condition is supposed to displace oil and increases recovery [25]. Making better wetting characteristics and improvement of fluid flow through permeable medium can be obtained by injecting of water into the oil reservoir by using water –based EOR method called Smart Water [26].
Oil recovery can be increased greatly by the application of Smart Water in both carbonates and sandstones [19]. It can be seen in figures 3.1 and 3.2.

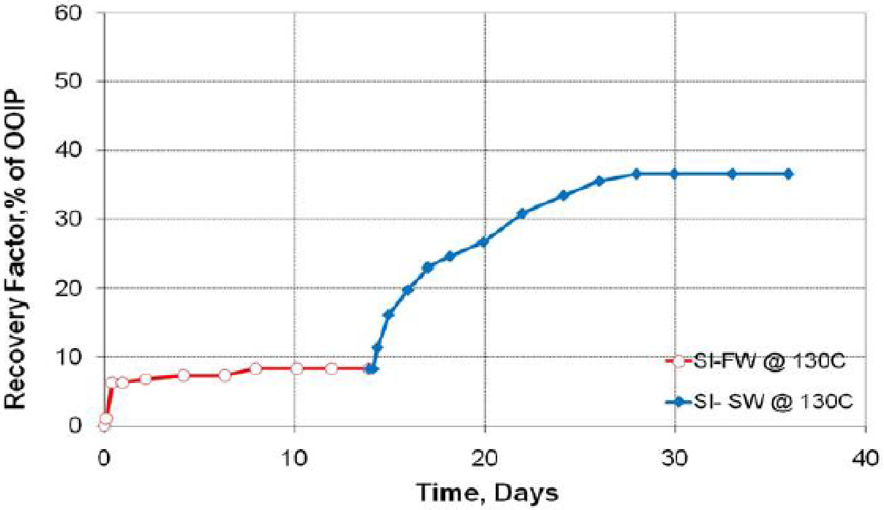


Figure 3.1: Spontaneous imbibition of formation water, FW, and seawater, SW, into a reservoir limestone core at 130 ºC [27].

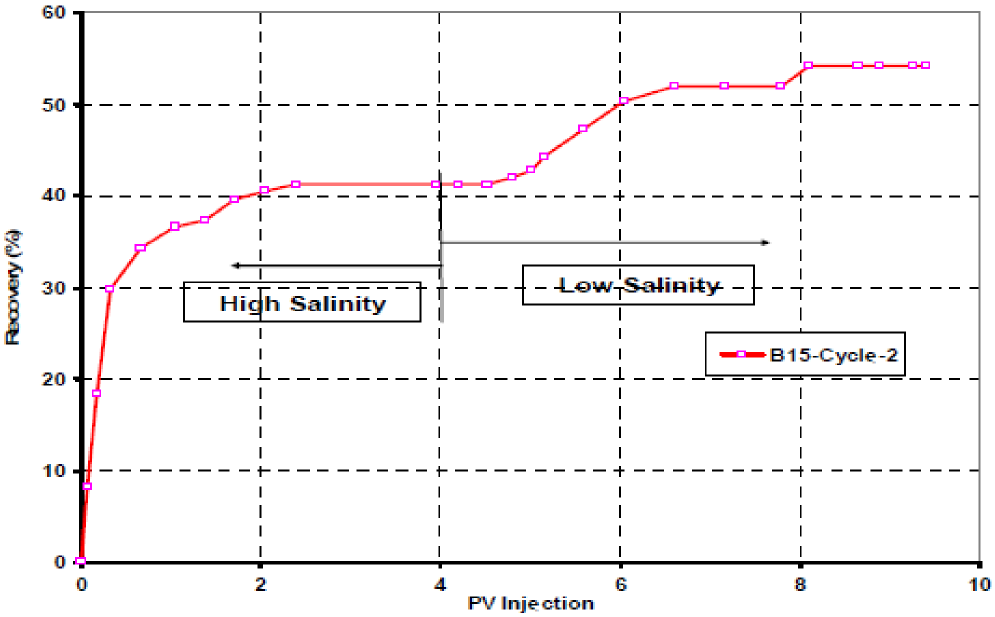


Figure 3.2: Low salinity effects in sandstone [28].

The content of Smart water is modified ionic composition of injected brine. The technique is cheap, environmentally friendly, and no expensive chemicals are used and there are no problems with the injection. To be commercially valuable water flooding process should begin with injecting of smartest water at the start of waterflooding [19].

3.2 Smart Water mechanism

The mechanism for the Smart water effect within carbonates has been registered well [23, 26]. Interaction between ions and surface brings to wettability alteration. Wettability change is governed by carboxylic acid and surface and interaction of ions with each other and finally oil recovery is improved [29]. The smart water mechanism is described in figure 3.3

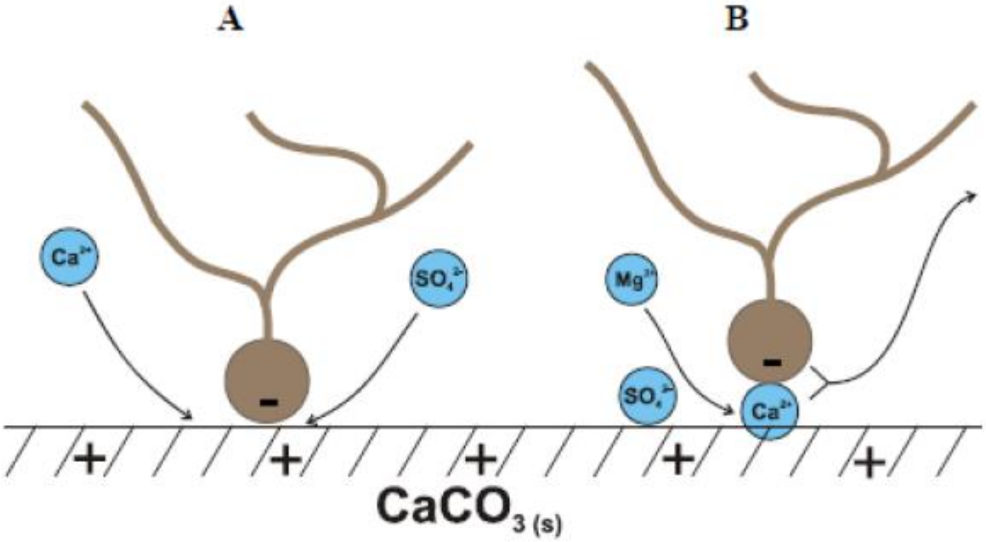


Figure 3.3: Proposed mechanism for how the wettability alters when injecting seawater. **A**: Proposed mechanism when Ca^{2+} and SO_4^{2-} are active. **B**: Proposed mechanism when $Ca^{2+}$and SO_4^{2-} and Mg^{2+} are active at high temperature [29].

Water phase only activates the potential determining ions. The surface absorbs the surface-active components of the crude oil in rock brine and oil system as shown in figure 3.3. A carboxylate is formed due to the hydrophilic group of the fixed carboxylic acid [30].

The offered mechanism indicates that seawater containing SO_4^{2-} adsorbs onto the chalk surface charged in a positive way and lessens the surface charge. It results in adsorption of more Ca^{2+} onto the chalk surface because of less electrostatic repulsion and creation of more Ca^{2+} next to the surface. Finally, Ca^{2+} ions interact with adsorbed carboxylic groups which are bounded to the surface and some carboxylic material releases [31].

By utilizing Smart Water, the chemical mechanism for wettability change in carbonates and sandstones varies due to big distinctions in the rock properties [32, 33]. 33000 ppm salinity seawater takes part as a wettability modifier in carbonates, unlike the former, wettability modifier in sandstones can be a low saline water > 2000 ppm, and it will make oil recovery better in tertiary water flood [34].

3.3 Wetting alteration by low salinity water

Several publications concern seawater acting as a wettability modifier at high temperatures [29, 35]. Strong affinity of potential determining ions (Ca^{2+}, Mg^{2+} and SO_4^{2-}) in the carbonate surface direction brings to the wettability change dependence. Oil recovery in chalk cores was improved by increasing of calcium concentration which was shown in the paper written by Fathi, et.al [36]. Because of surface reactivity increase, the temperature grows up and it brings to the improvement of Ca^{2+} activity [26].

At high temperature at 130° Ca^{2+} from the chalk surface can be substituted by Mg^{2+} in the seawater by influencing physical characteristics of the surface[30, 35] as illustrated in figure 3.3.

Wettability alteration process in carbonates is promoted by sulphate existence [23, 30]. The temperature increase influenced a symbiotic effect of Ca^{2+} and SO_4^{2-} on wettability alteration process [29]. The wettability will not be modified by Ca^{2+} or Mg^{2-} if there is no SO_4^{2-} in the injected fluid and vice versa if Ca^{2+} or Mg^{2+} do not exist then SO_4^{2-} is not active [31]. Zhang and Austad [30] investigate improved oil recovery in chalk with the increase of concentration of sulphate in seawater. The increase of water-wet characteristics in reservoir chalk by sulphate containing seawater was observed by the increase of positive capillary pressure [37].

Spontaneous imbibition and forced displacement describe improvement in oil recovery smart water composition. Oil recovery in imbibition test for carbonates was improved by the elimination of sodium chloride [26, 38]. The removal of 90% NaCl in the imbibing brine was suggested before the observation of crucial EOR effect [38]. Figure 3.4 shows the improvement of oil recovery by sulphate depletion in NaCl four times by spiking the imbibing brine [36].

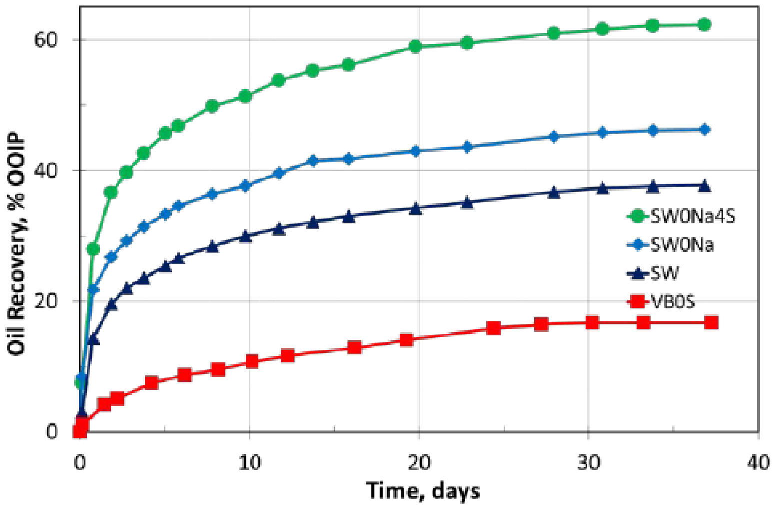


Figure 3.4: Improved recovery by water-based EOR, figure taken from [36]

- VB0S-Formation water
- SW-Seawater
- SW0Na-Seawater depleted in NaCl
- SW0Na4S-Seawater depleted in NaCl and spiked with 4 times sulfate

3.4 Field experiments

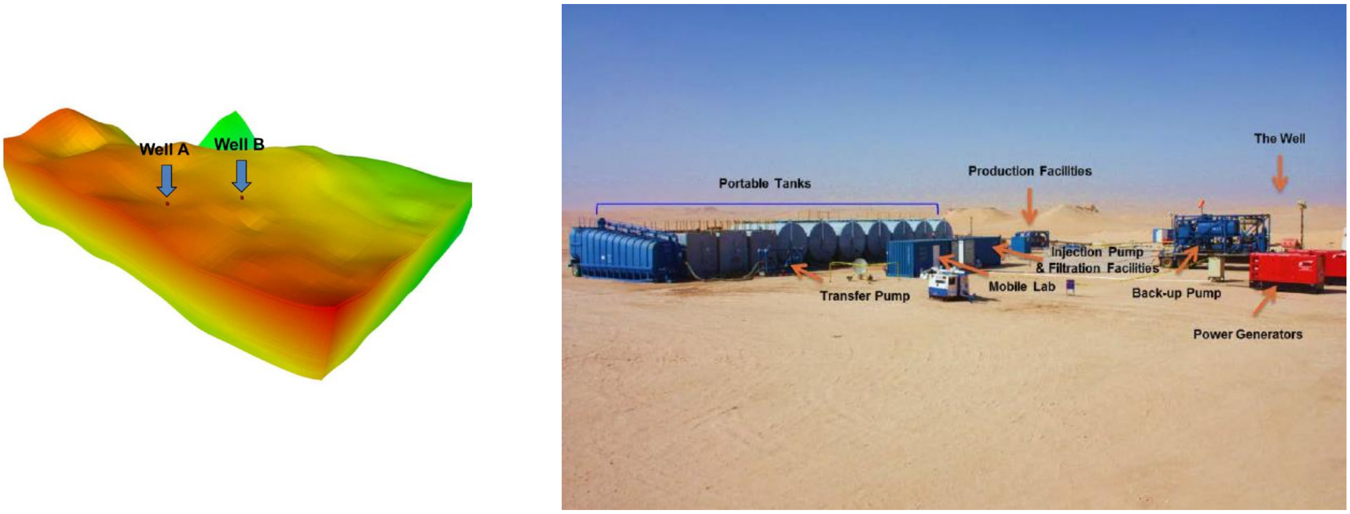
3.4.1 Ekofisk

The largest oil field in the southern part of Norwegian sector in the North Seas is Ekofisk. It was discovered in 1969 and in 1971 test production was started in the discovery well and three appraisal wells [39]. Ekofisk has been subjected to gas and water injection during 20 years. Waterflood project of 1.5billion (1903) has been expanded (1988), extended (1989) and optimized (1990) [40]. It has increased the recovery factor from the less than 20 % of the oil in place to the current estimate of more than 50% [41].

3.4.2 Saudi Aramco

Exploring of oil recovery increase potential by changing the salinity and ionic composition of the injected seawater has been studied out by Saudi Aramco’s research arm (the EXPEC Advanced Research Center) in the frame of Smart Water Flood. There are several reservoirs with natural water drives at Saudi Aramco’s disposal and over 60 years the company has implemented string of development of injection as a result of which the largest unique water injection infrastructure has been built. Seawater is a primary source of injection water and in Saudi Arabia current injection water faculties are used to change injected water properties and obtain incremental oil recovery potential.

Using the field seawater the impact of Smart Water on residue oil was determined by field tests. At the first stage oil saturation was moved in the direction of residual oil saturation by the introduction of seawater to the reservoir. At the second stage injection a slug of Smart water injection is carried out [42].



a) b)

Figure 3.5: (a) Relative location of selected wells for SmartWater Flood field tests, (b) Overall field preparation and logistics at the well site.

For measuring residual oil saturation Single-Well Chemical Tracer (SWCT) used as a tool. The results of two tests carried out in a carbonate showed the Smart Water Flood potential. Replication of house research results in the field scale was conformed with both field tests. Reduction of 7 saturation units in residual oil was demonstrated by Smart Water injection.

The field test was carried out in three stages in Well A within four weeks. Residual oil saturation was achieved by pumping a big quantity of field seawater in the first stage. The second stage was related to the validity and confirmation that no further oil will be mobilized by a lot of additional PV using durable field seawater injection. After completion of the second stage, oil saturation reduction was not observed. Finally, beyond field seawater, injection of Smart Water resulted in 7 saturation unit reduction in residual oil saturation.

Differently, designed field test at Well B was compared to the initial one at well A. For achievement of residual oil saturation first field seawater, then twice diluted seawater was injected. Reduction of 3 saturation units has been achieved in this step. Finally, 10 times diluted seawater was injected. The reduction at the last step was the same as the second step. As a result, 6 saturation unit reduction was obtained.

Comparison of total reduction in residue oil saturation of field test at Well A (7 saturation unit) with filed test results at Well B (6 saturation unit) has been revealed by injection of Smart Water.

Overall reduction in residual oil saturation was uncovered by injecting Smart water. The results noticed from field test carried out at Well A (7 saturation unit) were brought into comparison with the ones at Well B (6 saturation unit) [42].

