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Abstract

The initial wetting of carbonate reservoirs will affect the overall oil recovery and the potential of EOR methods linked to wettability alteration by the generation of positive capillary pressure. Polar acids in oil also effect the wettability alteration in carbonates.

Adsorption of polar acidic materials from oil onto a chalk surface at different temperatures is the main essence of this work. The role of only temperature, beside acid number, to wettability alteration of chalk is also presented. Crude oil with an AN of 0.35 mgKOH/g is flooded into three cores with 10 % initial water saturation at three different temperatures (50, 90 and 130 ^{0}C). Acid number of the effluent is observed to decrease to a low value for a short time, then increase slowly to the original acid number. The adsorption of acid is more or less equal at 90 and 50^{0}C and slightly lower at 130 ^{0}C. Wettability of the flooded cores were evaluated by spontaneous imbibition and ion-chromatography analysis, and the results show that the cores were more oil-wet. Our experimental results minimizes the effect of temperature on wettability alteration in chalk.

Theoretical understanding of enhanced oil recovery, carbonates and wettability is introduced in chapter 1, and discussed more in chapter 2. In chapter 3 different materials and methods for the experiments are explained. The results of the experiments are presented in chapter 4 and discussed in chapter 5. Finally, the conclusion of the experiments is presented in chapter 6.

Contents

Acknowledgement

I would like to express my greatest appreciation to Skule Strand, for introducing me to the world of "smart water" and enhanced oil recovery, which I am very enthusiastic about and find it very interesting. I would also recommend students at University of Stavanger to write their thesis with Skule Strand, who is very patient, helpful and makes the graphs understandable.

Paul Hopkins has been encouraging me throughout the semester and making AN measurements more interesting and survivable. I wish him and his girlfriend the best and good luck with their works in Stavanger.

I would also sincerely thank professor Tor Austad, that has created interest for "smart water" and EOR for students in his lectures. Further I would like to thank Jose Ferreire, Zahra Aghaeifar and Ivan "El loco" Torrijos for their help and guidance in the laboratory, and I wish them good luck in their works.

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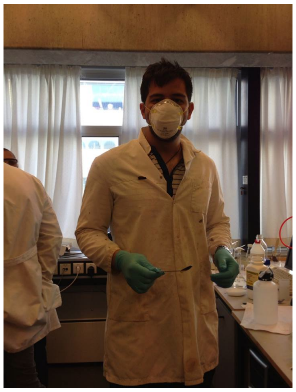

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Chapter 1

Introduction

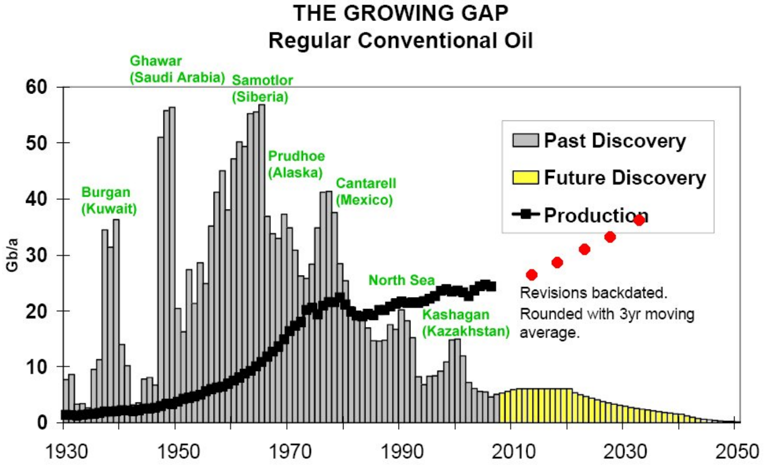

Figure 1.1: Discoveries and oil production since 1930 [44]

The world average oil recovery factor is stuck in the mid-30 per cent range and this comes from mature or maturing oil fields with reserves which does not keep the pace with the growing energy demand. This challenge opens a big room for advanced enhanced oil recovery (EOR) technologies, which might balance the demand-supply relations. [16]

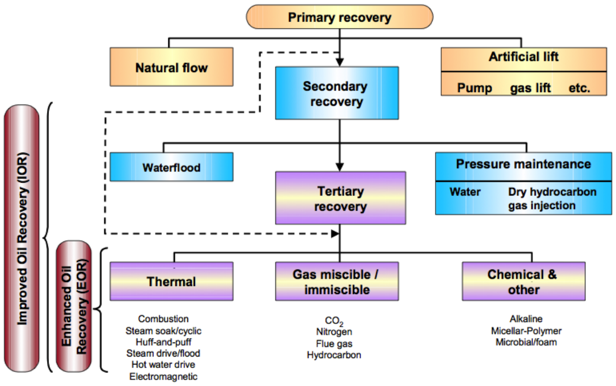

Figure 1.2: Proposed EOR/IOR definitions [31,16]

1.1 Reservoir Production

During oil production primary, secondary and tertiary recoveries covers a process from the start to a point where it is no longer economically feasible to produce hydrocarbons.[16]

Primary Recovery: first crop of oil

The main parameter in this process is the natural energy of the reservoir itself, i.e. primary recovery is the period when production is going on due to pressure decline and the accompanying evolution of dissolved gas, to the expansion of gas cap, or the influx of water. [31]

Secondary Recovery: second crop of oil

When the natural drive energy is no longer sufficient to maintain reservoir pressure, additional energy is required. This energy is usually obtained by injecting water or gas. Thus key element forces are physical, as opposed to thermal, chemical, solvent, interfacial tension, etc. [31] Secondary recovery should not change any property of the reservoir.

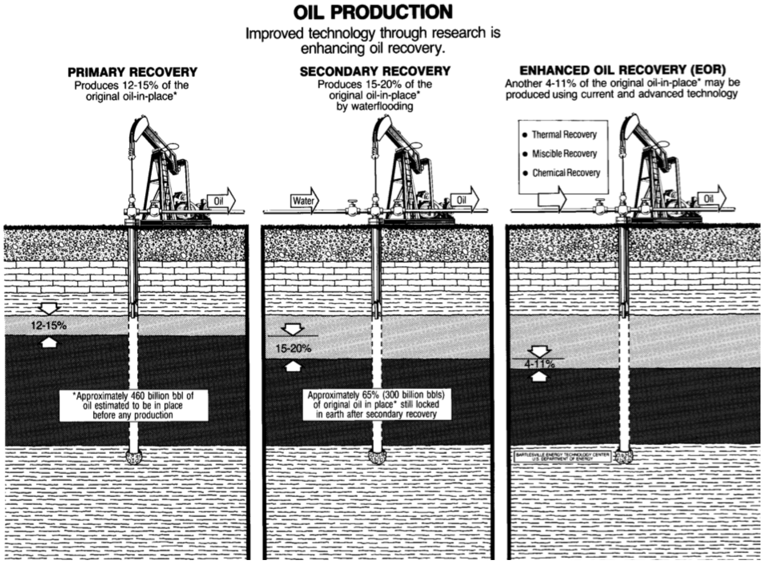

Figure 1.3: Steps in oil recovery, [42]

Tertiary Recovery: third crop of oil or EOR

The goal of tertiary recovery/EOR is to recover oil beyond secondary recovery, or what is left; since average oil recovery from primary and secondary recoveries is 1/3 of the oil originally present in the reservoir. The target using EOR will be then 2/3 of the original oil in place. However only 3.5% of the oil production (about 3 million barrels of oil per day) is obtained by EOR methods. The most popular method is *thermal methods*, which produces 2 million barrels, mainly in Canada (heavy oil), California, Venezuela etc.. CO_2*-EOR* is the second largest EOR method, followed by the *hydrocarbon gas injection* and *chemical* EOR methods. [16] Injection of seawater as a chemical wettability modifier should be categorized as a chemical process. It is an outstanding EOR fluid to chalk, which is discussed in chapter 2.2.1.

Tertiary recovery might be applied as a secondary operation in some cases. This action might be dictated by the nature of the tertiary process, availability of injectants and economical feasibility. For example, if a secondary recovery would diminish the overall efficiency, then secondary recovery might be bypassed. [14]

The recovery efficiency (E) of any EOR process is a function of macroscopic (E_V) and microscopic (E_d) displacement:

$$E = E_V * E_d. \tag{1.1}$$

Microscopic displacement is due to the change in oil saturation where the method has been active, while macroscopic displacement is more of a volumetric parameter and reflects the region the method has been active in. Macroscopic displacement is a product of both vertical and horizontal sweep efficiencies.

Several investigated EOR methods are listed in Table 1.1. Waterflooding is not shown as an EOR method here. But it is counted as an EOR method, since waterflooding might change the chemical equilibrium between crude oil, brine and the rock and improve the microscopic displacement.

EOR method	Authors	Year
Alkaline flooding	Cooke et al.	1974
Surfactants and polymers	Davis and Jones	1968
	Mueke	1979
	Lam et al.	1983
	Arriota	1983
	Hornof and Morrow	1987
	Gray and Dawe	1989
CO2 and other gas injection methods	Wang	1982
	Campbell and Orr	1983
	Orr and Taber	1984
	Bahralolom et al.	1985
	Peden and Husain	1985
	Bahralolom and Orr	1988
Foams	Mast	1972
	Owete	1982
	Wang	1984
	Owete and Bingham	1987
	Radke and Ranshoff	1988
	Huh et al.	1988
	Kuhlman	1988
	Manlow and Radke	1988
	Armitage and Dawe	1989
	Chambers and Radke	1990
Gels	Martin and Kovarik	1987
	Martin et al.	1988
Microbial techniques	Bryant and Doublas	1988
	Bryant et al.	1988

Table 1.1: Micromodel studies of EOR processes [6]

Chapter 2

Basic Principles of EOR in Carbonate Reservoirs

2.1 Carbonate Reservoirs

Secretions and shells from many small lime (CaO)-animals, plants and bacteria that are found in warm shallow water have formed many of the carbonate rocks. Formation occurs either by direct precipitation out of seawater or by biological extraction of calcium carbonate from seawater to form skeletal material. The result is then a very heterogeneous sediment with mixture of a wide range of particle sizes, shapes and mineralogies. [34, 19] [1]

Major minerals found in carbonate rock include calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and minor clay, and by these minerals carbonate reservoirs may be categorized as *limestone* with dominant calcite appearance, and *dolostone* with dolomite. [19, 11, 27]

More than 60% of the worlds oil and 40% of the worlds gas reserves are held in carbonates, which are mostly concentrated in Middle East. [29] The world's largest oil and gas fields which are composed of carbonate rocks are Ghawar Field, Saudi Arabia and South Pars/North Dome field, Iran & Qatar, respectively.

The average recovery for all reservoirs are 35%. However, it is recognized that recovery factors are higher for sandstone reservoirs than for carbonates.

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[1] Figure 2.1 is taken from http://www.slb.com/services

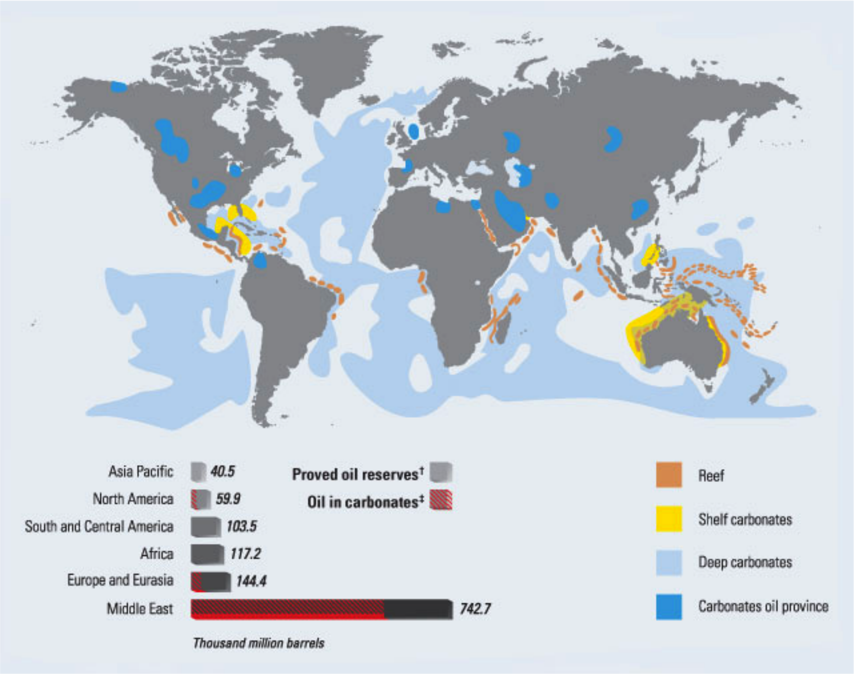


Figure 2.1: Distribution of oil from carbonate sources around the world

(a) The pools of Pamukkale; terraces of carbonate minerals in Turkey. [43]

(b) Scanning electron microscope (SEM) photograph of (Upper Cretaceous) chalk [45]

Figure 2.2: Pictures of carbonates in nature and under microscope

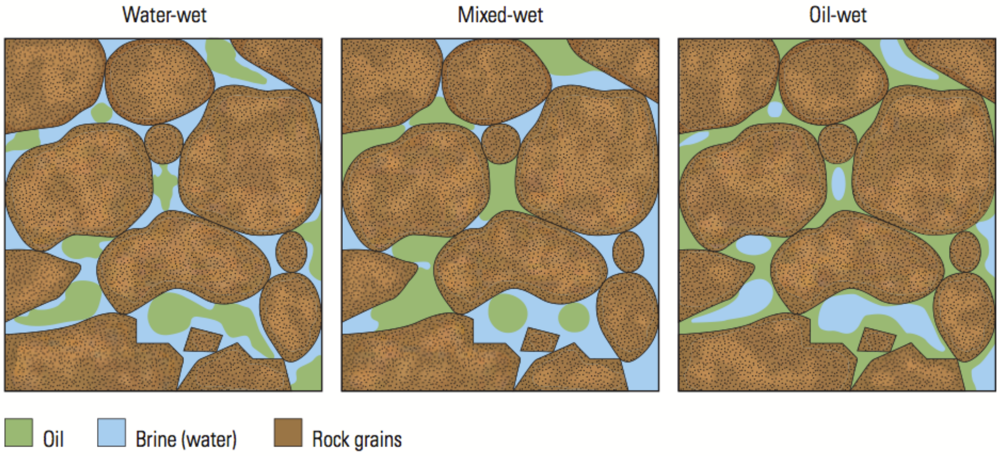


Figure 2.3: Wetting in pores. The three conditions shown have similar saturations of water and oil. [1]

2.1.1 Wettability

Definition

"The wettability of the rock is related to the affinity of its surface for water and/or oil."[9]

Petroleum reservoir is a complex system of several static interactions of water, oil, gas and the rock mineral solids. The combined effect of these interactions controls the saturation distribution and the contacts of fluids in a reservoir, which is an important parameter for the understanding of the reservoir. The *wettability* of a solid can be defined as the tendency of one fluid to spread on, or adhere to, the solid's surface in the presence of another immiscible fluid.

The wettability of a reservoir rock can be estimated quantitatively by measuring an angle, *wetting angle* (θ), which reflects an equilibrium between the interfacial tension of the two fluid phases and their individual adhesive attraction to the solid. *Interfacial tension* is a kind of two-fluid physical constant that can be altered by chemical changes, which is one of the principles exploited by the so-called enhanced oil recovery. [41]

In oil reservoirs, the rock can have three types of wettablity; *water-wet*, oil remains

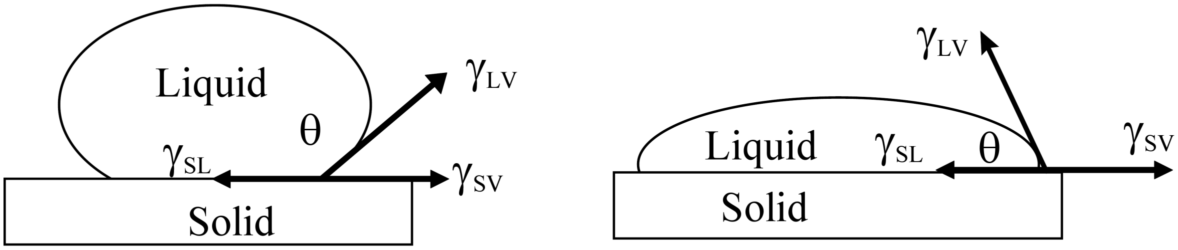


Figure 2.4: Examples of behavior of solid/liquid systems

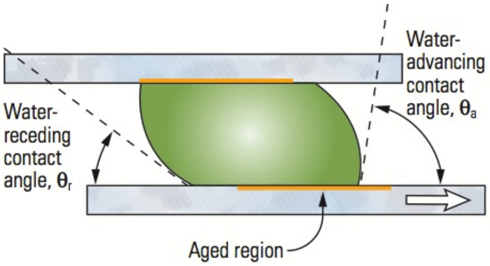


Figure 2.5: Sessile drop method

in the center of the pores, *oil-wet*, the oil remains in the center of the pores and *mixed-wet*, oil displaces the water from some parts of the surfaces, but is still in the centers of some water-wet pores. [1]

The wetting properties dictates the capillary pressure, P_c, and the relative permeabilities of water, k_{rw}, and oil, k_{ro}, which gives an influence on the two-phase flow in a porous medium. Studies show that a slightly water-wet system is optimal for oil recovery by waterflooding. [4]

Evaluation Methods

Numerous methods have been proposed for evaluating the wettability of a solid surface with regard to a fluid or a fluid system:

1. Methods based on thermodynamic definition of wetting. The thermodynamic definition of wetting relates to physicochemical reaction caused by intermolecular forces of attraction. Wettability, designated by γ_m, thus represents the

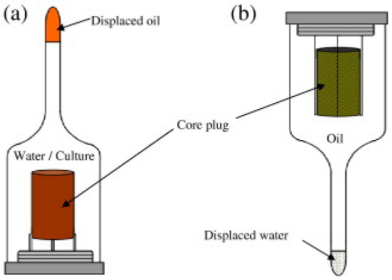


Figure 2.6: Apparatus for imbibition experiments in brine (a) and oil (b)

energy lost by the system during the wetting of a solid by a liquid. (Figure 2.4 [25])

When there is a contact angle θ, we have Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_m \tag{2.1}$$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} * cos\theta, \tag{2.2}$$

where γ_{LV} is the surface tension of the liquid.

It then suffices to separately evaluate γ_{LV}, cosθ or the product of them. Several methods are proposed for the measurements: by a tensiometer, strip method, capillarimetric method, dynamic Wilhelmy plate wettability technique etc. [9]

But such treatments for ideal systems cannot be implemented for actual reservoir systems due to the complexity of the rock, fluids, adsorption phenomena, etc.

2. Method based on contact-angle measurements. It is a popular technique in laboratories, where a drop of oil or water is placed on a flat surface of a solid with the same mineralogical nature as the reservoir considered. [9] The angle under static and dynamic conditions, θ, is then measured. When θ in water is small, the solid is water-wet. When it is large, the solid is said to be oil-wet. However, this method does not reflect the wettability of a heterogeneous solid, since heterogeneity will cause a variety in solid type over the rock.