4. Carbonate wetting

It is quite crucial to distinguish wettability between sandstones and carbonates. Sandstones usually possess a low pH and this leads to draw the basic components very easily. Notwithstanding, carbonates have a high pH and it entails to attract acidic components in an easier way [43]. There are multiple types of parameters to appoint the wetting of a carbonate reservoir. Carbonates are composed of diverse mineral components and all of which have a variety of wettability. Some of them such as heterogeneity, fracturing and recrystallization can modify wettability. Depending on the minerals in the rock and their distribution, it can be possible to obtain mixed wet situation [44]. Besides, 161 reservoir cores containing carbonate were checked and it was indicated that most of these reservoirs approximately 80% were described as neutral to oil wet [45].

4.1 Wettability by Crude Oil

The most essential wetting parameter is considered as the composition of the crude oil [46]. The polar compounds in the oil will attach to the rock surface when a rock keeps in touch with crude oil [44]. This will modify the wettability of rock to more the oil- wet conditions. The compounds containing nitrogen, oxygen or sulphur can change rock's wettability very often [47]. Crude oil is also composed of large size surfactants with diverse molecular weights and polarities. The polar organic acids and bases often found in the heavier crude oil fractions such as asphaltene fraction which has a significant influence on the wettability [25, 48]. Other factors that can impact on reservoir wetting, brine, crude oil and rock system are disjoining pressure, water solubility of polar components and prior water saturation [25, 49].

It has also been proved that on the contrary to the majority of sandstone reservoirs, water-wetting character of reservoirs containing carbonates seemed to increase because of the AN content which is decreasing with increased temperature, due to decarboxylation [30].Typical Filed examples is shown in the table 4.1.

Table 4.1: Field examples [30]

The Reservoir	Region	Temperature	AN	Wettability
Ekofisk	**North Sea**	**130° C**	**0.1 mgKOH/g**	**preferential water-wet**
Valhall	**North Sea**	**90° C**	**0.3-0.5 mgKOH/g**	**slightly water-wet**
Yates	**Texas**	**30° C**	**1.0 mgKOH/g**	**preferential oil-wet**

4.2 Acid and base number

The content of crude oil consists of surface-active components. A carbonate surface has interrelation with acidic and basic groups from chemistry and physics points of view [50]. The acidic components have negative charges and they are expressed by carboxyl (COO^-) and indicated by acid Number (AN) at the same time the base component given by (R_3NH^+) is positive and shown by base Number (BN) [46]. In the research, there was a tendency which described that the number of acid and base of crude oil raised with asphaltene concentration increase [51]. For determining the quality of crude oil consisting surface-active components the measures of the acid number (AN) and the base number (BN) can be taken. It can be carried out by potentiometric titration and there is unit mg KOH/g of oil [52]. Another research proved this by demonstrating that the water wettability in chalk is decreased by increasing AN [30].

Characteristic types of basic material may influence on the wettability. It was suggested that formation of acid-base complexes influenced on the wettability of chalk [53].

Crude oil AN impact on wettability features is given in figure 4.1. This effect can be observed in spontaneous imbibition of water into chalk cores saturated with various AN content oil. Imbibition rate and oil recovery reduce radically because of the AN increase [50].

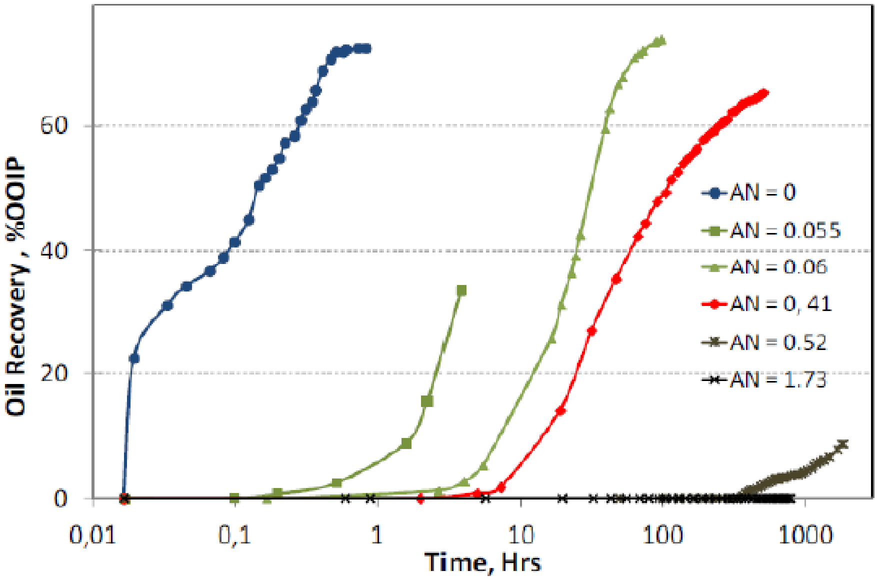


Figure 4.1: Spontaneous imbibition into chalk cores saturated with different oils [50].

Wettability was impacted by strong model base with the help of co-adsorption with the carboxylic acid on to the surface, decreasing the electrostatic repulsion and making possible increase adsorption of carboxylic substance on the surface and diminishing water-wetness. Growth of base number induced the increase of water wetness in larger basic molecules containing natural petroleum grounded oil [53].

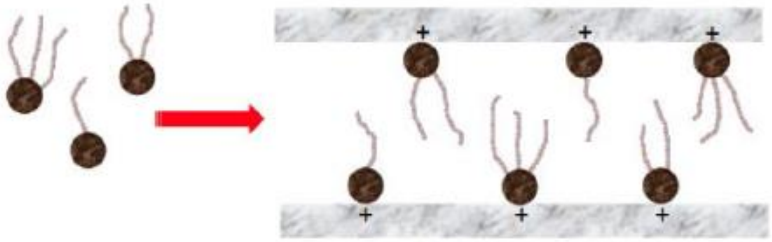
4.3 Adsorption of Oil Components

Buckley [46] described various modes of oil-wet condition establishing.

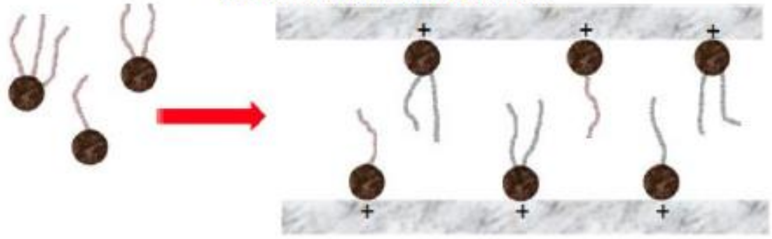
i. adsorption from the oil phase
ii. adsorption through the water phase
iii. adsorption from the oil/water interface
iv. surface precipitation

In the absence of water the adsorption processes are thought unrepelled, quick and independent on the temperature [54, 55]. It is considered that total adsorption and alteration in wettability depends on acid number and the chalk material, which ought to have a definite capacity limited to possible adsorption sites [50]. Effective grain size, shape and mass will have relation with the capacity, which is expressed in surface area terms [56].

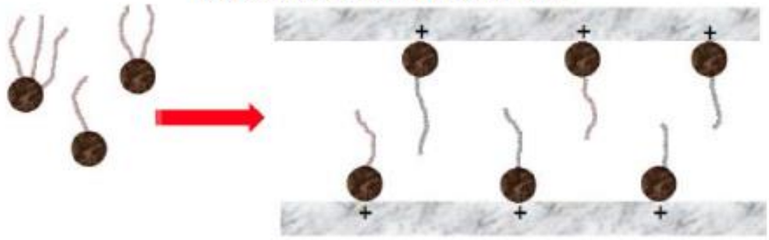
Various adsorption isotherms can express relationship which is the function of adsorbent concentration/pressure at constant temperature [57, 58]. In the initial stage, the rock surface will be attached to most of the negatively charged oil components, only the highest affinity acidic components will be able to complete when existing adsorption sites decrease. Figure 4.2 shows mechanism in adsorption of variety carboxylic group during oil saturation.



(a) Initial phase of adsorption.



(b) seconadry stage of adsorption.



(c) tertiary stage of adsorption.

Figure 4.2: Suggested mechanism in adsorption of different carboxylic group during oil saturation [59].

Yan et.al [60] investigated the effect of increasing cationic valences and decreasing initial water saturation too. Increased oil wetting was proved by the results and it will show that water will prevent access towards the surface, accessibility might be aided by ions found in the stern double layer by forming bridges to the surface. The ratio between resin and asphaltenes is considered very important and for organizing and forming a rigid film at the oil /water interface both of them are found capable [61, 62].The solubility in water is small, destabilization of the stern layer and influence on the adsorption process can be enabled by acid/ base reactions [25, 63]. The adsorption processes will be a function of pH, ionic strength, and concentration of the monomers and surface charge of the mineral. The acid base reaction of carboxylic group in water can be presented by equation 4.1 The equilibrium has pKa at ca 5pH.

$$\mathrm{RCOOH\ (aq)} + \mathrm{OH}^- \rightleftharpoons \mathrm{RCOO}^-\ \mathrm{(aq)} + \mathrm{H_2O\ (l)} \qquad (4.1)$$

Figure 4.3 shows the change in effluent oil acid and base number during oil flooding of an outcrop chalk material. Walrond (Msc 2015) reported that adsorption of acids was more pronounced than base components.

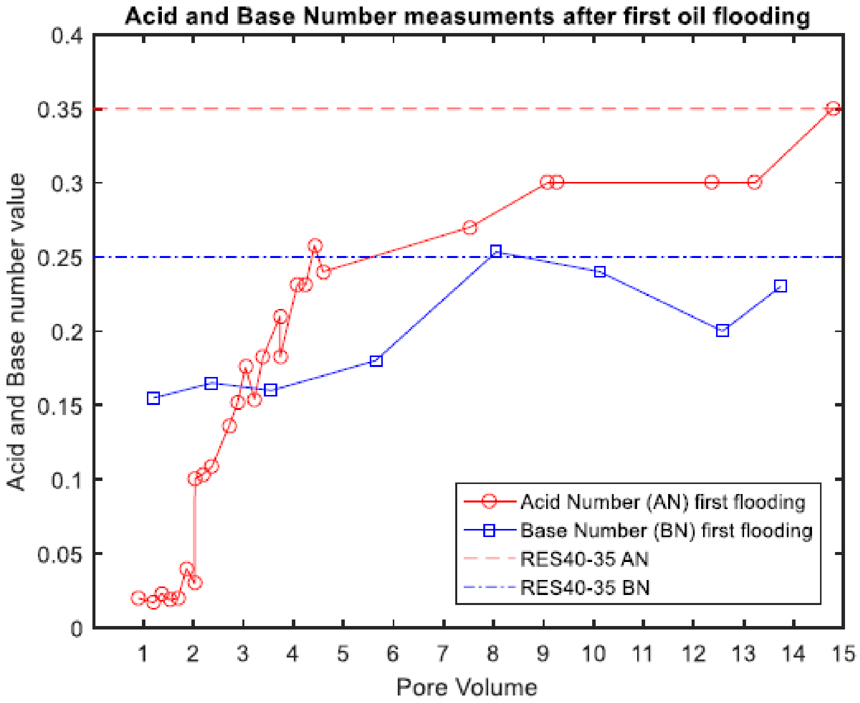


Figure 4.3: Acid and Base number change during oil flooding (Walrond Msc 2015)

5.Experimental materials and methods

The adsorption of polar components in crude oil onto chalk surface and the wettability alteration by oil flooding were performed in this thesis work. In this chapter, experimental methods involving the materials used, crude oils and outcrop chalk and so on. will be described.

5.1. Materials

5.1.1 Core data

Outcrop chalk samples from Stevns Klint (SK), near Copenhagen, Denmark, were utilized in this study as porous media. The cores in each experiment were drilled in the same direction and from the same block. The permeability of cores represented 1-5mD while porosity of cores accounted for 40-50%. SK chalks cores are low heterogeneity and often used as a reference rock in wettability and core experiments. They are quite similar to North Sea chalk reservoir [64]. Table 5.1 is presented Chalk core properties.

Table 5.1: Chalk core properties.

Chalk: Stevns Klint	**Unit**	**SK-0**	**SK-10**	**SK-100**
Dry weight	[gr]	102.35	97.54	108.03
Length	[cm]	6.94	6.40	7.35
Diameter	[cm]	3.74	3.75	3.77
Bulk Volume	[ml]	76.24	70.6	82.13
Saturation weight	[gr]	139.51	130.31	147.34
Pore Volume	[ml]	36.28	31.69	38.38
Porosity	[%]	47.59	44.84	46.73
Permeability	[mD]	1.43	1.27	1.50
Pump Rate	[ml/min]	0.1	0.1	0.1
Viscosity of water (20° C)	[cp]	1	1	1
Pressure drop	[mbar]	700	770	740
Initial water Saturation	[%]	0	10	100

5.1.2 Brines

The brines used in the experiments were prepared in the laboratory with de-ionized (DI) water and variety salts. Firstly, carbonate, chlorite and sulphate salts are all dissolved in DI water separately to avoid precipitation during mixing. Then, all solution was mixed to one solution and diluted to 1.00 L. Finally, the brines are filtered using with a 0.22 µm Millipore filters. The density is measured by using the Anton Parr DMA 4500 Density Meter. Table 5.2 shows the composition of all the different brines.

VB0S, Synthetic Valhall formation water, without sulphate. The brine is used to get 0 %, 10% and 100% initial water saturation and imbibing fluid during spontaneous and forced imbibition for all cores

SW0T, Seawater without sulphate (SO_4^{-2}) and thiocyanate (SCN^-), used initially in the chromatographic wettability test.

SW1/2T, Seawater containing equal amounts of SO_4^{-2} and SCN^-, 12mM.

Table 5.2: Properties and composition of brines used

Chemical Composition of the Brines mixed			
	VB0S	**SW0T**	**SW1/2T**
Salt	m, g/L	m, g/L	m, g/L
SSW	64.71	38.67	38.67
NaCl	57.7	26.79	23.41
Na_2SO_4	0	0	1.71
LiCl	0	0	0.51
KSCN	0	0	1.17
$NaHCO_3$	0.781	0.17	0.17
KCl	0.395	0.75	0.75
$MgCl_2*6H_2O$	1.58	9.05	9.05
$CaCl_2*2H_2O$	4.26	1.91	1.91
Density (Measured)	1.042	1.023	1.023
Ion Composition	mM	mM	mM
HCO_3^-	9	2	2
Cl^-	1066	583	583
SO_4^{2-}	0	0	12
SCN^-	0	0	12
Mg^{2+}	8	45	45
Ca^{2+}	29	13	13
Na^+	997	460	427
Li^+	0	0	12
K^+	5	10	22

5.1.3 Oil Samples

Heidrun oil

The biodegraded Heidrun crude oil with AN=2.78 and BN=0.74 mgKOH/ was used as the base crude oil. The acid number is the essential wetting parameter for chalk. If the acid number can vary, it may change the initial wetting of the chalk core.

RES40

The oil was prepared by blending 60% Heidrun Crude Oil and 40% n-heptane. The acid and base numbers were AN = 1.80 and BN = 0.42 mg KOH/g oil. Dilution of crude oil with heptane is made to reduce oil viscosity and hence required pressure to displace the oil.

Res40-0

The oil was prepared by using 90 gr silica gel was adding in RES40 over 3 days in order to reduce the acid number down to 0. In the subsequent stage, oil mixture was placed in a centrifuge at ca. 35 mph about 1 hour followed by filtering through a 0.65 µm Millipore filter as part of flow capacity improvement.

RES40-0.4

The oil RES40-0 was mixed by Res40 oil sample to get RES40-0.4 with AN=0.4mg KOH/g oil and BN=0.35 mg KOH/g oil. The Res 40-0.4 oil was used for oil flooding. The densities, acid and base numbers of all the oil samples were measured and presented in Table 5.3.

Table 5.3: Oil properties

Oil type	ρ (g/cm^3)	AN (mg KOH/g oil)	BN (mg KOH/g oil)
Heidrun	0.886	2.8	0.74
RES40	0.809	1.8	0.4
RES40-0	0.801	0	0
RES40-0.4	0.803	0.4	0.35

5.1.4 Chemicals

The following different chemicals were used during experiment work.

.

- Heptane was used to dilute crude oil and cleaned the lines in the set-ups.
- Silica gel was used to dry the cores in the desiccator, and Silica powder was used to reduce the AN of the crude oil.
- Chemicals were used for acid number and base number measurement and are presented in Appendix A Table A.1.1 and Table A.1.2

5.2 Methods

5.2.1 Core Preparation

The cores were drilled in the same direction from same block. Next, the chalk cores were shaved to 37-38 mm in diameter by using a lathe and cut the same length approximately 6.9-7 cm by a saw.