3. Method based on spontaneous imbibition. The spontaneous imbibition is largely controlled by capillary pressure, P$_c$, which is proportional to the interface tension and the cosine of the contact angle between two fluids. As shown in Figure

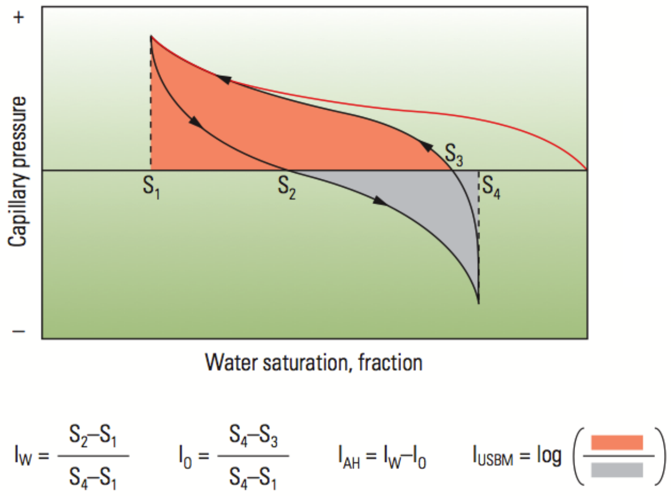


Figure 2.7: Amott and USBM measurements methods [1]

2.6 [2], the core is set in an apparatus and is surrounded by either the wetting fluid or not-wetting, where the volume of the displaced fluid is measured. Measurements of spontaneous imbibition rate provide a useful supplement to Amott indices or USBM wettability numbers. [11]

$$P_c = \frac{2 * \sigma * cos\theta}{r} \tag{2.3}$$

4. Method based on imbibition and displacement experiments. This method for evaluation of wettability was proposed by Amott [9] and is also called the Amott wettability measurement. This method consists of four different steps; spontaneous and forced imbibition, spontanoeus and forced drainage. The followings are needed to determine Amott-Harvey index for wettability:

1. The amount of imbibed water into the core is measured during spontaneous imbibition into an oil saturated core at irreducible water saturation, S_2 in Figure 2.7,
2. The volume of water forcibly imbibed into the core during forced imbibition, S_3 in Figure 2.7
3. The amount of produced water during spontaneous drainage, S_1 in Figure 2.7
4. The amount of water produced during forced drainage, S_4 in Figure 2.7.

	Oil-wet	Neutral wet	Water-wet
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°

Table 2.1: Comparison of Amott-Harvey index, USBM wetting index and contact angle measurements

$$I_w = \frac{S_2 - S_1}{S_4 - S_1} \tag{2.4}$$

$$I_o = \frac{S_4 - S_3}{S_4 - S_1}. \tag{2.5}$$

The difference between the water ,I_w, and oil, I_o, indices gives the Amott-Harvey index, I_{AH}, where the water and oil indices are termed as the ratios of spontaneous imbibition and drainage to total saturation change for water and oil, respectively. (Figure 2.7) [30]

5. USBM (U.S. Bureau of Mines.) test By the results of Gatenby and Marsden (1957), Donaldson (1969) proposed this method that makes use of the areas under the capillary-pressure curves [9], where USBM wetting index, I_{USBM} is the logarithm of the ratio of the area under spontaneous drainage curve to the area over forcibly imbibition curve. (Figure 2.7) [30]

Both the Amott method and USBM method has no validity as an absolute measurement, but it is industry standard for comparing wettability of various cores. A comparison of both methods are introduced in Table 2.1. [13]

6. Method based on chromatographic wettability test. Even though both Amott and USBM tests for wettability are common within the petroleum industry, they show a remarkable differences near the neutral wetting condition. [13, 5]

However a new method for chalk wettability has been developed by Strand et al., by the chromatographic separation between a non-adsorbing tracer, SCN^-, and adsorbing SO_4^{2-} at the water-wet areas of the surface. The area between the effluent

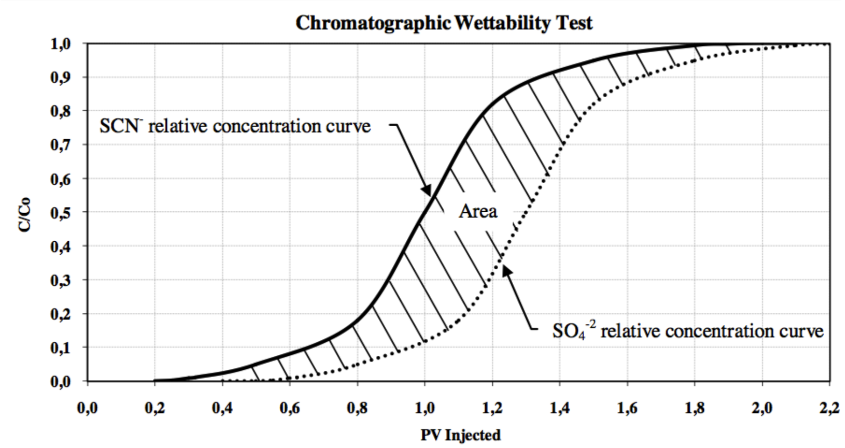


Figure 2.8: Schematic illustration of the chromatographic wettability test separation between SCN$^-$ and SO$_4$^{2}−

curves for SCN^- and SO_4^{2-} in a chalk core at residual oil saturation is proportional to the area contacted by water during flooding. Thus the ratio between this area and a corresponding area from a water-wet core will give a water index between 0 and 1, where 0 is completely oil-wet and 1 is completely water-wet. This test is preferred for cores close to neutral wettability. (Figure 2.8) [30, 32]

2.1.2 Acid and Base Numbers

Definition

Acid number - the quantity of base, expressed in milli- grams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared non-aqueous basic buffer solution. [22]

What does AN indicate?

One simple analysis of the composition of oil is SARA, where crude oil is divided into *saturate, aromatic, resin* and *asphaltene* fractions. The saturate fraction contains the non-polar material, like linear, branched and cyclic saturated hydrocarbons, while aromatics contain more polarizable aromatic rings. The remaining fractions, resins and asphaltenes, have polar substituents and also carboxylic groups. The carboxylic acid groups, i.e. the acid number, AN, is an important property of crude oils. It is important for oil's quality because conductivity, corrosivity and some other properties of the oils are dependent on AN. Furthermore, AN appears also to be a crucial wetting parameter for the reservoir. [10, 36, 39]

2.1.3 Wettability in carbonates

Treiber et al. evaluated the wettability of 50 oil reservoirs (mostly American reservoirs). Of the carbonate reservoir crude oil-water systems they tested, 8 percent were water-wet; 8 percent intermediate; and 84 percent oil-wet. Carbonates constitute 45 percent of the reservoir systems, but they constitute 58 percent of those found to be oil-wet in the publication. [35]

Carbonate reservoir rocks are made of a complex matrix with various mineral types, and this variety makes it difficult to describe the wettability of the rock. However some parameters are important to help understand and interpret rock wettability. These parameters are listed as: saturation (geological) history, crude oil etc.

Because of the *saturation history* of a rock there might be some areas in the rock, which has never been touched by oil during the oil-migration. These areas will be water-wet areas. Other areas might have been touchefd and changed to be oil-wet, since the primary condition of carbonate are water-wet prior to oil migration. [1] Carbonate rocks (calcite and dolomite crystals) are generally hydrophobic, if subjected to choice of oil or water, they will prefer oil and become oil wet. Electrostatics will control the surface charges in a rock/fluid interaction. Carbonate particles usually adsorb organic coating which protect them from dissolution in the slightly acidic formation waters. [20]

Crude Oils are also complex mixtures, and some of the organic molecules in oil can adsorb to high-energy surfaces, which might further alter the wettability on surface. Especially the carboxylic group (usually resins and asphaltenes), which adsorbs strongly to onto the carbonate surface by displacement of water. The acid number, *AN*, of the crude oil plays also a major role in wetting carbonates, and it has been observed that the water wetness decreases as the AN increases. [18, 39]

Decarboxylation is a process which leads to the generation of carbon dioxide, which again produces carbonic acid in the presence of water. [3] Both decarboxylation

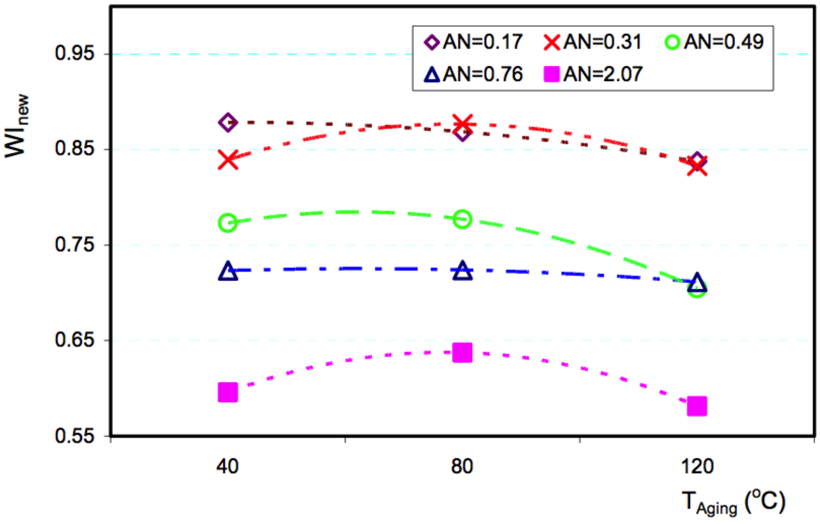


Figure 2.9: Correlation between wettability index and aging temperature, by Zhang et al. 2005.

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

Table 2.2: Field examples, from Hoegnesen 2005.

and other type of decomposition of carboxylic acids present in crude oil, which leads to decreasing AN, take place in as the temperature increases. Various types of clay minerals and CaCO3 behaves as a catalyst in this process. Thus temperature in itself is not a direct factor for wettability alteration, but indirectly affects the wettability of chalk reservoirs. A correlation from experiments made by Zhang et al. shows how wettability is not dependent on temperature: Fig 2.9. Field data are shown in Table 2.2. [39, 15]

To sum up, in chalk reservoirs AN of oil is the most important parameter for wettability. Unlike sandstone reservoirs, 90 % of carbonate oil reservoirs are characterized as neutral to preferential oil-wet, and with an oil recovery around 30 %. [39, 7]

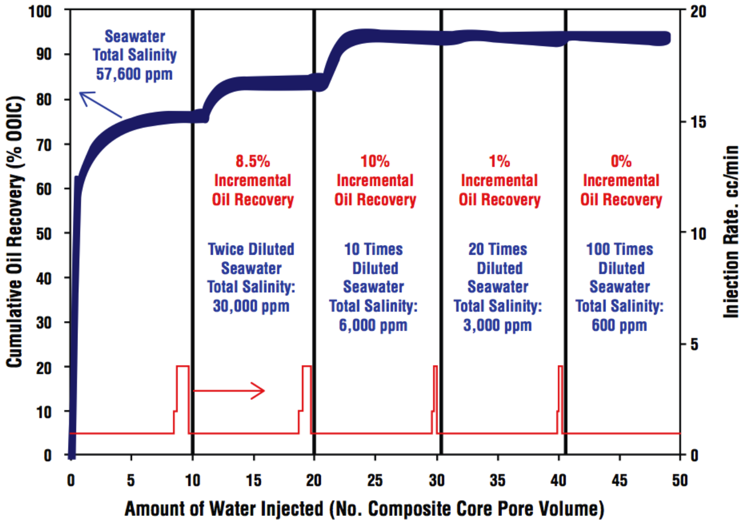


Figure 2.10: Obtaining more oil recovery from a core by more diluting injected seawater (about 60,000 ppm salinity). But there is a limit

2.2 E.O.R. in Carbonates

Ion reactivity with the carbonate rock surface is very complex and depends on different factors including rock mineralogy, reservoir conditions, oil composition, what has been injected in the reservoir, and others."
-Ali Yousef

2.2.1 Recovery by EOR Waterflooding

Initially, the main reasons for waterflooding were to give a pressure support to the reservoir to avoid gas evolving from oil ($P_{res} > P_b$) and displace the oil by viscous forces. This categorizes waterflooding as a secondary recovery. But studies show that water, different from formation water, changes the chemical equilibrium in brine/rock/crude oil systems and this makes waterflooding a tertiary recovery. [4]

Waterflooding is known as the most succesful method for oil recovering, and reasons can be listed as:

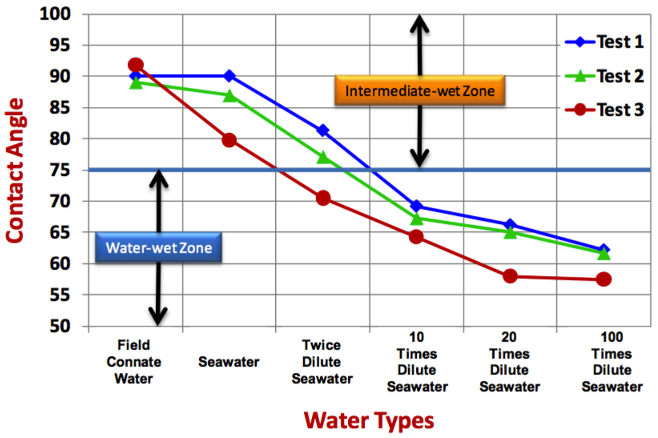


Figure 2.11: Reduced salinity water is observed to change the wettability of a rock toward water-wet.

- Water is an efficient injectant for displacing oil of light to medium gravity,
- Water is easy to inject,
- Water is available, and most importantly inexpensive,
- Compared to other IOR methods, waterflooding involves much lower capital investment and operating costs. [37]

In the oil industry, smart water has been synonymous with low-salinity waterflooding to increase oil recoveries. The goal is to understand how to control rock wettability by changing the ionic composition of the injected seawater. Researchers have found that chemicals other than sodium chloride are the critical factors: the core-flood tests showed that using dilution to halve the salinity increased the incremental recovery by 8 %. Further increasing the dilution added 10% to the incremental recovery (Figure 2.10). Studies of changes on the rock surface showed the main reason for the gains was a change in the wettability from ”slightly oil-wet” to ”strongly water-wet”. [26] Carbonate rock wettability alteration has also been observed with twice diluted seawater and also 10 times diluted seawater. (Figure 2.11) [37]

SmartWater is not simply low salinity water, and ionic composition of field injection water plays an important role in the rock wettability alteration process. [37] Generally, the difference in oil recovery potential for different carbonate reservoirs is attributed to variation between conditions of reservoirs, primarily the reservoir

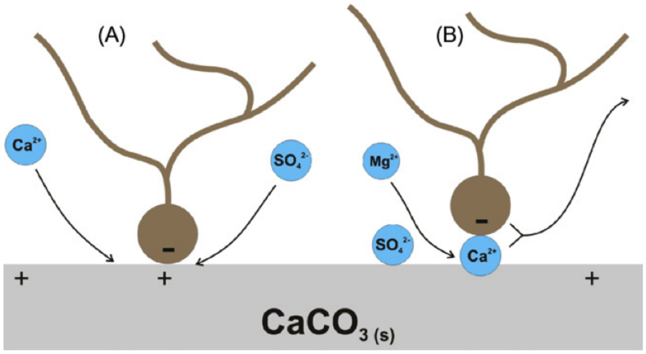


Figure 2.12: Schematic model of the suggested mechanism for the wettability alteration induced by seawater. (A) Proposed mechanism when Ca^{2+} and $SO_4{}^{2-}$ are active at lower and high temperature. (B) Proposed mechanism when Mg^{2+} and $SO_4{}^{2-}$ are active at higher temperatures. [40]

temperature, the chemistry of initial formation water, oil properties, rock surface reactivity and the reservoir heterogeneity. [38]

2.2.2 Proposed Mechanisms

Impact of the potential determining ions Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$

Based on experimental facts , this mechanism is proposed by Zhang et al., and explains the alteration by the potential determining ions in seawater, Mg^{2+}, Ca^{2+} and $SO_4{}^{2-}$. (Figure 2.12) Ca^{2+} and $SO_4{}^{2-}$ ions have great influence on the surface charge, and can turn the wettability of the rock during waterflooding. At high temperatures, Mg^{2+} is strong potential determining ion towards chalk, and can substitute Ca^{2+}, where the substitution increases as the temperature increases. This substitution releases the carboxylic groups attached to the surface, i.e. the water-wetness of the rock improves.

To sum up, the key parameters in seawater are Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$, where to improve the oil recovery, sulphate must act together with either Ca^{2+} or Mg^{2+}. In both ways, the efficiency increases as the temperature increases. The main mechanism is that these ions releases the attached carboxylic groups on surface (which gives an oil-wet nature to the rock), and creates a water section on the rock surface. [40]

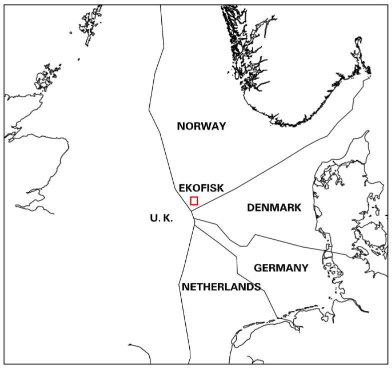


Figure 2.13: Map of North Sea with Ekofisk location [17]

Further studies show that oil recovery by spontaneous imbibition of seawater depleted in NaCl is increased from 37 to 47% of OOIP compared to ordinary seawater. This shows that not only Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$, but also NaCl has an effect on waterflooding efficiency: water depleted in NaCl is even more effective. [4]

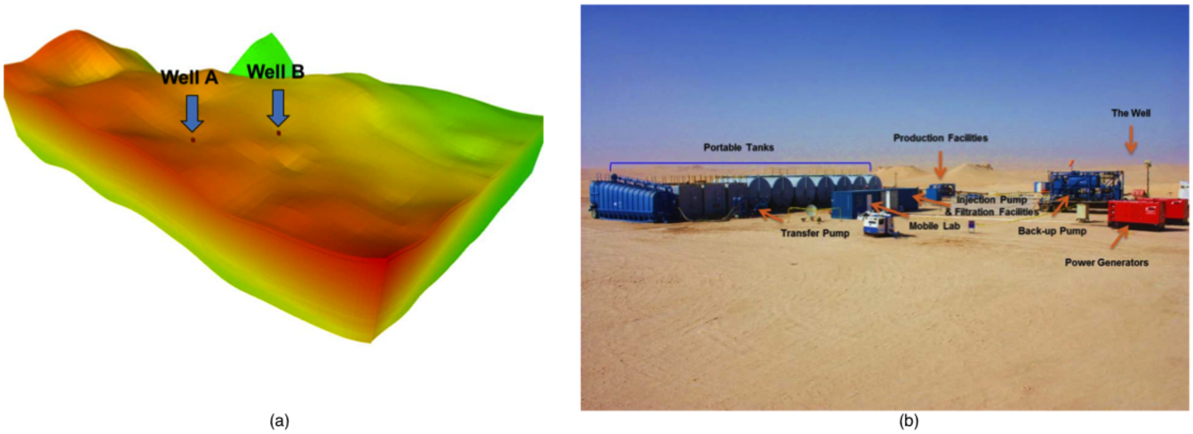
2.2.3 Field Experiments

Ekofisk

Ekofisk was discovered in 1969 and test production was started in 1971 from the discovery well and three appraisal wells. [17] During its first 20 years, Ekofisk has undergone both gas and water injection. The initial $1.5-billion waterflood project (1983) has been expanded (1988), extended (1989) and optimized (1990). [33] It has boosted the recovery factor from less than 20 per cent of the oil in place to the current estimate of more than 50 per cent. [21]

Saudi Aramco Field Trials

Saudi Aramco started a R&D program to find ways to increase oil recovery in carbonates by changing the salinity and ionic composition of the injected seawater to maintain pressure and push oil toward producing wells. [26] Several Saudi Aramco reservoirs have natural water drives and a string of development of injection has been implemented over the past 60 years, which has resulted in unique water injection infrastructure. The primary source of the injection water is seawater, thus the potential



(a) (b)

Figure 2.14: (a) Relative location of selected wells for SmartWater Flood field tests, (b) Overall field preparation and logistics at the well site.

of obtaining incremental oil recovery by waterflooding is significant considering the large oil resources and current injection facilities in Saudi Arabia. [37]