5.2.2 Initial core cleaning

The cores were initially cleaned with flooding 5 PV with DI water at rate of 0.1 ml /min for removing dissolvable salts, especially SO_4^{2-} which could affect the wettability. During the flooding, effluent was tested for sulphate by a batch test utilizing Ba^{2+}, where any feasibly sulphate would visually generate precipitation of $BaSO_4(s)$. Equation 5.1 represents the chemical reaction for a batch test. Next, the cores were placed in an oven at 90°C for drying to constant weight.

$$Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightleftharpoons BaSO_4\,(s) \tag{5.1}$$

Permeability measurement was performed by using Darcy’s law equation (5.2) during the core cleaning. The high permeability indicates that fluids pass through rocks easily.

$$k=\frac{q\mu L}{A\,(\Delta P)} \tag{5.2}$$

where

k= permeability

q=flow rate

μ=fluid viscosity

L=length

A=cross-sectional area

ΔP=pressure drop

5.2.3 Initial water saturation by desiccator

5.2.3.1 Establishing 100% Initial Water Saturation (Swi=100%)

A dried chalk core was placed a desiccator and the gas was removed using a vacuum pump as illustrated in figure 5.1 The brine (VB0S) was then introduced to the core under vacuum and the core was equilibrated before the pressure was released.

5.2.3.2 Establishing 10% initial water saturation (Swi=10%)

The core was saturated with 10 times diluted VB0S brine. Then the core was placed in a desiccator with silica gel and water was evaporated by silica gel as an adsorbent. When the core weight equal to 10% initial water saturation (Swi=10%) with VB0S was reached, the core was placed in sealed container and equilibrated for a minimum of 3 days to reach an even ion distribution [65]. For core Swi=0%, has no initial water saturation and therefore was not used for desiccation.

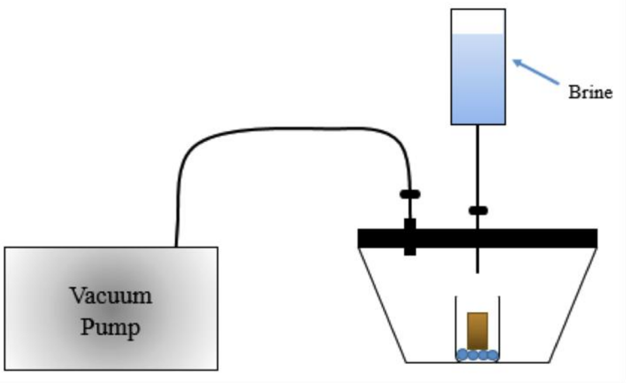


Figure 5.1: Vacuum pump by Frida Layti (BSc 2015)

5.2.4 Adsorption of polar components by oil flooding

The chalk with Swi=0%, Swi=10% and Swi=100% saturated VB0S were placed in a protective rubber sleeve and mounted in the core holder inside a heating cabinet illustrated in figure 5.2. Confining pressure and Backpressure was set at 10 bar and 20 bar respectively during oil flooding at 50°C. All cores were flooded 15PV oil in one direction and a constant rate of 0.1 ml/min. Effluent samples of produced oil were collected using an auto-sampler and the volume oil produced were calculated based on produced oil by weight and oil density. The AN and BN in effluent samples were analyzed.

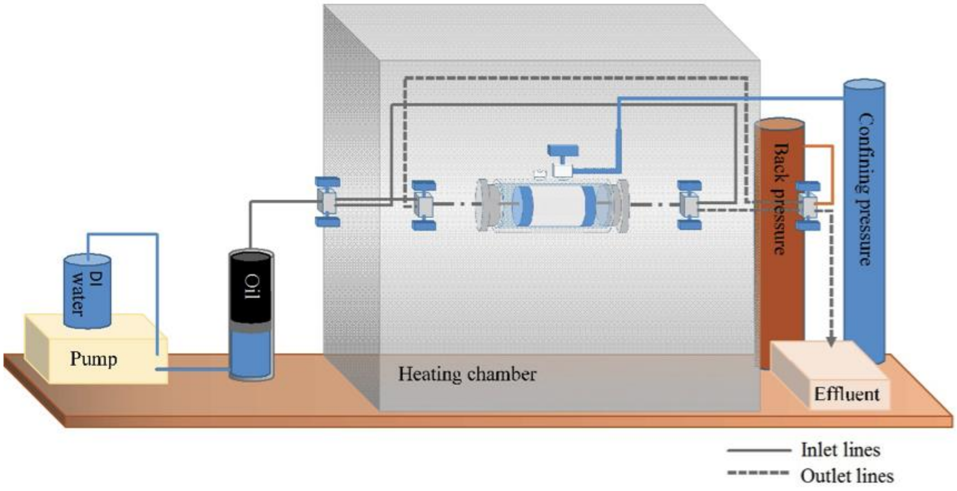


Figure 5.2: Oil saturation and flooding setup by Ingrid Omland (BSc 2015).

5.2.5 Ageing of chalk cores

After the core has been flooded with 15 PV Crude Oil (Res 40-0.4), the cores were wrapped with Teflon tape and placed in a sealed aging cell surrounded by the same crude oil and aged 14 days at 50°C.

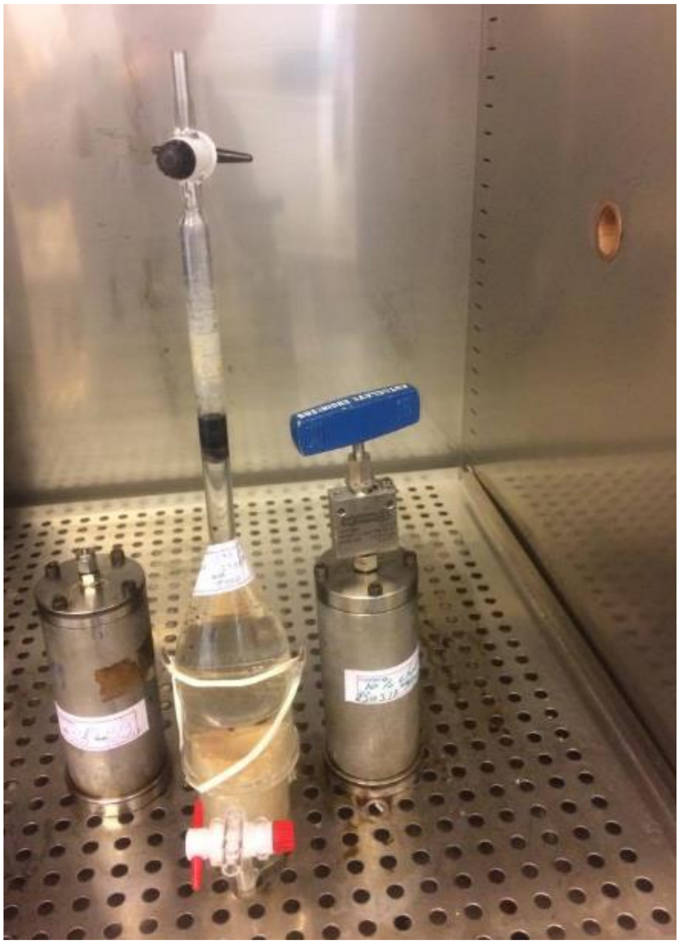


Figure 5.3: (middle) spontaneous imbibition SK-100; aging of SK-10 and SK-0 (left and right)

5.3 Oil displacement tests

5.3.1 Oil recovery by spontaneous imbibition

The wetting state of the core was evaluated by spontaneous imbibition. The aged core was immersed in formation water (VB0S) inside a steal Amott-cell and placed in heating chamber at 50 ˚C. No chemical induced wettability alteration should take place when the cores are imbibed with formation water. The produced oil was collected in a burette and the oil recovery as % OOIP (Original Oil in Place) versus time was recorded. The figure 5.4 illustrates spontaneous imbibition set up.

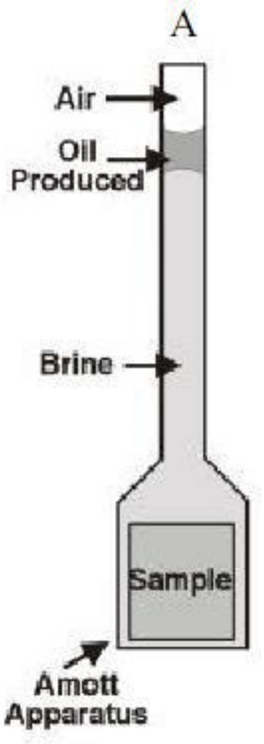


Figure 5.4: Spontaneous imbibition test in Amott glass cell. Aksulu (MSc 2010)

5.3.2 Oil recovery by forced imbibition

Following the spontaneous imbibition, the core was placed into Hassler core holder. Formation water (VB0S) is flooded through the core at rate of 1 PV/day at 50°C with a confining and back pressure of 20 and 10 bars, respectively. Produced fluid was collected in a burette and oil recovery was determined as a percentage of original oil in place (% OOIP) versus time. At the end, the flow rate was increased to push out any extra oil. Flow rates of each core is shown in table 5.4.

Table 5.4: PV and Injection rates during forced imbibition

Core	**PV**	**1 PV/day**	**2 PV/day**	**4 PV/day**
SK-0	36.28 ml	0.025 ml/min	0.05 ml/min	0.1 ml/min
SK-10	31.69 ml	0.022 ml/min	0.044 ml/min	0.088 ml/min
SK-100	38.38 ml	0.026 ml/min	0.052 ml/min	0.104 ml/min

5.4 Wettability test

5.4.1. Chromatographic Wettability test

The chromatographic wettability test determines the water-wet surface area inside a carbonate core and based on the measurement separation of a non-adsorbing tracer and sulphate [23]. The chromatographic wettability tests were performed at both 25°C and 50°C. The core was flooded with the brine SW0T until Sor residual oil saturation was reached following SW½T containing the tracer and sulphate with a flow rate of 1.0 mL/min. Effluent samples were collected and the area of separation between tracer and sulphate was determined by Ion chromatography analysis of the ion concentration. The results were compared to a completely water-wet system.

5.5 Chemical and Physical Analysis

5.5.1. Ion-chromatography analysis

Dionex ICS-5000+ Ion Chromatograph was used to analyze Ion concentration in the effluent of samples during SW1/2T flooding. All samples were diluted 500X, using a Gilson Gx–271 Liquid Handler, to stay in the linear region of the calibration curve. The software uses retention time which is travel time through the columns and it plots graph of conductivity versus retention time where the areas under each peak representing an ion corresponds to their relative concentrations. Sulphate has a retention time at 3.91 min while tracer (SCN^-) comes out at 13.60 min. The ion concentration in the effluent was calculated based on external standard method.

5.5.2 Determination of Acid Number and Base Number

The acid and base number measurement oil samples were done by potentiometric titrations, applying the modified versions of ASTM D2896 for base number (AN) and ASTM D664 for acid number (AN) titration developed by Fan and Buckley [52]. See Appendix A.1 for more details.

6. Results

The polar organic components present in the crude oil are the main parameters dictating reservoir wettability. The acidic and basic component could adsorb to rock surface and behaves as anchor molecules. In this project, the adsorption of polar organic components towards water wet chalk surface with different initial water saturation (0%, 10%, and 100%) has been evaluated.

6.1 Water wet chalk core

The initial water wetness of the outcrop chalk cores used in this study has previous been evaluated in the PhD thesis of the Paul Hopkins (2016). The chalk core with Swi=0.1 and saturated with n-C_7 (heptane) was done spontaneous imbibition with formation water (FW) as shown in figure 6.1.

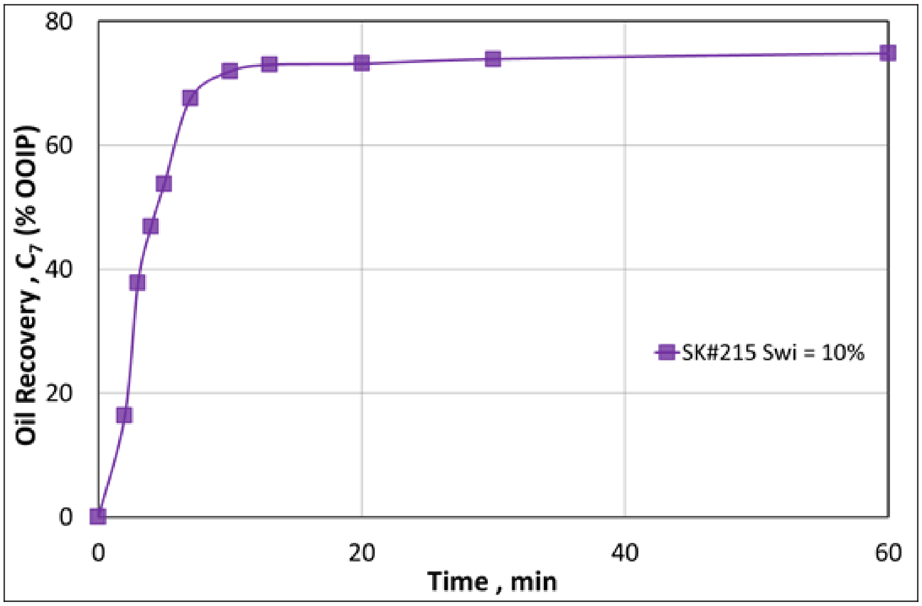


Figure 6.1: Spontaneous imbibition at ambient temperature of a completely water-wet chalk core. The core with Swi= 10 % was saturated with heptane (C_7) and spontaneously imbibed with DI water was used as FW. (Hopkins et al. 2016b)

The oil recovery of 75% was observed after only 30 minutes confirming strong capillary forces and SK outcrop core that behaved very water-wet.

The chromatographic test performed at ambient temperature on 100% water saturation SK reference core using SW0T-SW1/2T brines gave water-wet surface area of A_w=0.256, figure 6.2.

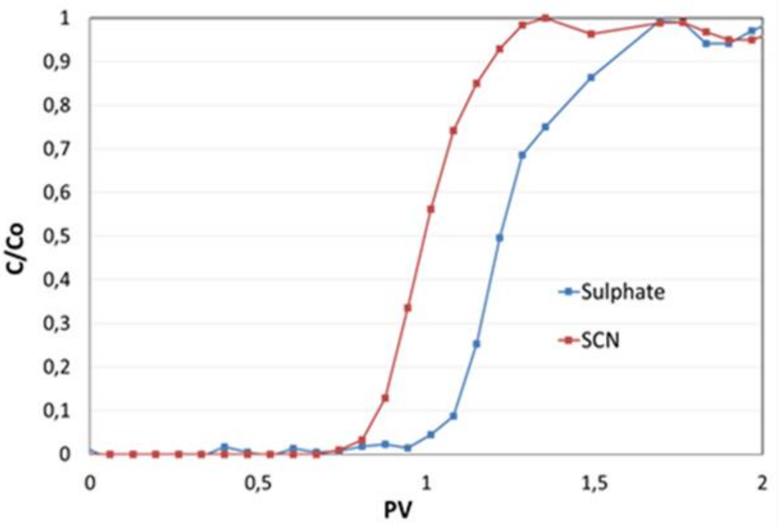


Figure 6.2: Chromatographic wettability test on a 100% water saturated core, (SK-REF1) The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected. Hopkins (PhD 2016).

It represents 100 % water wet surface area for a core which has not seen any oil containing polar organic components.

6.2 Adsorption of polar oil components onto water wet chalk surface

Three chalk cores (SK-0, SK-10 and SK-100) with initial water saturation of 0%, 10%, and 100% were flooded with 15 PV with Res40-0.4 oil at rate 0.1 ml/min at 50°C.The RES40-0.4 have Acid Number = 0.40 mgKOH/g and Base Number=0.35 mgKOH/g. The adsorption of polar organic components was tested by analyzing effluent oil samples. The change in water wetness of the chalk cores was evaluated by spontaneous, forced imbibition and chromatographic wettability tests.