The concept of field trials is to determine the effect of waterflooding on residual oil saturation. To achieve this, field seawater is first introduced to the reservoir to move oil saturation toward the residual oil saturation. Then, injection of a slug of smartwater is started, where it should mobilize the oil after the seawater injection. Single Well Chemical Tracer (SWCT) was selected as a tool for residual oil saturation measurements. [37]

These tests in carbonate reservoirs showed an increase in the oil recovery:

- Both field tests confirmed that in-house research results can be replicated in a field scale. Injection of SmartWater revealed a reduction of 7 saturation units in residual oil.
- The field trial at Well A was designed in three stages over a four-week period. First seawater was introduced, then additional large volume was injected to validate and confirm that no further oil is mobilized. At last SmartWater was injected, and this gave *7 saturation unit reduction* in the residual oil saturation beyond field seawater.
- The design of the field trial at Well B was different; First field seawater was injected to achieve residual oil saturation, then twice diluted seawater was injected. This step gave a reduction of 3 saturation units. At last 10 times

diluted seawater was injected. Last step gave the same reduction as the second step. Thus *a reduction of 6 saturation units* was obtained. [37]

Chapter 3

Experimental Procedure

3.1 Materials

3.1.1 The porous media

Four outcrop cores from Stevns Klint chalk nearby Copenhagen, Denmak, is used as the porous medium for the experiments. More than 98 % of the cores consist of $CaCO_3$. The cores have a low permeability in the range of 1-2 mD. This material is quite similar to the North Sea chalk reservoirs. Physical parameters of the cores are presented in Table 3.1.

Chalk cores	T1	T2	T3	T4
Dry weight, gr	101.47	104.63	104.35	103.73
Length, cm	6.5	6.375	6.3	6.48
Diameter, cm	3.9	3.79	3.81	3.8
Bulk volume, cc/ml	77.65	71.92	71.83	73.49
Saturated weight, gr	136.85	137.63	134	137.92
Pore volume, ml	35.27	32.90	29.56	34.09
Porosity	45 %	46 %	41 %	46 %

Table 3.1: Chalk cores physical properties, conditions for core flooding and desired weight for certain initial water saturation

3.1.2 Crude oils

The high AN oil (AN = 1.8 mgKOH/g), RES40, was made by diluting crude oil from Heidrun sandstone reservoir (AN = 3.0 mgKOH/g) with heptane at a volume ration of 40/60 heptane/crude. Some of the RES40 was steered with silica powder (10 % of the oil mass) for 3 days, then the same amount of silica powder was added for 2 more days to obtain RES40-0 (AN = 0.17 mgKOH/g). Then RES40-0.35, oil used in our experiments, was made by mixing RES40 and RES40-0 in a proper, calculated ratio. Crude oils were centrifuged and filtered through a 2 μm Millipore filter.

Crude Oil	AN
RES40	1.8 mgKOH/g
RES40-0	0.17 mgKOH/g
RES40-0.35	0.35 mgKOH/g

Table 3.2: Crude oils

3.1.3 Brines

The brines used for experiments were prepared in the laboratory with DI water, and salts with an order of chlorides, sulphates and carbonates. The terminology is as follows;

- **VB0S**, Valhall (carbonate) formation water, used in chalk cores.
- **SW0T**, Seawater without SO_4^{-2} & SCN^-, used in chromatographic wettability tests
- **SW1/2T**, Seawater containing 24 mM of SO_4^{-2} & SCN^-, used in chromatographic wettability tests.

Chemical composition of the brines is presented in Table 3.3.

	VB0S	SW0T	SW1/2T
Salt	m, g/L	m, g/L	m, g/L
NaCl	57.70	26.79	23.41
Na_2SO_4	0	0	1.71
KSCN	0	0	1.17
LiCl	0	0	0.51
$NaHCO_3$	0.781	0.17	0.17
KCl	0.395	0.75	0.75
$MgCl_2$	0.74	4.24	4.24
$CaCl_2$ (dry)	3.213	1.44	1.44
$BaCl_2$	0	0	0
$SrCl_2$	0	0	0
$MgCl_2x6H_2O$	1.58	9.05	9.05
$CaCl_2x2H_2O$	4.26	1.91	1.91
$BaCl_2x2H_2O$	0	0	0
$SrCl_2x6H_2O$	0	0	0
Density (measured)	1.040	1.024	1.024
Ions	mole/L	mole/L	mole/L
HCO3-	0.009	0.002	0.002
Cl-	1.066	0.583	0.538
SO4 2-	0	0	0.012
SCN-	0	0	0.012
Mg2+	0.008	0.045	0.045
Ca2+	0.013	0.013	0.013
Na+	0.997	0.450	0.427
K+	0.005	0.01	0.022

Table 3.3: Chemical composition of the brines used

3.1.4 Chemicals

The following chemicals were used:

- Heptane: which is used to dilute crude oil.
- Silica; which is used to treat oil to lower the AN, and dry a fully water saturated core to desired water saturation.
- Acid and base number solutions: are shown in chapter 3.3.1

3.2 Experimental Methods

3.2.1 Removal of initial sulphate

In order to remove soluble salts, especially sulphate, the cores were flooded with 250 mL of distilled water at ambient temperature. [24] The effluent during flooding was tested for sulphate with $BaCl_2$, where any possible sulphate would visually create precipitation of $BaSO_4(s)$.

3.2.2 Initial water saturation by desiccator technique

After drying at 90 ^{0}C to constant weight, the cores were vacuumed and saturated with 10xdiluted VB0S to both measure the pore volume (PV) and saturate the cores with formation water.

The saturated cores were placed in a vacuum desiccator container with silica gel, that vaporized the pure water steady throughout the whole core. When the desired weights were achieved, the cores had an initial water saturation of 10% (S_{wi}=0.1).

3.2.3 Adsorption of polar components by oil flooding

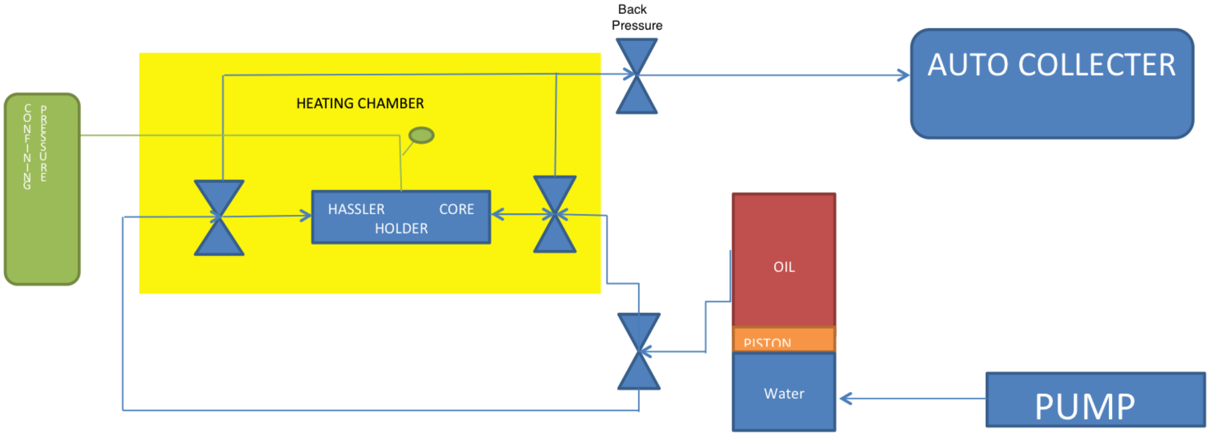


Figure 3.1: Schematic diagram of core flooding set-up

The cores with 10% formation water saturation were then put in a system shown in Figure 3.1, where they were set vacuumed and then saturated with crude oil (RES40-0.35) from both sides at ambient temperature. The system was then heated to test temperature (50, 90 and 130 ^{0}C) and the cores were flooded in one direction with a pump pressure not exceeding 15 bars and pump rate of 4 PV/day. Back pressure was 10 bars, while confining pressure was 30 bars. The effluent was then collected with an auto-sampler in sealed vials (6 ml in each). The samples were stored and measured for AN or BN. [1]

After core-flooding for about 12 PVs, the injection was stopped and the cores were equilibrated for 48 hours. The floodings were started again with the same rate for more pore volumes. If there is any change in adsorption of polar components due to equilibration, this would show up on the results.

3.2.4 Aging

After oil flooding the cores were wrapped with teflon tape and stored in oil (RES40-0.35) for aging at the test temperature for 14 days. Pressure of 8 bars was needed during the aging of the core at 130 ^{0}C.

3.2.5 Spontaneous imbibition

After aging the cores for 14 days, spontaneous imbibition was performed by immersing the cores in formation water (VB0S) in a sealed steel cell. The tests were performed at test temperatures, with a back pressure of 10 bars. The produced oil was then collected in burettes, and oil recovery vs time was determined. (Figure 3.2)

No chemical interaction and wettability alteration should take place when the cores are imbibed with formation water.

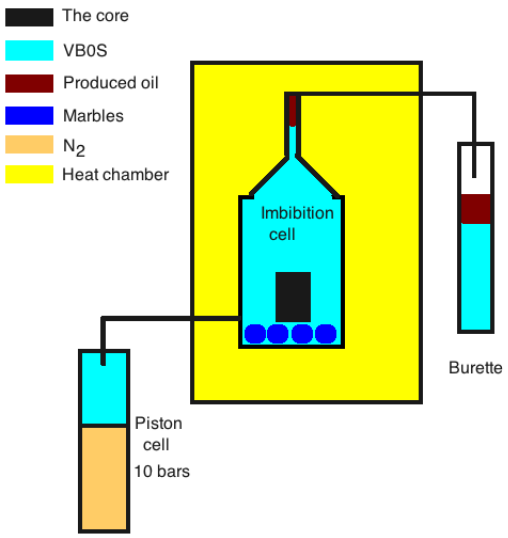


Figure 3.2: Schematic diagram of spontaneous imbibition set-up at high temperature in steel cell

3.2.6 Chromatographic wettability test

The chromatographic wettability test for carbonates, described previously in chapter 2.1.1, studies the reactivity of $SO_4{}^{-2}$ towards limestone surface, i.e. this test determines the water-wet fraction of the rock surface.

Flooding steps for this test is as follows:

1. Brine = SW0T. Rate = 0.2 ml/min. Volume = at least 2 PV, until no more oil production is observed.
2. Brine = SW0T. Rate = 1 ml/min. Volume = at least 2 PV.
3. Brine = SW0T. Rate = 0.03 ml/min. Pumping during night.
4. Brine = SW0T. Rate = 0.2 ml/min. Volume = 1.5 PV. To have a dynamic equilibrium in the system.

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[1] Due to problems in the software and the flow, at 130 ^{0}C the effluent was weighted with the glasses to have the exact volume in PV.

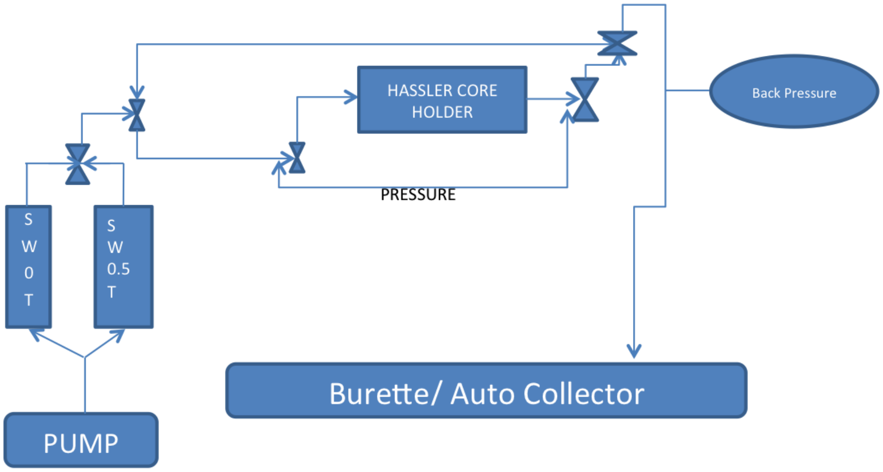

Figure 3.3: Schematic diagram of chromatographic wettability test flooding set-up

5. Brine = SW1/2T. Rate = 0.2 ml/min. Volume = 88 ml in 44 glasses. The effluent is sampled in the auto collector.
6. Brine = SW0T. Rate = 0.2 ml/min

The relative concentration is then plotted against injected pore volume, where the area , A_{wet}, between the curves of $SO_4{}^{2-}$, and tracer, SCN^-, is directly proportional to the water-wet area inside the core. The ratio of A_{wet} and the corresponding area for a completely water-wet reference core, A_{ref}, is a measure of the water-wet fraction of the core, WI:

$$WI = \frac{A_{wet}}{A_{ref}} \tag{3.1}$$

where WI=0 is completely oil-wet, WI=0.5 is the neutral wetting state, and WI=1 is completely water-wet.

Dead volume measurements

The dead volume of the system is important to measure, so that the right value of concentration is plotted against the injected volume. During this measurement, the system was divided into sections shown in Figure 3.4. A dummy core was installed

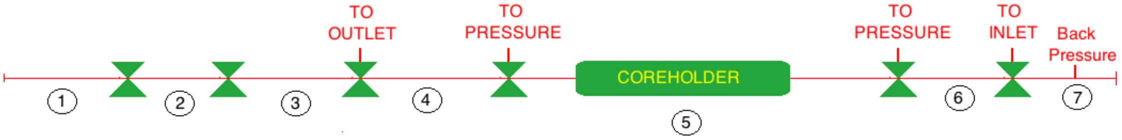

Figure 3.4: The system is divided by sections and each section is measured

in the core holder, and all valves were closed. The inlet was attached to a burette. The valves are opened one by one, and the injected volume is measured. Since the last section has a back pressure, the brine was injected by a pump and the difference between the effluent and injected volume gives the dead volume of the last section. Dead volume of the sections are measured as: section 1 - 2.5 mL, section 2 - 0.3 mL, section 3 - 0.2 mL, section 4 - 3.0 mL, section 5 - 1.5 mL, section 6 - 2,9 mL and section 7 - 0.89 mL.

Total dead volume is then 11.29 mL (Input = 4.5 mL, output = 6.79 mL).

3.3 Chemical Analysis

3.3.1 Acid number measurements

An auto-titrator was used to measure the acid and base number for the different crude oils, and the effluent during oil flooding. This method involves potentiometric titrations using an internal standard.

Experimental materials

- Auto-titrator: Mettler Toledo DL55
- Titrant: 0.05 M tetrabutyl ammonium hydroxide in ethanol
- Spiking solution: 0.5 g stearic acid diluted to 100 ml with acid titration solvent
- Standard solution: 0.2 g KHP dilute to 500 ml DI water
- Titration solvent: 6 ml DI water & 494 ml 2-propanol & 500 ml toluene

Titration procedures

Before the measurements the auto-titrator needs to be calibrated and standardized. Then the samples are tested and compared to a blank with known AN, which was introduced to the system. Thus samples with low AN can be tested easier.

- **Calibration.** pH meter calibration with ph 4, pH 7 and pH 10 buffers,
- **Standardization.** Titrant standardization with 50ml KHP standard solution,
- **Blanking.** 0.85 g spiking solution in 40 g solvent titration with standardized titrant,
- **Testing.** ca. 0.80 g crude oil in 40 g solvent titration with 0.85 g spiking solution.

Calibration and standardization procedures are carried once, while blanking is done after roughly each 30 testings.

Calculations

The molarity concentration of titrant (N) is calculated as:

$$N = \frac{1000 * W_{KHP}}{204.23 * V_{eq,std}}, \tag{3.2}$$

where, W_{KHP} is the amount of KHP in standard solution, and $V_{eq,std}$ is the amount of titrant (ml) consumed at the equivalent point (software). The acid number (AN) in terms of mg KOH/g oil is the calculated as:

$$AN = \frac{(V_{eq} - b_{eq}) * N * 56.1}{W_{oil}}, \tag{3.3}$$

where, V_{eq} is the amount of titrant consumed by crude oil sample and 0.85 g spiking solution at the equivalent point (software during testing), b_{eq} is the amount of titrant (ml) consumed by 1 ml spiking solution at the equivalent point (software during blanking) and W_{oil} is the amount (g) of oil used. At least 3 testings are done for obtaining one value.

Base number measurements

The method for BN measurements is the same as for AN measurements, with only a difference in the experimental materials.

3.3.2 Ion-chromatography analyses

The glasses containing the effluent of SW1/2T flooding during chromatographic wettability test were diluted 200 times and analyzed for concentration of ${SO_4}^{2-}$, and tracer, SCN^-, using Dionex ICS-300 Ion Chromatograph. The apparatus measures the conductivity in samples with a flow rate of 1.0 mL/min. A graph of conductivity vs retention time comes automatically, where each peak in the graph represents an ion. Sulphate retention time is at 3.91 min, while thiocyanate (SCN) retention time is at 13.60 min. The area of a peak value in a sample related to the are of a peak value at the same retention time in a reference sample, gives the relative concentration of the ion.

Chapter 4

Chronology and Results of the Experiments

4.1 Adsorption of polar acidic components onto chalk surfaces

The chalk cores with 10 % initial water saturation (S_{wi}=0.1) were saturated with oil (RES40-0.35) in both directions. Then the cores were flooded in one direction (4 PV/day), and the effluent fractions were collected. After 3 days the injections were stopped and the systems were equilibrated for 2 days to observe any increased adsorption at static condition. The experiments were done in three different temperatures: 50 ^{0}C, 90 ^{0}C and 130 ^{0}C.

At the start of the flooding acid number of the effluents were immediately reduced to a low value and stay there for a while. This is when adsorption of acidic material from oil onto the chalk surface is at peak value. Then the adsorption decreases slowly to the plateau value for AN, reached at 0.35 mgKOH/g.

No increase in adsorption at static condition at any temperature was observed when the injection continued.

Flooding at 50 ^{0}C

AN decreases immediately from 0.35 to 0.06 mgKOH/g, and is stable for 2.5 pore volumes. After 9 pore volumes injected, AN increases to the plateau value (0.35 mgKOH/g), i.e. 9 pore volumes is needed to reach the full adsorption.

The acid number results at 50 ^{0}C is presented in Figure 4.1.

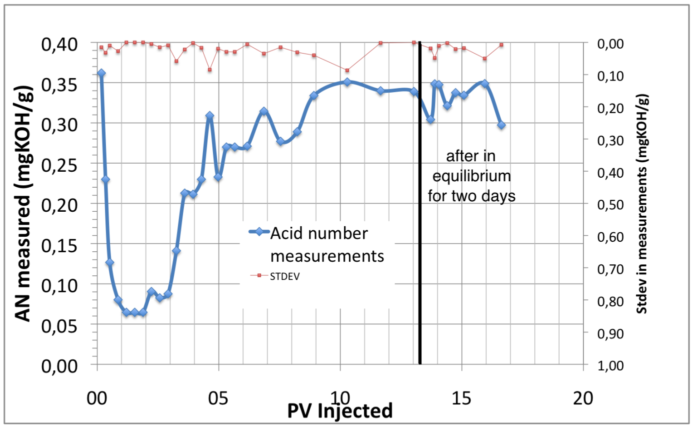

Figure 4.1: Acid number measurements (with corresponding standard derivation) from the effluent oil during flooding core T1 at 50 ^{0}C.

Flooding at 90 ^{0}C

The lowest value for acid number is 0.0 mgKOH/g at 90 ^{0}C, and this full adsorption of acidic components is maintained for only 1.5 pore volumes. Later adsorption decreases, and the core had full capacity of adsorbed species after 11 pore volumes injected.