6.2.1 Adsorption of polar organic components: core without initial water saturation

The core without initial water saturation, SK-0 was flooded totally 15 PV with Res40-0.4 oil. The effluents were analyzed for AN and BN content and the results are presented in figure 6.3

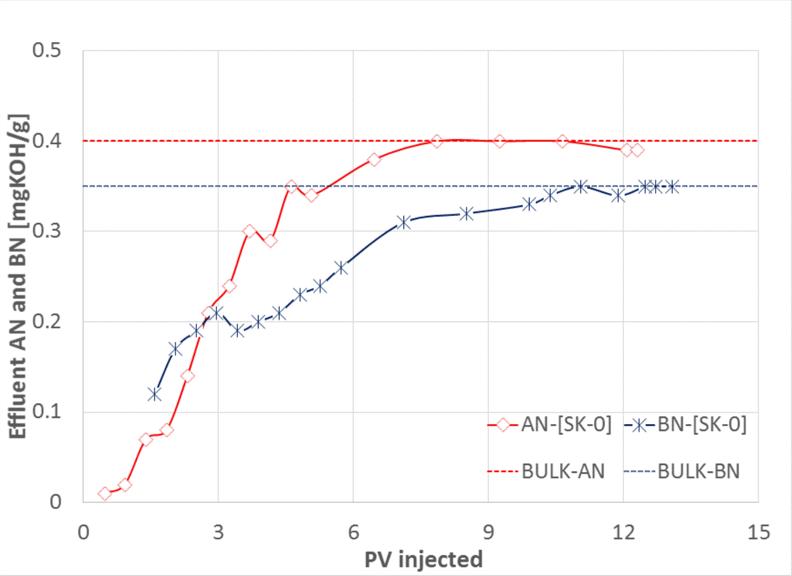


Figure 6.3: The adsorption of polar organic material during oil flooding with Res40-0.4 containing AN=0.40 mgKOH/g and BN=0.35 mgKOH/g. The chalk Core-SK0 was flooded at 50°C with a flow rate of 0.1ml/min. The AN and BN in the effluent samples are presented vs. PV injected.

The Acid Number (AN) in the first effluent sample is close to zero. The AN increases gradually and reaches a plateau equal to the injected value after 8 PV is injected, confirming that all retention of acidic components is connected to adsorption. The total amount of Acid adsorbed could be quantified using the trapezoidal method, giving an area of AN_{ads}=1.51 (PV*mgKOH/g).

The Base number in first effluent sample was 0.12 mgKOH/g and increases gradually to the plateau value of 0.35 mgKOH/g after 11 PV injected.

The results confirmed that both acidic and basic components immediately interact within the crude oil/brine/rock system and could affect the rock wettability.

Oil recovery and wettability without initial water saturation core

After core SK-0 has been flooded with 15 PV crude oil (RES40-0.4), the core was aged for 14 days at 50 ˚C. After aging, spontaneous imbibition with formation water (VB0S) as imbibing brine. The oil recovery was measured and presented in figure 6.4.

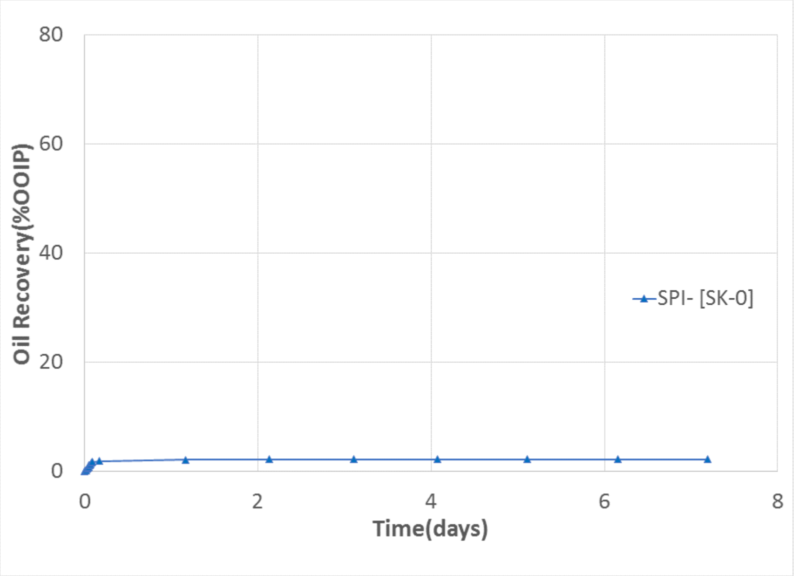


Figure 6.4: Oil Recovery on core SK-0 by spontaneous imbibition using VB0S as imbibing fluid. The SPI test was performed at 50 ˚C

Only 2.2 % OOIP oil was produced. Most of this produced oil could be linked to thermal expansion. The adsorbed polar components reduced the core wettability from strong water wet to a fractional wetting with no positive capillary forces.

After the spontaneous imbibition, the core was mounted in a core holder and a forced imbibition (FI) test was performed using VB0S as flooding brine. The test was done at 50 ˚C with a flooding rate at 1 PV/day. The oil recovery results are presented in figure 6.5

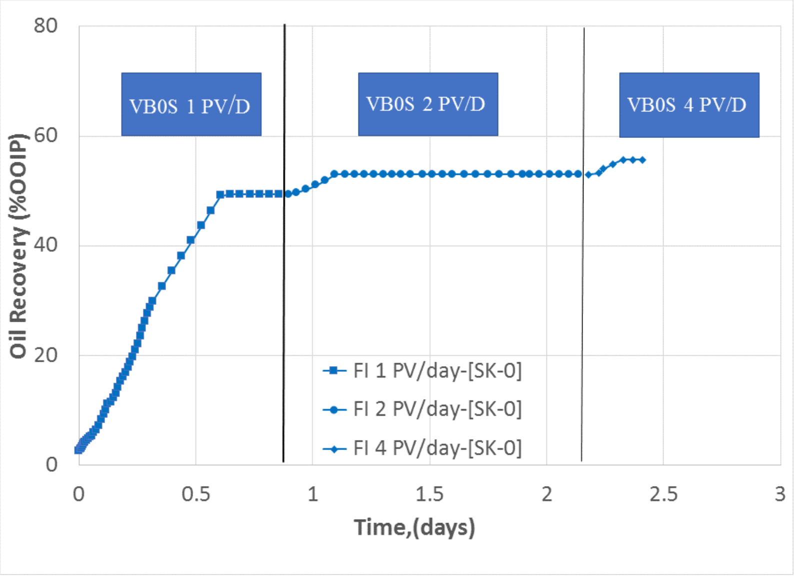


Figure 6.5: Oil recovery test at 50 ˚C on core SK-0, the core was flooded with VB0S at a rate of 1 PV/D. After the oil recovery plateau was reached, the injection rate was increased 2 PV/D and 4 PV/D.

The core SK-0 was flooded with VB0S brine at rate 1PV/D (0.025 ml/min). The recovery reached a plateau of 50% after 1 PV/D. By increasing the injection rate to2 PV/D, 3% extra oil was recovered, 4 PV/D gave also an extra recovery with a total recovery of 56%.

Spontaneous and forced imbibition gave a total final oil production of 19.9 ml. The spontaneous and forced imbibition experiments presented together are shown in figure 6.6.

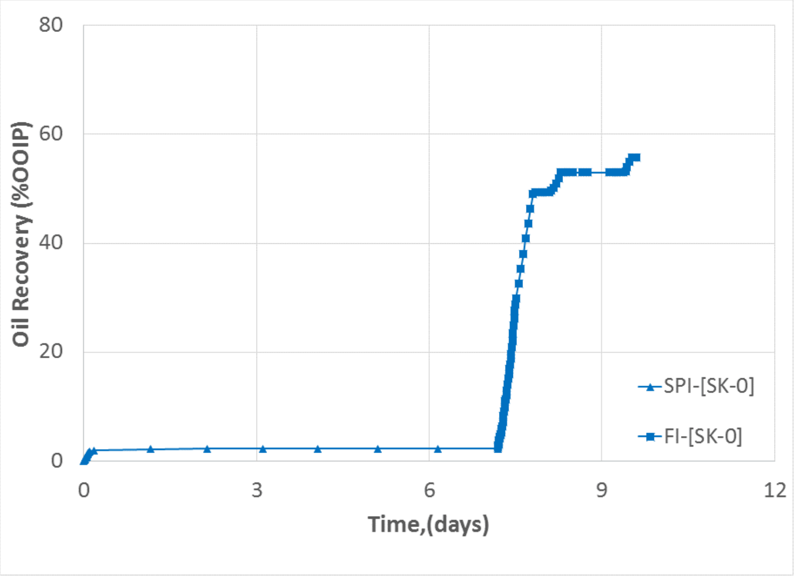


Figure 6.6: Oil recovery after both spontaneous imbibition and forced imbibition with VB0S on core SK-0. The experiments were performed at 50 ˚C.

Chromatographic Wettability test SK-0

After the force imbibition experiment, a chromatographic wettability test was performed on core SK-0 at ambient temperature (20°C). The core was flooded SW0T followed by SW1/2T brine at rate of 0.1ml/min. Effluent fractions were collected and analyzed SO_4^{2-} and SCN^- concentrations by ion chromatograph. The water-wet surface area inside the core was determined based on the separation between the effluent concentration curves of the tracer and sulphate, illustrated in figure 6.7 Aw [SK-0] = 0.09

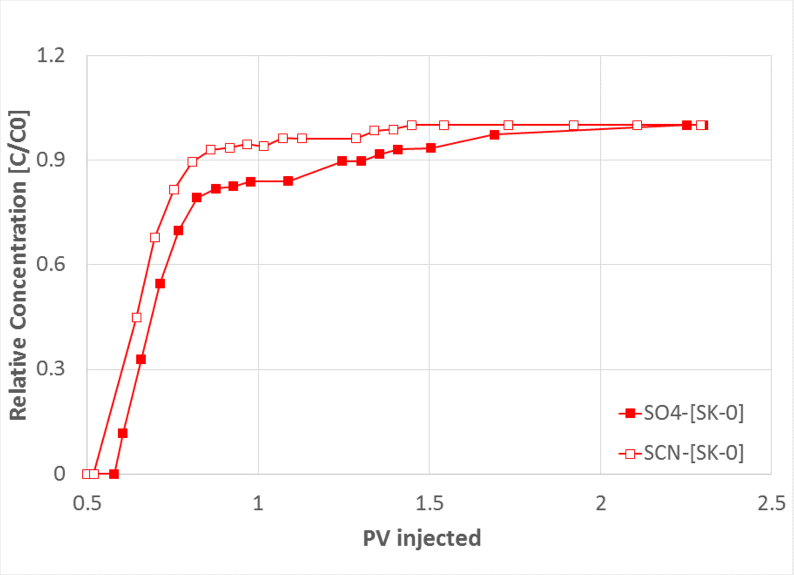


Figure 6.7: Chromatographic wettability test performed at ambient temperature on core SK-0. The core was flooded at a rate of 0.1 ml/min with SW0T - SW½T.The relative effluent concentrations of SCN- and SO_4^{2-} are plotted vs. PV injected.

The A_w was calculated to 0.09 which is far less than A_w=0.256 for a completely water wet chalk core. It confirms that the core wetting is on the oil wet side.

6.2.2 Adsorption of polar organic components: initially 10% water saturation core.

The core SK-10 with Swi=0.1 was flooded 15PV with crude oil (RES40-0.4) at 50°C.The results of adsorption of acidic and basic material onto the outcrop chalk core are shown in figure 6.8.

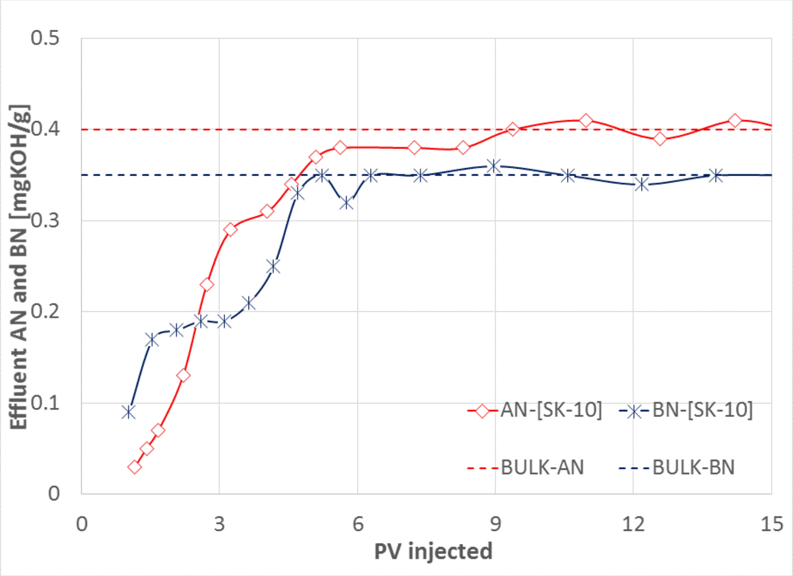


Figure 6.8: The adsorption of polar organic material during oil flooding with Res40-0.4 containing AN=0.40 mgKOH/g and BN=0.35 mgKOH/g. The chalk Core-SK10 was flooded at 50°C with a flow rate of 0.1ml/min. The AN and BN in the effluent samples are presented vs. PV injected.

From beginning, the effluent AN is very low and close to zero. There is a sharp rise to AN=0.38 (mgKOH/g) after 5 PV injecting. Continuing flooding, the AN increases towards the originally injected value of 0.40 when is reached at 9 PV. Total area is determined by trapezoidal method; AN_{ads} [SK-10]=1.33 (PV*mgKOH/g).

The first effluent BN is close to 0.1(mgKOH/g) and there is a gradual rise in effluent BN value and the adsorption equilibrium of basic crude oil components onto the chalk surface is reached after 5 PV.

Oil recovery and wettability on initially 10% water saturation core

After the crude oil injection (15PV) the core SK-10 was aged for 14 days. Spontaneous imbibition test was performed, as shown in figure 6.9

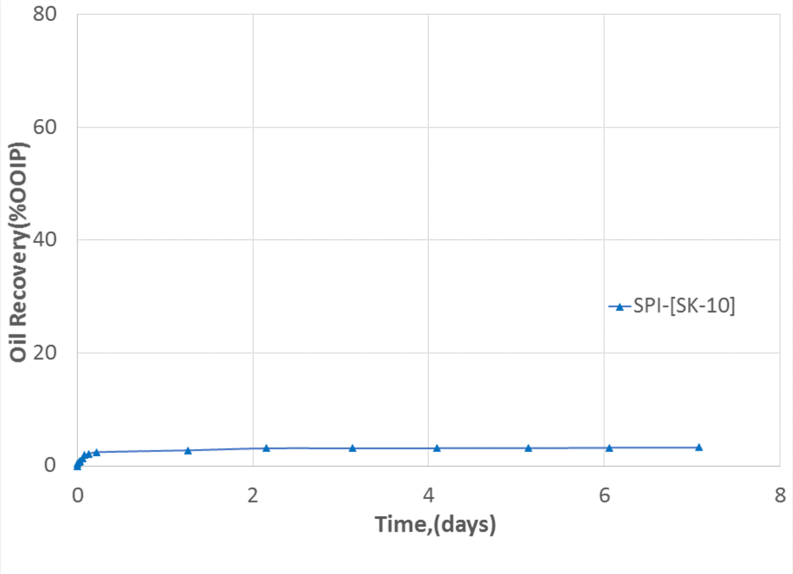


Figure 6.9: Oil Recovery on core SK-10 by spontaneous imbibition using VB0S as imbibing fluid. The SPI test was performed at 50 ˚C.

The oil recovery of SK-10 is a little higher than SK-0. The recovery plateau is established at 3.3% after 2 days while the recovery was 2.2% for core SK-0.

When the oil recovery plateau was reached by spontaneous imbibition, a forced imbibition experiment with VB0S was started. The core SK-10 produced 55 % OOIP at injection rate of 1 PV/D as presented in figure 6.10.

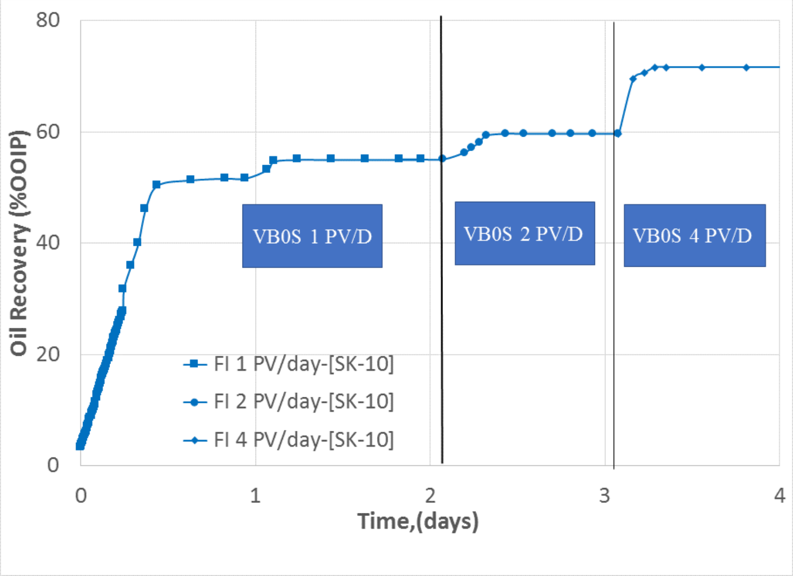


Figure 6.10: Oil recovery test at 50 ˚C on core SK-10, the core was flooded with VB0S at a rate of 1 PV/D After the oil recovery plateau was reached, the injection rate was increased 2 PV/D and 4 PV/D.

The ultimate oil recovery of 55 % at 1PV/D is close to the recovery observed in SK-0 which was 50 %. The injection rate was then changed to 2 PV/day, and the core produced around 5 % extra oil, resulting in overall recovery of 60 % OOIP with an injection rate of 4 PV/D the recovery reached 71 % OOIP.
Total oil production for core SK-10 was 20.24 ml. The spontaneous and forced imbibition results are presented together in figure 6.11.

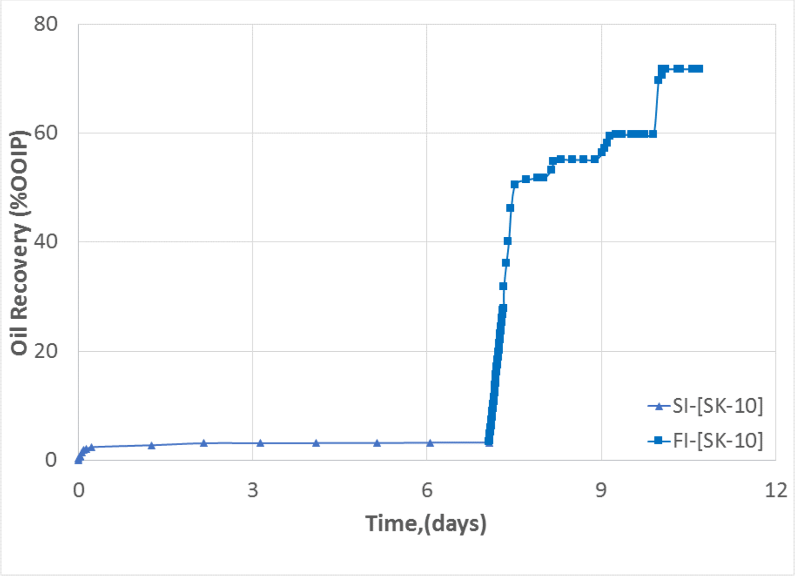


Figure 6.11: Oil recovery after both spontaneous imbibition and forced imbibition with VB0S on core SK-10. The experiments were performed at 50 ˚C

Chromatographic Wettability test SK-10

After the forced imbibition experiment, chromatographic wettability test was performed on core SK-10. The experiment was conducted at 50° degree. The results are presented in figure 6.12

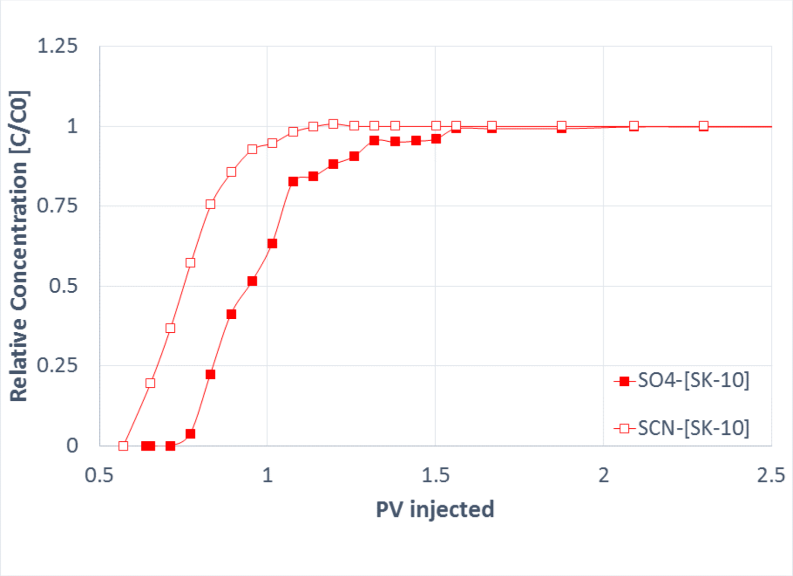


Figure 6.12: Chromatographic wettability test performed at 50° C on core SK-10. The core was flooded at a rate of 0.1 ml/min with SW0T - SW½T.The relative effluent concentrations of SCN- and SO_4^{2-} are plotted vs. PV injected.

The area between tracer and sulphate curves were A_{wet}=0.20 with is much larger than observed for core SK-0 which was only A_w=0.09. This indicates that a core with 10% initial water saturation adsorbs less polar components and behaves somewhat more water wet, as observed specifically regarding water wet surface area but also indicated by SPI tests on core SK-0 and SK-10.

6.2.3 Adsorption of polar organic components: initially 100 % water saturation core.

During the oil flooding, the brine produced fluid was FW, by a period with both oil and water after 0.4 PV injected as presented figure 6.13. After 0.8 PV injected, only oil was produced with S_{wr}=0.3. After 1.7 PV, S_{wr}=0.25 was established.

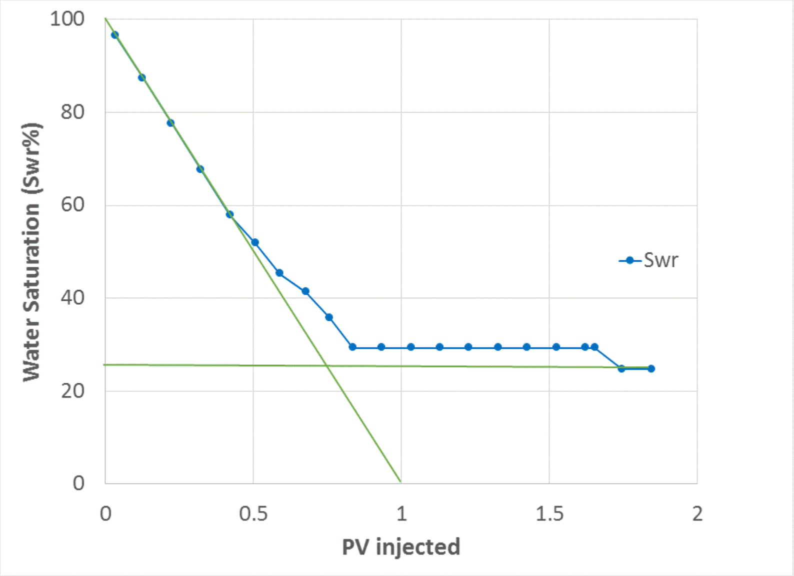


Figure 6.13: Water Saturation in SK-100 during oil injection

The core SK-100, water saturation decreases gradually to 0.30 after 0.8 PV injected and initially Swi=0.25% after 1.8 PV injected. The effluents were analyzed in measurement AN and BN and the results are shown in figure 6.14.

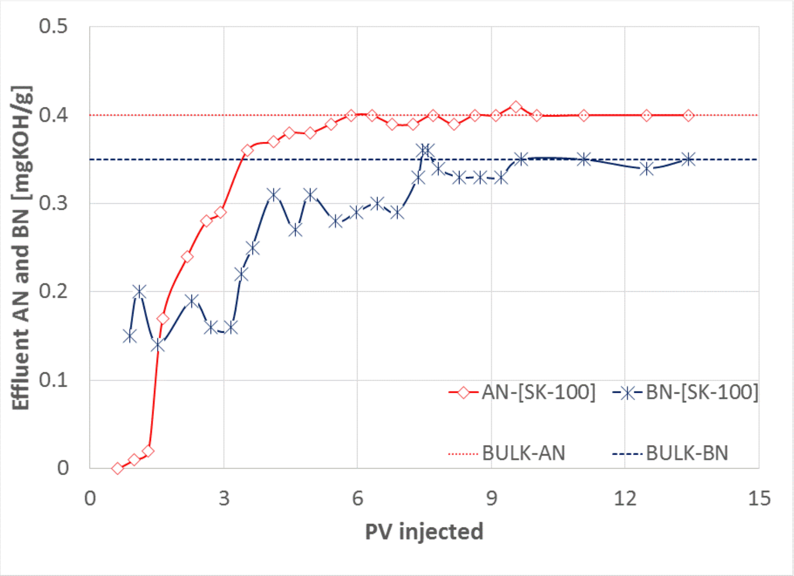


Figure 6.14: The adsorption of polar organic material during oil flooding with Res40-0.4 containing AN=0.40 mgKOH/g and BN=0.35 mgKOH/g. The chalk Core-SK100 was flooded at 50°C with a flow rate of 0.1ml/min. The AN and BN in the effluent samples are presented vs. PV injected.

Th first effluent oil sample has an AN=0 after 0.62 PV injected and the AN increase steadily to the injecting value. Moreover, the adsorption equilibrium is reached after 6 PV flooded which are earlier compared to the other cores and the total adsorption area is lower than in the two previous cores: The calculated area is ANads=0.92 (PV*mgKOH/g).

The effluent BN starts close to 0.15 (mgKOH/g) for the first 3 PV, and increases gradually towards injected value. After 7.5 PV, following the same behavior as the two previous cores.

Oil recovery and wettability on initially 100% water saturation core

The core SK-100 had the highest SPI and behaved somewhat more water-wet than other 2 cores and imbibed 9.30% OOIP as shown in figure 6.15

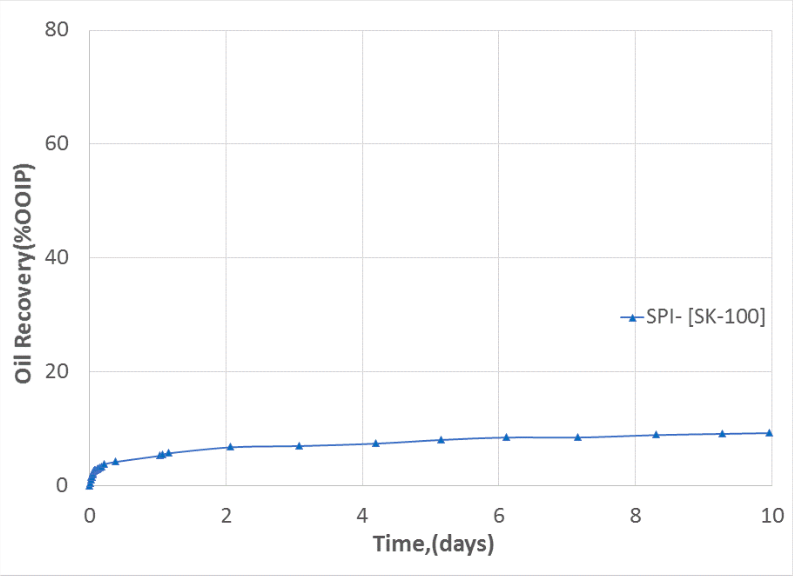


Figure 6.15: Oil Recovery on core SK-100 by spontaneous imbibition using VB0S as imbibing fluid. The SPI test was performed at 50 ˚C.

After spontaneous imbibition, forced imbibition with VB0S brine was performed. As seen in figure 6.16, the oil recovery reaches a plateau of 56% OOIP with an injection rate of 1 PV/D. After increasing injection rate to 2 PV/day and 4 PV/day an ultimate recovery of 71% OOIP was reached which was the same recovery as observed for core SK-10 core.

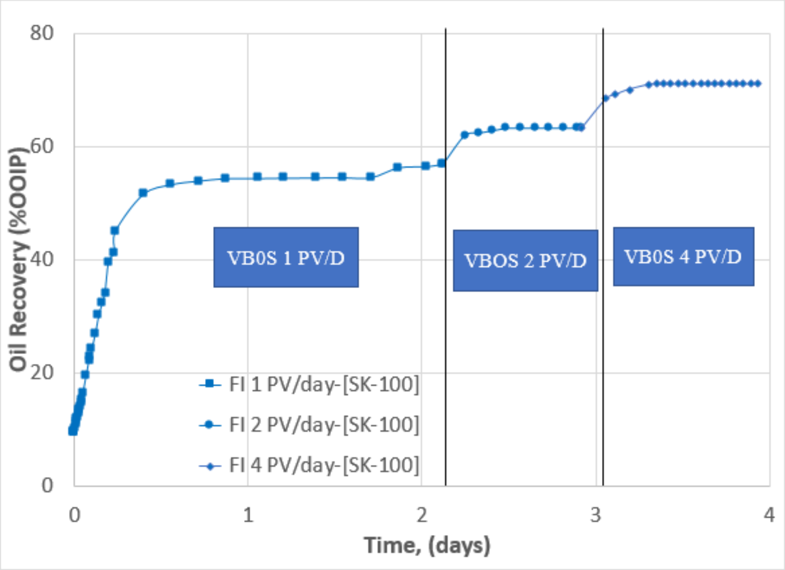


Figure 6.16: Oil recovery test at 50 ˚C on core SK-100, the core was flooded with VB0S at a rate of 1 PV/D After the oil recovery plateau was reached, the injection rate was increased 2 PV/D and 4 PV/D.

Overall, the spontaneous and forced imbibition recovered a total 28.78 ml oil, which was matching 71 % of OOIP. The figure 6.17 shows the spontaneous and forced imbibition results.

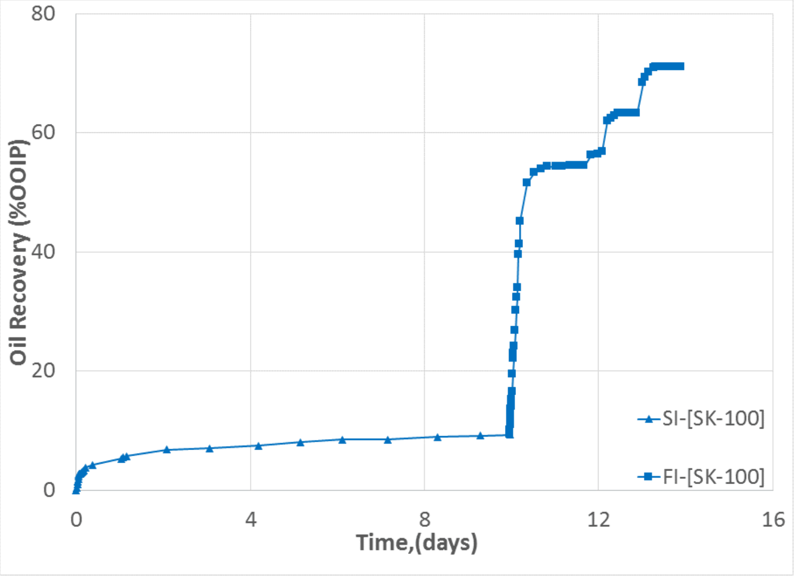


Figure 6.17: Oil recovery after both spontaneous imbibition and forced imbibition with VB0S on core SK-100. The experiments were performed at 50 ˚C.

Chromatographic Wettability test SK-100

The chromatographic wettability test was performed after FI test which is presented in figure 6.18. The test was performed at 50°C. The area between the tracer and sulphate curve was calculated to $A_W = 0.22$.