90 ^{0}C test reaches the plateau value latest, comparing to other tests. Thus more total adsorption is observed. Some of the increase in adsorption might occur because of a power shutdown during the flooding.

The acid number results at 90 ^{0}C is presented in Figure 4.2.

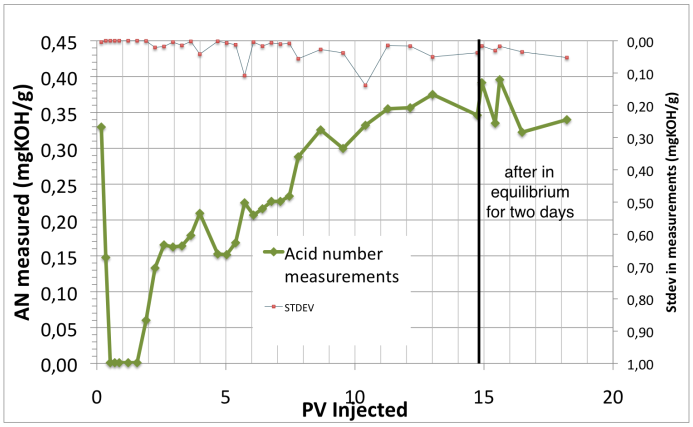

Figure 4.2: Acid number measurements (with corresponding standard derivation) from the effluent oil during flooding core T2 at 90 ^{0}C.

Flooding at 130 ^{0}C

Results show a generally lower adsorption of polar components at 130 ^{0}C. Here acid number is at its lowest (0.04 mgKOH/g) for only 1 pore volume, and total adsorption is reached after 6 pore volumes. [1]

The acid number results at 130 ^{0}C is presented in Figure 4.3.

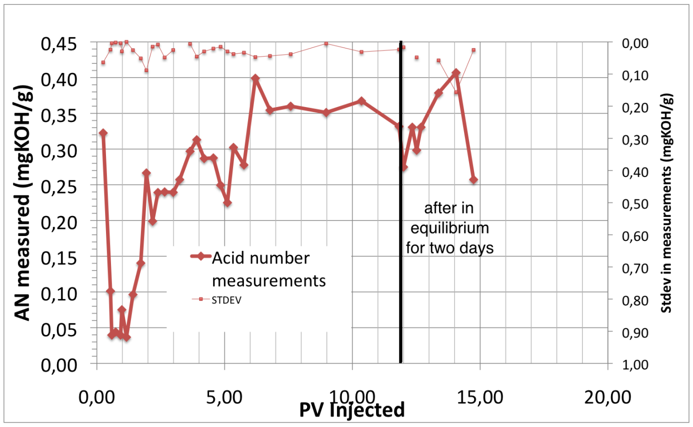

Figure 4.3: Acid number measurements (with corresponding standard derivation) from the effluent oil during flooding core T4 at 130 ^{0}C.

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[1] During 130 ^{0}C flooding a continuos flow was not obtained.

4.2 Wettability

4.2.1 Spontaneous imbibition

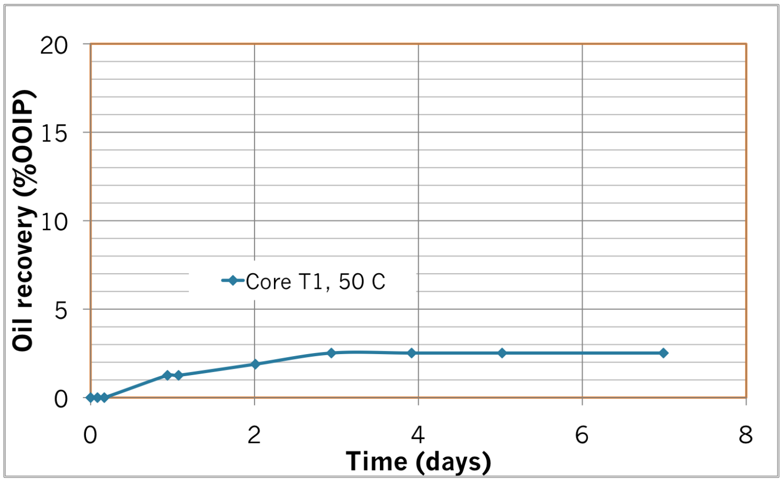

Figure 4.4: Spontaneous imbibition test done with core T1 at 50 ^{0}C, after aging in 14 days.

After the crude oil injection (at least 15 PV), the cores were aged at the test temperatures (50 ^{0}C, 90 ^{0}C and 130 ^{0}C) for 14 days. The cores were put for imbibition in an Amott cell using formation water as the imbibing fluid.

Spontaneous imbibition for T1 at 50 ^{0}C, T2 at 90 ^{0}C and T4 at 130 ^{0}C, is roughly the same. 50 ^{0}C test after 3 days, 90 ^{0}C test after 6-8 days and 130 ^{0}C test after 3-4 days reaches the plateau in oil recovery. The cores produce less than 10 % of OOIP, which is only due to thermal expansion. Thermal expansion is discussed further later in chapter 5.

The results are shown in Figures 4.4, 4.5, 4.6 and Tables A.4, A.6.

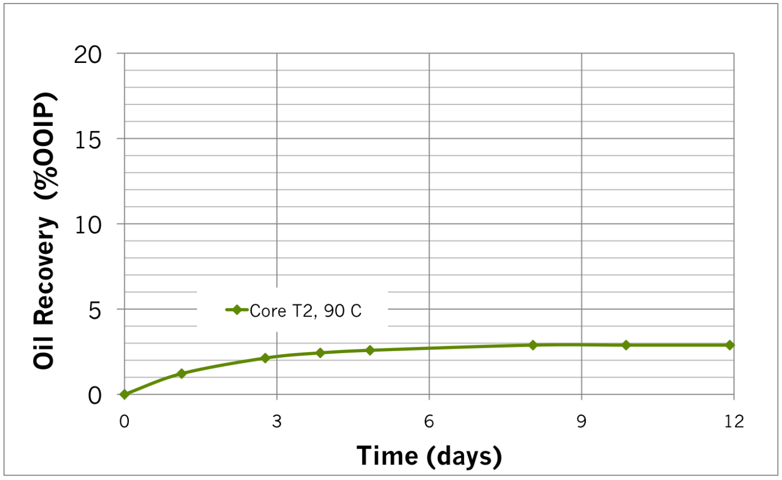

Figure 4.5: Spontaneous imbibition test done with core T2 at 90 ^{0}C, after aging in 14 days.

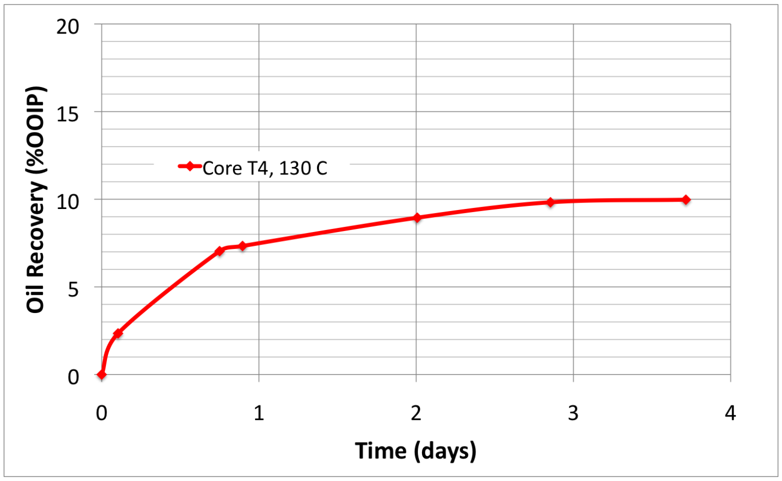

Figure 4.6: Spontaneous imbibition test done with core T4 at 130 ^{0}C, after aging in 14 days.

4.2.2 Ion-chromatography analysis

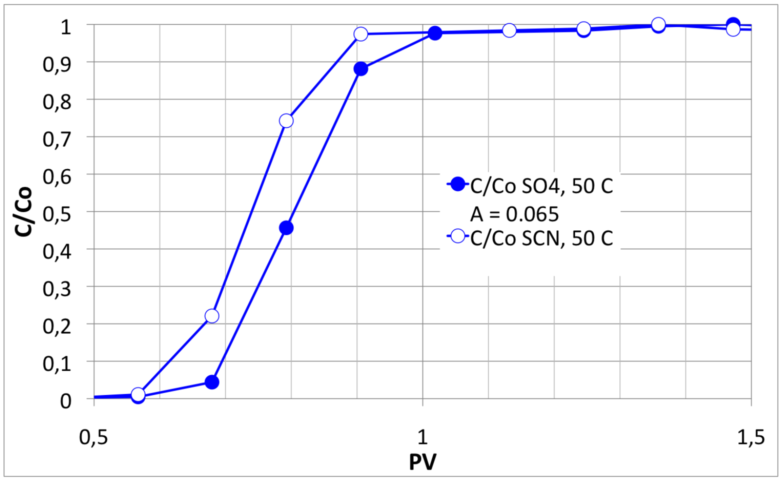

Figure 4.7: Chromatographic wettability analysis after spontaneous imbibition at 50 ^{0}C using formation water. The core had been flooded 18 PV with oil with AN of 0.35 mgKOH/g.

After the spontaneous imbibition the cores were flooded with seawater without sulphate and SCN$^-$ (SW0T) to reduce the oil saturation to S_{or} and have a chemical and physical equilibrium in the core. Then SW1/2T brine is injected and the effluent fractions are collected and measured for SO_4 and SCN concentrations. The area between the relative concentrations will determine the water wet area inside the core. Figures 4.7 and 4.8 show the results from 50 ^{0}C and 90 ^{0}C tests, respectively.

Test	S_{or}	A_{wet}	WI	Wettability
T1 @ 50 ^{0}C	0.25	0.065	0.201	oil-wet
T2 @ 90 ^{0}C	0.30	0.073	0.225	oil-wet
Clean reference core [12]	-	0.324	1	completely water-wet

Table 4.1: Data from the chromatographic wettability test

Table 4.1 shows the calculated area between SO_4 and SCN concentration graphs, A_{wet}, and the wettability index of the cores, WI. Clean reference core value is taken from Fathi et al.