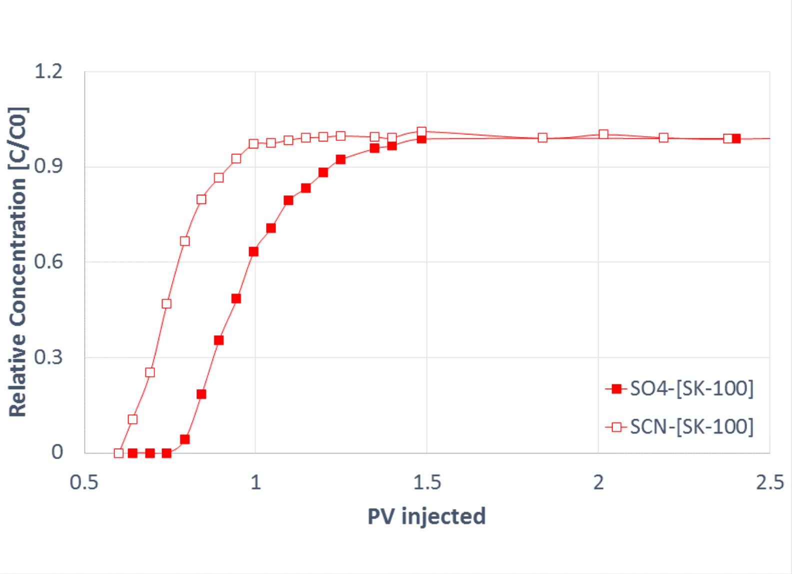


Figure 6.18: Chromatographic wettability test performed at 50°C on core SK-100. The core was flooded at a rate of 0.1 ml/min with SW0T - SW½T.The relative effluent concentrations of SCN- and SO_4^{2-} are plotted vs. PV injected.

The results confirm that the water wet surface area was somewhat larger than for core SK-10, but much larger compared to SK-0.

7. Discussion of the results

7.1 Adsorption of acidic polar organic components onto chalk surfaces

The results from adsorption tests are compared in Figure 7.1. All tests were carried out at the same temperature, but at different initial water saturations core. All tests illustrate the same trend, with strong adsorption of acidic components. The AN in oil effluents starts off near zero and increases gradually to the initial value of AN=0.4 mgKOH/g.

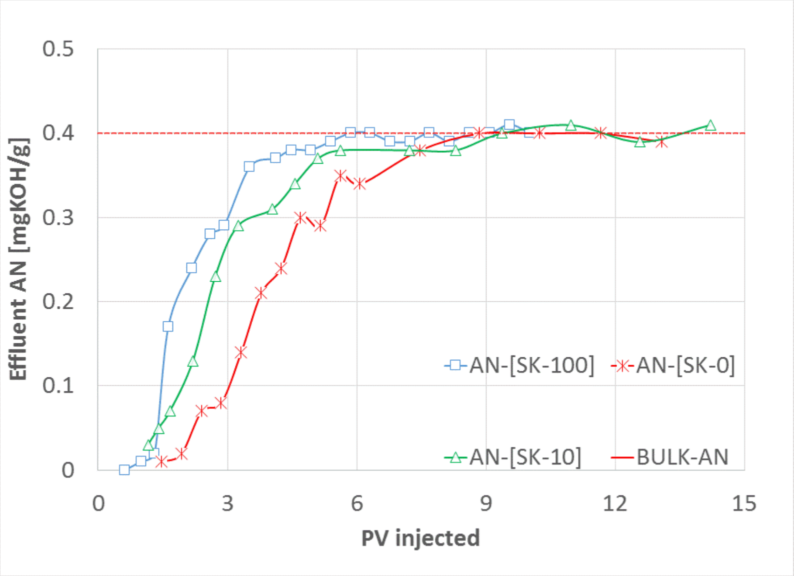


Figure 7.1: Comparing AN measurement for three chalk cores at 50°C.

The core with Swi=0 adsorbs most polar components and the adsorption decreases with increasing Swi. By increasing Swi, the sites at the rock surface available for adsorption seem to be reduced as shown in table 7.1.

Table 7.1: Adsorption of Acidic Polar Components

Core	**SK-0**	**SK-10**	**SK-100**
Swi	0	10	25*
AN_{ads}	1.51	1.33	0.92

7.2 Adsorption of basic polar organic components onto chalk surfaces

Base Number (BN) measurement illustrates a smaller variation compared to the adsorption of acidic components as presented in figure 7.2.

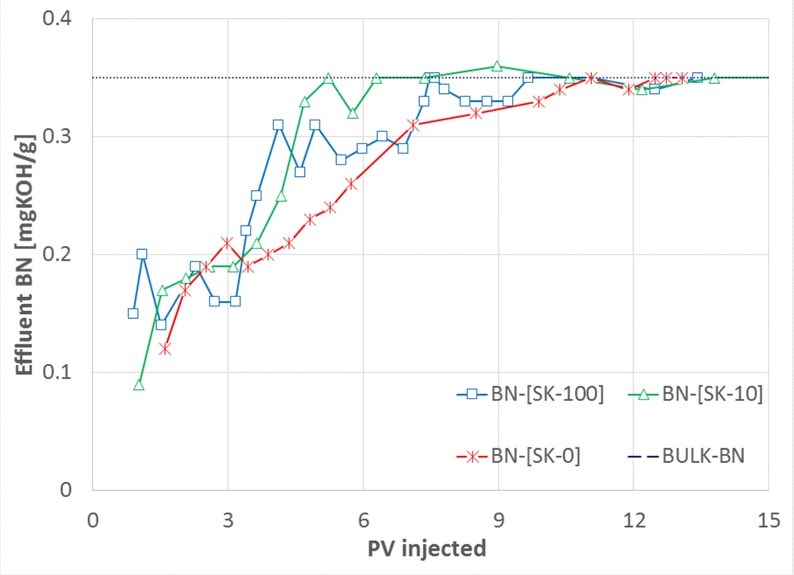


Figure 7.2: Comparing BN measurement for three chalk cores at 50°C

The Acid adsorption is function of Swi and easily available sites on the rock surface, which is not the case for base adsorption. It confirms that the observed base adsorption could be linked to acid/base molecule interaction instead of direct adsorption to positive charged mineral surface. At alkaline conditions, non-charged base components should not have large affinities towards positive charged mineral sites [53]**.** The BN_{ads} is presented in table 7.2.

Table 7.2: Adsorption of Basic Polar Components

Core	**SK-0**	**SK-10**	**SK-100**
Swi	0	10	25*
BN_{ads}	1.20	0.93	1.04

7.3 Oil Recovery by spontaneous and forced imbibition

After flooding the chalk cores with 15 PV crude oil and establishing an adsorption equilibrium with basic and acidic components, all cores had fractional wetting close to neutral. The core with highest Swi adsorbed least amount if acidic components and behaved most water wet, based on SPI tests. The core with Swi=0 adsorbed most acidic components and imbibed least amount of oil as shown in figure 7.3**.**

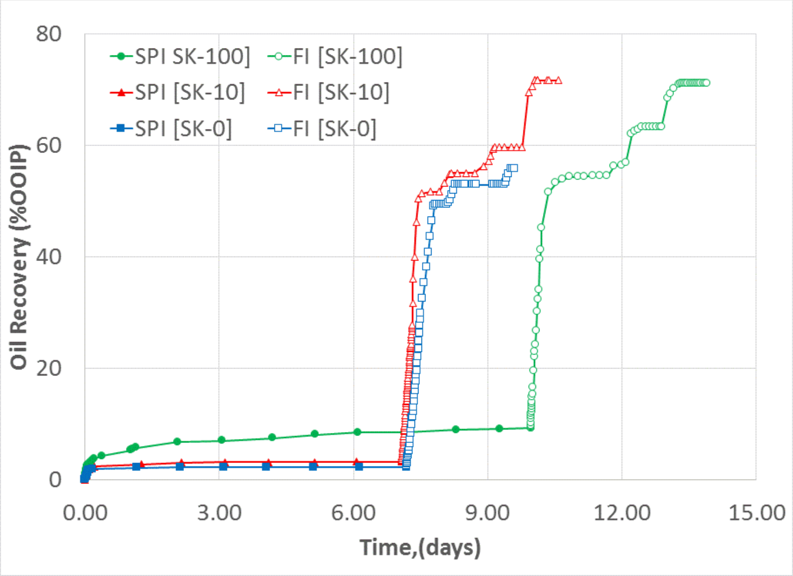


Figure 7.3: Spontaneous and forced imbibition of three cores

FI tests on all cores using VB0S which should not promote any wettability alterations, gave oil recovery of 50-56% OOIP for all 3 cores at a rate of 1PV/D. The cores SK-10 and SK-100 that adsorbed less polar components gave the highest ultimate oil recovery when injection rate was increased ,71% OOIP.

7.4 Chromatographic wettability test

The chromatographic wettability test quantifies the water wet surface (Aw) inside a core. The Aw is dependent on water wet surface area but also test temperature and the composition of the tracer brine system. The chromatographic tests were performed at 2 different temperatures in this study, and were able to compare the results and convert them to WI, Aref values for completely water wet cores at 50° C have been estimated. Based on results from both published and nonpublished work, Aref value at 50° C has been estimated for SW0T/SW1/2T brine system. The measured results are presented in table 7.3.

Table 7.3: Aw water wet core with SW0T/SW1/2T and SW0T/SW1T different temperature

Temperature	**Aw water wet core**	
	SW0T/SW1/2T	**SW0T/SW1T**
20° C	0.256	0.190
40° C		0.223
70° C		0.304

The estimated Aref at 50° C, for SW0T/SW1/2T is shown in figure 7.4.

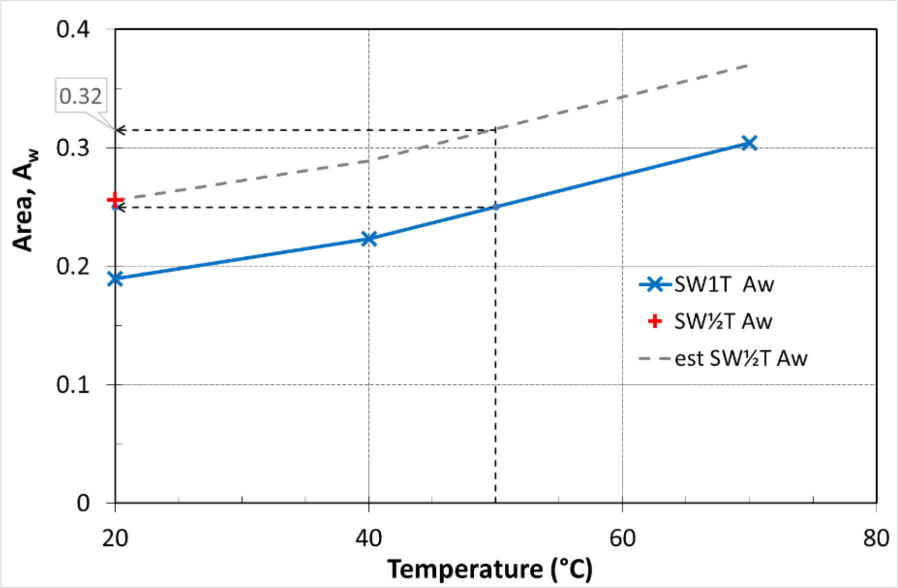


Figure 7.4: Average area for core REF2 at 50°C

Knowing that, the completely water wet SK core has A_{ref} = 0.256 and A_{ref} = 0.32 at 25°C and 50°C degree respectively, a Wetting Index (WI) WI = A_w/A_{ref} for each core can be calculated as shown in table 7.4

Table 7.4: WI for three cores and corresponding wettability

Core	Aw	Temperature	Aref	WI	Wettability
SK-0	**0.09**	**25°**	**0.256**	**0.35**	**More oil wet**
SK-10	**0.20**	**50°**	**0.320**	**0.62**	**Slightly water wet**
SK-100	**0.22**	**50°**	**0.320**	**0.69**	**More water wet**

Based on the results from chromatographic test the SK-0 core that adsorbed most polar components and hardly imbibed any water should behaved more oil wet. Core SK-10 and SK-100 have much higher water wet surface area that could explain a higher ultimate oil recovery with high injection rates.

Previous studies carried out by Wakwaya (MSc 2016) and Layti (BSc 2015), demonstrated that 0% and 10% initial water saturation cores injected with 15 PV of crude oil (RES40, AN = 0.34) towards one direction. The result shows in the table 7.5. SK1=Wakwaya (MSc 2016) and SK2=Layti (BSc 2015)

Table 7.5: Comparison at 0% and 10% initial water saturation.

Test	Aw	Aref	WI new	Wettability
SK- 0	**0.09**	**0.256**	**0.32**	**More oil wet**
SK1-(Swi=0%)	**0.09**	**0.2302**	**0.382**	**More oil wet**
SK- 10	**0.20**	**0.32**	**0.62**	**Slightly water wet**
SK2-(Swi=10%)	**0.15**	**0.255**	**0.58**	**Slightly water wet**

Additionally, it is significant to emphasized that core with 10% initial water saturation the core Swi=10% was done by ion chromatography tests at ambient temperature as opposed to my experiment. It would be interesting to see corresponding result on the wetting index for SK-10 and SK-100 at ambient temperature. PhD student Jon Endre Slejeset has the credit for carrying out my experiment on the Chromatographic wettability test.

7.5 Summary

15 PV of crude oil is flooded at 50 °C into outcrop chalk with different initial water saturation of 0%, 10% and 100% and the adsorption of acidic polar components onto chalk was monitored during injecting. The wettability inside the cores was analyzed by spontaneous, forced imbibition and ion-chromatography. The outcomes from this research are summarized in the following table 7.6.

Table 7.6: Summary of the experimental results

Core	**AN_{ads}**	**SPI [%OOIP]**	**Oil Recovery [%OOIP] 1 PV/D**	**Ultimate oil Recovery [%OOIP] 4 PV/D**	**WI**	**Wettability**
SK-0	**1.51**	**2.2**	**50**	**55**	**0.35**	**More oil wet**
SK-10	**1.33**	**3.3**	**55**	**71**	**0.62**	**Slightly water wet**
SK-100	**0.92**	**9.3**	**56**	**71**	**0.69**	**More water wet**

Chalk cores SK=0 and SK=10 should very low recovery by SPI, which could be explained by thermal expansion of oils are close to $1*10^{-3}$/°C. When the core is heated from ambient to 50°C should expect an oil expansion of 2-3 % OOIP. The water-wet area that was obtained from the chromatographic wettability tests, indicated that cores SK-100 and SK-10 was water-wet in comparison to the SK-0.

Conclusion

1. The cores wettability is dramatically effected by crude oil containing polar organic components.
2. The adsorption of polar components happens immediately.
3. By increasing Swi, the total adsorption of Acidic polar components reduced.
4. The cores initially 100% saturation core behaved more water wet with increasing Swi, confirmed by both SPI and chromatographic wettability test.
5. The core without Swi adsorbed most polar components, did not imbibe oil and behave oil wet based on the chromatographic wettability test.
6. The oil recovery at low injection rate did not differentiate between oil wet cores, and cores that are mixed wet or slightly water wet.
7. The most water wet cores showed highest ultimate oil recoveries with increased injection rates.

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Appendix A Laboratory Apparatus and Their Uses

A.1 Automatic titrator

Mettler Toledo DL55 auto-titrator which was shown in figure A.1 was used in measurement of oil sample Acid and Base Number and applied the modified versions of ASTM D2896 for base number (BN) and ASTM D664 for acid number (AN) titration developed by Fan and Buckley [52].Titration solvent and spiking solution are required to measure for Acid and Base number. Chemical description each AN and BN show the table A.1.1 and table A.1.2.

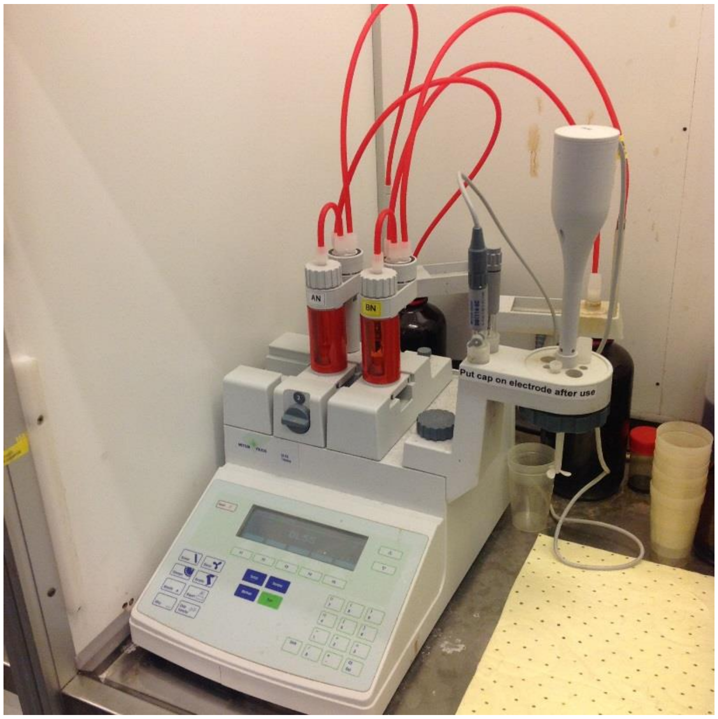

Figure A.1: Illustration of Mettler Toledo DL55

A.1.1 Calculations

The molarity concentration of titrant (CKOH) is evaluated as;

$$\mathrm{C_{KOH}}\,[\,\mathrm{mol}\,/\mathrm{L}] = 1000 * \frac{W_{KHP}[\mathrm{g}]}{204.23 V_{st}[\,\mathrm{ml}]} \tag{A.1.1}$$

Where, W_{KHP} is weight (grams) of KHP in 50 ml of standard solution, and V_{st} is volume titrant used to neutralize the standard solution. The constant 204.23 is molar mass (grams/mole) of KHP, while 1000 is a conversion factor from milligrams to grams. Next, the acid number (AN) is calculated as follows;

$$\mathrm{AN}\,[\,\mathrm{mol\ KOH/g}] = \frac{[\,\mathrm{V_t} - \mathrm{V_b}]\mathrm{C_{KOH}}56.1}{w_{Oil}} \tag{A.1.2}$$

V_t is the amount (ml) of the titrant required to neutralize the crude oil and V_b is the amount needed to equilibrate the blanks. W_{Oil} is weight of oil used and the number 56.1 is molar mass of KOH. The method of BN measurement is the similar calculation as AN measurement but only difference can be seen in the experimental materials.

Chemical and Physical Analysis

A.1.1 Acid Number solutions

Table A.1.1: Chemicals for AN measurements

Solution	Chemicals	Chemical Formula	Description
Titrant	Potassium Hydroxide 2-propanol	KOH>85% $CH_3CHOHCH_3$	2.8g KOH dilute to 1000 ml with 2-propanol
Spiking Solution	Stearic acid Acid titration solvent	$CH_3(CH_2)_{16}COOH$	0.5g Stearic acid dilute to 100 ml with acid titration solvent
Standard Solution	Potassium Hydrogen Phthalate (KHP) DI-water	$HOOCC_6H_4COOK$	0.2g KHP diluted to 500 ml with DI-Water
Titration Solvent	DI-water 2-propanol (HPLC) Toluene (HPLC)	$CH_3CHOHCH_3$ $C_6H_5CH_3$	6 ml DI-Water with 494 ml 2-propanol and with 500 ml Toulene
Electrode Electrolyte	Potassium chloride DI-water	KCl	Mettler DG-114 3M KCl in DI water

A.1.2 Base Number solutions

Table A.1.2: Chemicals for BN measurements

Solution	Chemicals	Chemical Formula	Description
Titrant	Perchloric acid Acetic anhydride Acetic acid	$HClO_4$ (70%) $(CH_3CO)_2O$ $CH_3CHOHCH_3$	5mlHClO4, 15ml(CH3CO)2O diluted to 1000 ml with Acetic acid
Spiking Solution	Quinoline Decane	C_9H_7N $CH_3(CH_2)_8CH_3$	0.5g Quinoline dilute to 100 ml with Decane
Standard Solution	Potassium Hydrogen Phthalate (KHP) Acetic acid	$HOOCC_6H_4COOK$ $CH_{33}COOH$	0.2 g KHP dilute to 250 ml with Acetic Acid
Titration Solvent	Methyl Isobutyl Ketone (MIBK)	$CH_3CHCH_2COHCH_3$	provided in the lab
Electrode Electrolyte	sodium perchlorate 2-propanol	$NaClO_4$ $CH_3CHOHCH_3$	Mettler DG-113 saturated sodium perchlorate in 2-propanol

A.2 Centrifuge

The Centrifuge was used to separate unconsolidated particles from the crude oil samples. Centrifugal force was applied the centrifuge when rotating at great speed and the particles were arranged due to gravity.

Figure A.2: Illustration of the centrifuge

A.3 Filtration pump

The crude oil and brines were filtered through a 0.65µm and 0.22µm Millipore filters respectively. The Filtration process is to remove undissolved salts and large particle impurities from the brine which may block the chalk core pore throats during flooding.

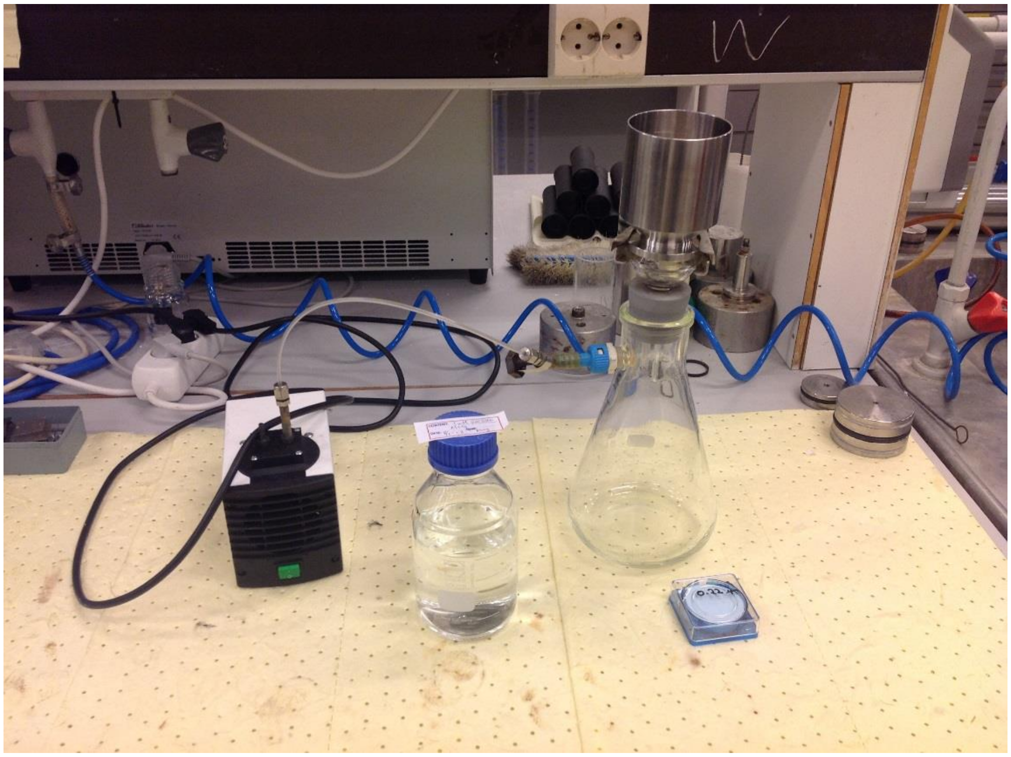

Figure A.3: Illustration of filtration setup

A.4 Vacuum pump

Vacuum pump was used to saturate the cores with formation water to establish initial water saturation. Before saturation process, the core was placed in a vacuum pump and evacuated to eliminate any trapped fluids inside the sealed volume.

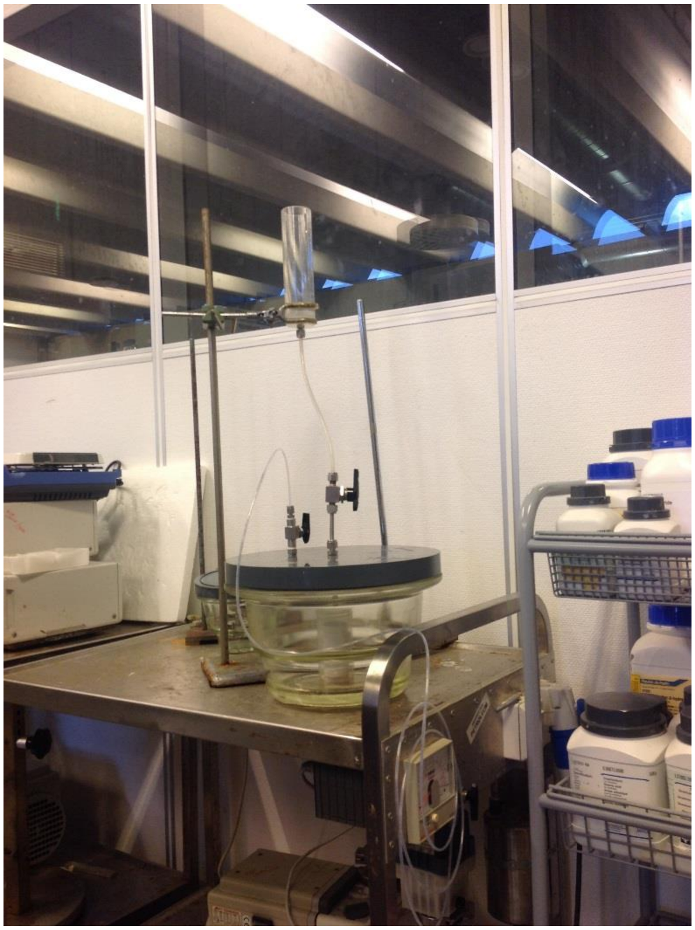

Figure A.4: Illustration of Vacuum pump

A.5 Desiccator

Desiccator with silica-gel was used to establish 10% initial water saturation of the core.
The core was placed in a desiccator with silica gel and water was evaporated by silica gel as an adsorbent. The amount of water vaporized depended on the quantity of silica adding, because if the silica was altered very often, it led to reach the core 10% initial water saturation (Swi=10%) with VB0S in a short time.

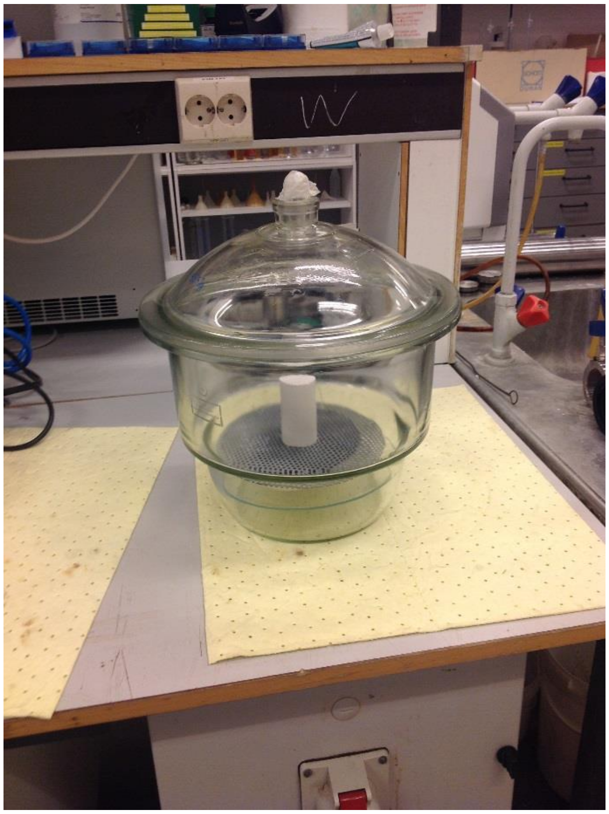

Figure A.5: Illustration of the desiccator

A.6 Density Instrument

The fluids density was measured using Anton Paar DMA 4500 density meter as shown figure A.6 at 20°C. Initially, the apparat was cleaned with spirit and following acetone. Next, the small amount brine and oil sample was injected into tube and the density was determined.

Figure A.6: Illustration of Anton Paar DMA 4500

A.7 Hassler core holder

It was used for core cleaning procedure. The chalk core was placed in a protective rubber sleeve in a central position and mounted inside the Hassler core holder as illustrated in figure A.7.

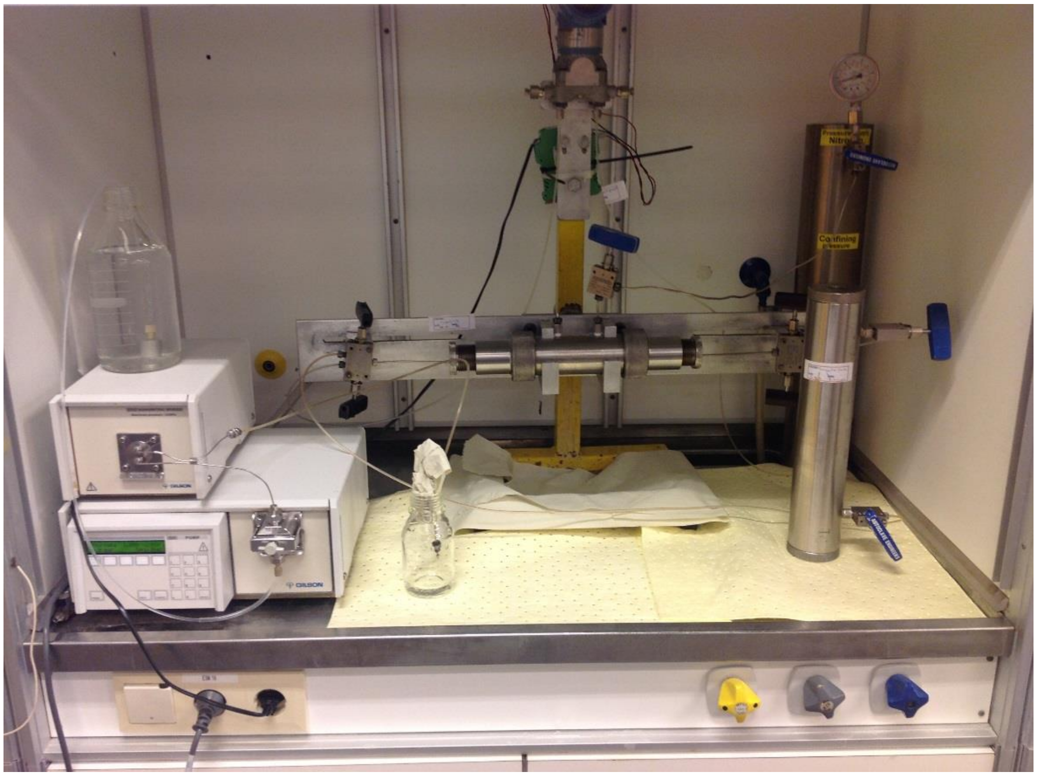

Figure A.7: Illustration of Hassler Core holder

Appendix B

Experimental data

Table B.1: **Acid Number and Base Number data SK-0**

PV (AN)	AN	PV (BN)	BN
0.48	0.01	1.59	0.12
0.93	0.02	2.05	0.17
1.40	0.07	2.51	0.19
1.85	0.08	2.97	0.21
2.32	0.14	3.43	0.19
2.78	0.21	3.89	0.20
3.24	0.24	4.36	0.21
3.70	0.30	4.81	0.23
4.16	0.29	5.27	0.24
4.62	0.35	5.73	0.26
5.08	0.34	7.11	0.31
6.46	0.38	8.51	0.32
7.85	0.40	9.90	0.33
9.25	0.40	10.37	0.34
10.65	0.40	11.06	0.35
12.08	0.39	11.89	0.34
12.32	0.39	12.48	0.35

Table B.2: Acid Number and Base Number data SK-10

PV (AN)	AN	PV (BN)	BN
1.16	0.03	1.03	0.09
1.41	0.05	1.54	0.17
1.67	0.07	2.07	0.18
2.21	0.13	2.59	0.19
2.72	0.23	3.11	0.19
3.24	0.29	3.64	0.21
4.04	0.31	4.17	0.25
4.57	0.34	4.70	0.33
5.10	0.37	5.23	0.35
5.63	0.38	5.77	0.32
7.23	0.38	6.30	0.35
8.29	0.38	7.36	0.35
9.37	0.4	8.97	0.36
10.97	0.41	10.57	0.35
12.58	0.39	12.18	0.34
14.21	0.41	13.80	0.35
15.42	0.4	15.42	0.35

Table B.3: Acid Number and Base Number data SK-100

PV (AN)	AN	PV (BN)	BN
0.63	0	0.89	0.15
1.00	0.01	1.10	0.20
1.31	0.02	1.52	0.14
1.63	0.17	2.29	0.19
2.18	0.24	2.71	0.16
2.61	0.28	3.16	0.16
2.92	0.29	3.40	0.22
3.52	0.36	3.64	0.25
4.12	0.37	4.12	0.31
4.48	0.38	4.60	0.27
4.94	0.38	4.94	0.31
5.40	0.39	5.51	0.28
5.86	0.40	5.98	0.29
6.32	0.40	6.43	0.30
6.78	0.39	6.89	0.29
7.24	0.39	7.35	0.33
7.69	0.4	7.47	0.35
8.16	0.39	7.81	0.34
8.63	0.40	8.28	0.33
9.10	0.40	8.75	0.33
9.56	0.41	9.21	0.33
10.01	0.40	9.67	0.35
11.07	0.40	11.07	0.35
12.47	0.40	12.47	0.34
13.42	0.40	13.42	0.35

Spontaneous and Forced imbibition data

Table B.4: Spontaneous imbibition SK-0 T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
15-Apr	12:48	0.0	0.00	0.00	0.00
15-Apr	13:08	0.3	0.01	0.05	0.14
15-Apr	13:18	0.5	0.02	0.10	0.28
15-Apr	13:30	0.7	0.03	0.20	0.55
15-Apr	13:50	1.0	0.04	0.24	0.66
15-Apr	14:00	1.2	0.05	0.30	0.83
15-Apr	14:10	1.4	0.06	0.40	1.10
15-Apr	14:25	1.6	0.07	0.45	1.24
15-Apr	14:35	1.8	0.07	0.50	1.38
15-Apr	14:45	2.0	0.08	0.60	1.65
15-Apr	15:00	2.2	0.09	0.65	1.79
15-Apr	17:00	4.2	0.18	0.70	1.93
16-Apr	16:44	27.9	1.16	0.80	2.21
17-Apr	16:00	51.2	2.13	0.81	2.23
18-Apr	15:33	74.7	3.11	0.81	2.23
19-Apr	14:33	97.7	4.07	0.81	2.23
20-Apr	15:30	122.6	5.11	0.81	2.23
21-Apr	16:30	147.6	6.15	0.81	2.23
22-Apr	17:30	172.6	7.19	0.81	2.23

Table B 5: Force imbibition SK-0, 1 PV/day q=0.025 ml/min T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
24-Apr	12:40	0.000	0.00	0.81	2.23
24-Apr	14:13	0.550	0.02	1.41	3.89
24-Apr	14:20	0.667	0.03	1.51	4.16
24-Apr	15:00	1.333	0.06	1.91	5.26
24-Apr	15:30	1.833	0.08	2.31	6.37
24-Apr	15:45	2.083	0.09	2.61	7.19
24-Apr	16:00	2.333	0.10	3.01	8.30
24-Apr	16:15	2.583	0.11	3.31	9.12
24-Apr	17:00	3.333	0.14	4.11	11.33
24-Apr	17:15	3.583	0.15	4.41	12.16
24-Apr	17:45	4.083	0.17	5.11	14.08
24-Apr	18:00	4.333	0.18	5.51	15.19
24-Apr	18:45	5.083	0.21	6.41	17.67
24-Apr	19:00	5.333	0.22	6.81	18.77
24-Apr	19:15	5.583	0.23	7.11	19.60
24-Apr	19:30	5.833	0.24	7.61	20.98
24-Apr	19:45	6.083	0.25	8.01	22.08
24-Apr	20:00	6.333	0.26	8.51	23.46
24-Apr	20:30	6.833	0.28	9.51	26.21
24-Apr	21:00	7.333	0.31	10.41	28.69
24-Apr	22:15	8.583	0.36	11.81	32.55
24-Apr	23:15	9.583	0.40	12.81	35.31
25-Apr	0:15	10.583	0.44	13.81	38.07
25-Apr	1:15	11.583	0.48	14.81	40.82
25-Apr	2:15	12.583	0.52	15.81	43.58
25-Apr	3:15	13.583	0.57	16.81	46.33
25-Apr	10:15	20.583	0.86	17.91	49.37

SK-0, 2 PV/day q=0.05 ml/min T=50°C

25-Apr	11:15	21.583	0.90	17.91	49.37
25-Apr	14:00	24.333	1.01	18.51	51.02
25-Apr	15:00	25.333	1.06	18.81	51.85
25-Apr	16:00	26.333	1.10	19.21	52.95

SK-0, 4 PV/day q=0.1 ml/min T=50°C

26-Apr	11:00	52.333	2.18	19.21	52.95
26-Apr	12:00	53.333	2.22	19.31	53.22
26-Apr	12:30	53.833	2.24	19.61	54.05
26-Apr	13:30	54.833	2.28	19.91	54.88
26-Apr	14:30	55.833	2.33	20.21	55.71

Table B.6: Spontaneous imbibition SK-10 T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
7-Apr	11:21	0	0	0	0
7-Apr	11:26	0.1	0	0.1	0.35
7-Apr	11:54	0.6	0.02	0.2	0.7
7-Apr	12:04	0.7	0.03	0.25	0.88
7-Apr	12:44	1.4	0.06	0.4	1.4
7-Apr	13:24	2.1	0.09	0.55	1.93
7-Apr	14:24	3.1	0.13	0.6	2.1
7-Apr	16:34	5.2	0.22	0.7	2.45
8-Apr	17:34	30.2	1.26	0.8	2.8
9-Apr	15:00	51.7	2.15	0.9	3.16
10-Apr	14:34	75.2	3.13	0.9	3.17
11-Apr	13:34	98.2	4.09	0.91	3.18
12-Apr	14:34	123.2	5.13	0.91	3.19
13-Apr	12:43	145.4	6.06	0.93	3.26
14-Apr	13:12	169.9	7.08	0.94	3.3

Table B 7: Force imbibition SK-10, 1 PV/day q=0.022 ml/min T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
15-Apr	14:08	0.000	0.000	3.31	3.33
15-Apr	14:35	0.400	0.017	3.8	5.05
15-Apr	15:10	0.983	0.041	4.54	7.64
15-Apr	15:40	1.483	0.062	5.15	9.78
15-Apr	15:55	1.650	0.069	5.4	10.66
15-Apr	16:05	1.900	0.079	5.7	11.71
15-Apr	16:20	2.067	0.086	6	12.76
15-Apr	16:35	2.400	0.100	6.55	14.69
15-Apr	16:40	2.483	0.103	6.7	15.22
15-Apr	17:05	2.900	0.121	7.35	17.50
15-Apr	17:40	3.400	0.142	8.05	19.95
15-Apr	17:50	3.567	0.149	8.2	20.48
15-Apr	18:15	4.067	0.169	8.8	22.58
15-Apr	18:35	4.400	0.183	9.4	24.68
15-Apr	19:00	4.817	0.201	10	26.79
15-Apr	19:15	4.983	0.208	10.2	27.49
15-Apr	19:30	5.233	0.218	10.6	28.89
15-Apr	19:40	5.400	0.225	10.75	29.42
15-Apr	20:00	5.817	0.242	11.3	31.35
15-Apr	21:00	5.900	0.246	12.6	35.90
15-Apr	22:00	6.900	0.288	14	40.81
15-Apr	23:00	7.900	0.329	15.3	45.37
16-Apr	0:40	8.900	0.371	17.3	52.38
16-Apr	5:20	10.567	0.440	18.7	57.29
16-Apr	16:33	25.617	1.067	19.6	60.45
17-Apr	10:42	39.100	1.629	20.2	62.55

SK-10, 2 PV/day q=0.044 ml/min T=50°C

17-Apr	13:22	43.767	1.824	20.2	62.55
17-Apr	14:22	46.767	1.949	20.6	63.95
17-Apr	15:22	47.767	1.990	20.9	65.00
17-Apr	16:22	48.767	2.032	21.2	66.06
17-Apr	19:00	49.767	2.074	21.6	67.46

SK-10, 4 PV/day q=0.088 ml/min T=50°C

18-Apr	12:30	67.900	2.829	21.7	67.81
18-Apr	13:30	69.900	2.913	22.1	69.21
18-Apr	14:00	70.900	2.954	22.2	69.56
18-Apr	15:00	72.400	3.017	22.5	70.61
18-Apr	17:00	73.900	3.079	22.8	71.06

Table B.8: Spontaneous imbibition SK-100 T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
27-Mar	10:50	0.0	0.00	0.00	0.00
27-Mar	11:00	0.2	0.01	0.10	0.43
27-Mar	11:20	0.5	0.02	0.25	1.07
27-Mar	11:32	0.7	0.03	0.35	1.49
27-Mar	11:52	1.0	0.04	0.45	1.92
27-Mar	12:05	1.3	0.05	0.55	2.35
27-Mar	12:15	1.4	0.06	0.60	2.56
27-Mar	13:00	2.2	0.09	0.65	2.77
27-Mar	13:30	2.7	0.11	0.70	2.99
27-Mar	14:00	3.2	0.13	0.73	3.09
27-Mar	14:30	3.7	0.15	0.75	3.20
27-Mar	15:00	4.2	0.17	0.80	3.41
27-Mar	16:00	5.2	0.22	0.90	3.84
27-Mar	20:00	9.2	0.38	1.00	4.27
28-Mar	11:30	24.7	1.03	1.25	5.33
28-Mar	12:30	25.7	1.07	1.30	5.55
28-Mar	14:30	27.7	1.15	1.35	5.76
29-Mar	12:30	49.7	2.07	1.6	6.83
30-Mar	12:30	73.7	3.07	1.65	7.04
31-Mar	15:30	100.7	4.19	1.75	7.47
1-Apr	14:30	123.7	5.15	1.9	8.11
3-Apr	14:30	171.7	7.15	2.0	8.53
4-Apr	18:00	199.2	8.30	2.1	8.96
5-Apr	17:30	222.7	9.28	2.15	9.17
6-Apr	10:00	239.2	9.97	2.18	9.30

Table B 9: Force imbibition SK-100, 1 PV/day q=0.026 ml/min T=50°C

Date	Time (min)	Time (hrs)	Time (days)	Oil production (ml)	Recovery (%OOIP)
7-Apr	12:06	0.000	0.00	0	9.30
7-Apr	13:06	0.000	0.00	0.04	9.47
7-Apr	13:18	0.200	0.01	0.2	10.15
7-Apr	13:37	0.517	0.02	0.7	12.29
7-Apr	13:53	0.783	0.03	1.1	13.99
7-Apr	14:00	0.900	0.04	1.3	14.85
7-Apr	14:07	1.017	0.04	1.4	15.27
7-Apr	14:19	1.217	0.05	1.7	16.55
7-Apr	14:45	1.650	0.07	2.4	19.54
7-Apr	15:07	2.017	0.08	3	22.10
7-Apr	15:32	2.433	0.10	3.5	24.23
7-Apr	16:00	2.900	0.12	4.1	26.79
7-Apr	16:30	3.400	0.14	4.9	30.20
7-Apr	17:00	3.900	0.16	5.4	32.34
7-Apr	17:20	4.233	0.18	5.8	34.04
7-Apr	17:50	4.733	0.20	7.1	39.59
7-Apr	18:37	5.517	0.23	7.5	41.30
7-Apr	18:50	5.733	0.24	8.4	45.14
7-Apr	22:38	9.533	0.40	9.9	51.54
8-Apr	2:27	13.350	0.56	10.3	53.24
8-Apr	6:14	17.133	0.71	10.45	53.88
8-Apr	10:02	20.933	0.87	10.55	54.31
9-Apr	6:04	40.967	1.71	10.59	54.48
9-Apr	9:52	44.767	1.87	11	56.23

SK-100, 2 PV/day q=0.052 ml/min T=50°C

9-Apr	13:41	48.583	2.02	11.05	56.44
9-Apr	19:00	53.900	2.25	12.35	61.99
10-Apr	8:32	67.533	2.81	12.65	63.27
10-Apr	10:28	69.467	2.89	12.65	63.27

SK-100, 4 PV/day q=0.104 ml/min T=50°C

10-Apr	11:00	70.000	2.92	12.65	63.27
10-Apr	14:21	73.350	3.06	13.85	68.39
10-Apr	15:48	74.800	3.12	14.05	69.24
10-Apr	17:37	76.617	3.19	14.25	70.09
10-Apr	21:24	80.400	3.35	14.46	71.00

Chromatography data

Table B.10: Ion chromatography SK-0 at 25°C

		SO4		SCN	
Sample	PV corrected	C/C0	Area under curve	C/C0	Area under curve
6	0.50	0	0	0	0
7	0.58	0.0000	0	0.4485	0.0179
8	0.60	0.1180	0.001455656	0.6776	0.0084
9	0.66	0.3300	0.008844426	0.8148	0.0218
10	0.71	0.5453	0.014979678	0.8943	0.0246
11	0.77	0.6983	0.018808334	0.9300	0.0250
12	0.82	0.7924	0.021341876	0.9355	0.0252
13	0.88	0.8179	0.023020241	0.9451	0.0266
14	0.93	0.8242531	0.020868662	0.9396	0.0238
15	0.98	0.8386018	0.020667267	0.9629	0.0237
17	1.09	0.8401961	0.046844345	0.9616	0.0536
18	1.25	0.8975909	0.070352186	0.9616	0.0754
19	1.30	0.8975909	0.024538649	0.9849	0.0269
20	1.35	0.9167225	0.025061675	0.9876	0.0270
21	1.41	0.93	0.025077778	1.0000	0.0269
23	1.50	0.9342598	0.044413862	1.0000	0.0475
25	1.69	0.972523	0.09050115	1.0000	0.0931
27	2.25	1.00	0.281733085	1.0000	0.2817
		Total area	0.7384	Total area	0.8292

Area in between two curves
0.09

Table B.11: Ion chromatography SK-10 at 50°C

		SO4		**SCN**	
Sample	PV corrected	C/C0	Area under curve	C/C0	Area under curve
7	0.7	0.000	0	0.3690	0.0110
8	0.8	0.038	0.0011	0.5725	0.0284
9	0.8	0.225	0.0079	0.7564	0.0402
10	0.9	0.412	0.0193	0.8569	0.0490
11	1.0	0.515	0.0292	0.9292	0.0562
12	1.0	0.635	0.0346	0.9488	0.0565
13	1.1	0.826	0.0446	0.9832	0.0590
14	1.1	0.844	0.0505	1.0003	0.0599
15	1.2	0.881	0.0513	1.0003	0.0595
16	1.3	0.907	0.0551	1.0003	0.0617
17	1.3	0.957	0.0569	1.0003	0.0611
18	1.4	0.952	0.0586	1.0003	0.0614
19	1.4	0.955	0.0588	1.0003	0.0617
20	1.5	0.962	0.0579	1.0003	0.0605
21	1.6	0.962	0.0584	1.0003	0.0608
23	1.7	1.000	0.1034	1.0003	0.1055
25	1.9	1.000	0.2084	1.0003	0.2085
27	2.1	1.000	0.2149	1.0003	0.2150
29	2.3	1.000	0.2063	1.0003	0.2064
31	2.5	1.000	0.2143	1.0003	0.2144
		Total area	1.5316	Total area	1.7365

Area in between two curves
0.20

Table B.12: Ion chromatography SK-100 at 50°C

		SO4		SCN	
Sample	PV corrected	C/C0	Area under curve	C/C0	Area under curve
6	0.6	0	0	0	0
7	0.7	0.000	0	0.2529	0.0066
8	0.7	0.000	0.0000	0.4701	0.0177
9	0.8	0.042	0.0011	0.6670	0.0292
10	0.8	0.186	0.0056	0.7980	0.0362
11	0.9	0.355	0.0137	0.8663	0.0422
12	0.9	0.485	0.0217	0.9256	0.0463
13	1.0	0.634	0.0279	0.9726	0.0474
14	1.0	0.708	0.0338	0.9748	0.0491
15	1.1	0.794	0.0379	0.9849	0.0494
16	1.1	0.834	0.0410	0.9927	0.0498
17	1.2	0.883	0.0446	0.9938	0.0516
18	1.2	0.923	0.0448	0.9983	0.0495
19	1.3	0.958	0.0944	0.9950	0.1000
20	1.4	0.967	0.0485	0.9916	0.0501
21	1.5	0.989	0.0857	1.0118	0.0877
23	1.8	0.990	0.3484	0.9905	0.3525
25	2.0	0.990	0.1760	1.0028	0.1771
27	2.2	1.000	0.1738	0.9927	0.1743
		Total area	1.1989	Total area	1.4166

Area in between two curves
0.22