During this test, residual oil saturations were also measured. Half of concentration of SCN appears at (1-S_{or}) pore volumes injected.

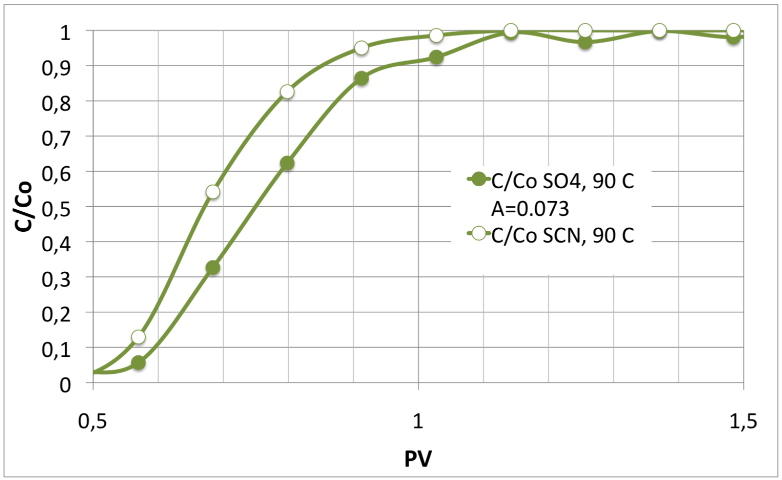

Figure 4.8: Chromatographic wettability analysis after spontaneous imbibition at 90 ^{0}C using formation water. The core had been flooded 18 PV with oil with AN of 0.35 mgKOH/g.

Chapter 5

Discussion of the Results

Adsorption of polar acidic components onto chalk surfaces

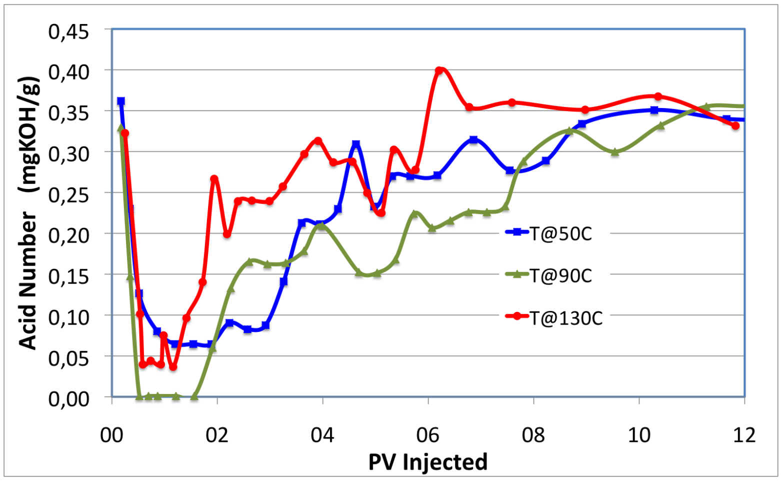

Figure 5.1: Comparing AN measurements from flooding core T1, T2 and T4 at 50 ^{0}C, 90 ^{0}C and 130 ^{0}C, respectively.

The results from adsorption tests are compared in Figure 5.1. The tests were performed at 50 ^{0}C, 90 ^{0}C and 130 ^{0}C.

All tests have roughly the same pattern, where adsorption of polar components starts immediately and decreases gradually , but 90 ^{0}C test adsorbs more acid than the other ones. Some of it might be explained by the power shut down during the

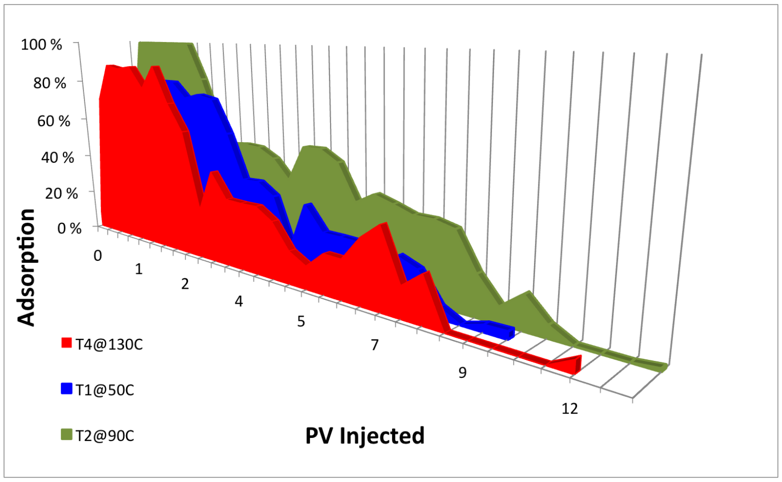

Figure 5.2: Comparing acid adsorption during flooding core T1, T2 and T4 at 50 ^{0}C, 90 ^{0}C and 130 ^{0}C, respectively.

flooding.

Adsorption of acids can be calculated mathematically; if AN$_{plateau}$ is the highest acid number, then there is no adsorption at this value. When acid value is 0, then there is full adsorption onto the core. Thus adsorption for a given sample nr x, should be like:

$$Adsorption_x = \frac{AN_{plateau} - AN_x}{AN_{plateau}}, \tag{5.1}$$

where AN$_x$ is the acid value at sample nr x. By the help of eq. 5.1 Figure 5.2 is plotted. In this figure adsorption of each flooding is compared. Total adsorption of each test is described by the area of adsorption by PV:

$$Totaladsorption = \int Adsorption * Volume. \tag{5.2}$$

The total adsorption of acidic components for each flooding is presented in Table 5.1 and Figure 5.3. The adsorptions of acidic components is twice at 90 ^{0}C than at 130 ^{0}C.

The experiments showed that at least 10 pore volume of a crude oil with AN ca. 0.35 had to be injected , before the adsorption capacity of the chalk was reached.

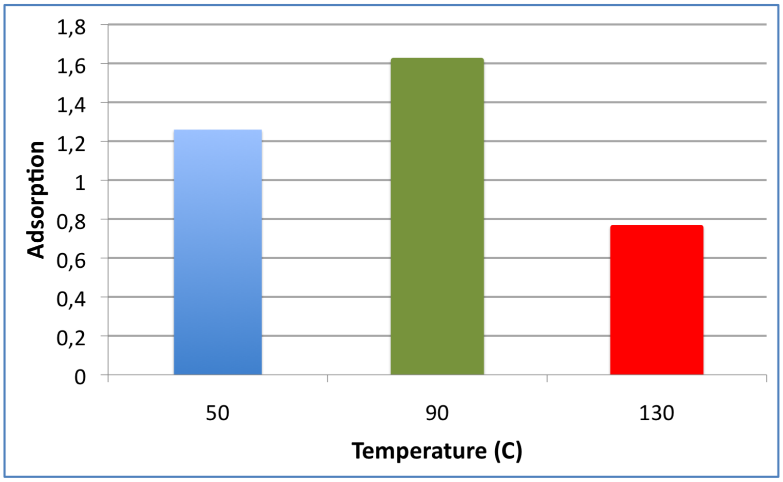

Figure 5.3: Adsorption and temperature

Flooding	Total adsorption ($\frac{mgKOH}{g} * PV$)
T1 @ 50 ^{0}C	1.3
T2 @ 90 ^{0}C	1.6
T4 @ 130 ^{0}C	0.8

Table 5.1: Total adsorption in each flooding

We should not expect that the amount of adsorbed material on the rock surface is related to the acid number observed in the crude oil. This trend might also be seen in reservoirs also, when oil flooding and oil effluent refer to oil migration and oil production, respectively. However, care must be taken to use outcrop cores to mimic reservoir wettabilities.

Wettability results

The cores produces less than 10 % of OOIP, which might be only due to thermal expansion of the oil; oil is expected to increase by around $1*10^{-3}$ of the original volume by each Celsius degree the temperature is increased. Thus 1% of oil recovery per 10 ^{0}C during spontaneous imbibition is excepted, i.e. at 50 ^{0}C 2.5 %, at 90 ^{0}C 6.5 % and at 130 ^{0}C 10.5 % oil production occurs due to thermal expansion.

Counting thermal expansion, no oil is produced from the cores during spontaneous imbibition, which indicates that there is no wettability alteration and the cores are oil-wet. This was approved further by ion-chromatographic analysis: wettability index of the cores were 0.201 after flooding at 50 ^{0}C, and 0.225 after flooding at 90 ^{0}C.

Test	Adsorption	SI production	WI	Wettability
T1 @ 50 ^{0}C	1.3	3 %	0.201	oil-wet
T2 @ 90 ^{0}C	1.6	3 %	0.225	oil-wet
T4 @ 130 ^{0}C	0.8	10 %		

Table 5.2: Comparison of the test results

It would be interesting to see the wettability index for 130 ^{0}C test, and how WI and adsorption is connected to each other in different temperatures.

Earlier studies done by Fathi et al., show that cores flooded with 1.5 pore volume of crude oil (RES40, AN = 1.9) in each direction have much higher water wettability (WI = 0.61) than in our experiments. In experiments done by Zhang et al., the same procedure was carried on: the cores were flooded with 1.5 -2 pore volumes of crude oil (AN = 0.17) in each direction, and the wetting index was around 0.85 at 40, 80 and 120 ^{0}C. It is important to mention that in both experiments the cores were aged for 4 weeks, contrary to 2 weeks as in our experiments.

Chapter 6

Conclusion and Suggestions

Conclusions

The results of the experimental study can be summarized as:

1. During oil flooding, adsorption of polar acidic components onto chalk surfaces is slightly larger at 90 ^{0}C compared to 50 and 130 ^{0}C: $T=90\ ^0C > T = 50\ ^0C > T=130\ ^0C$,
2. Based on Amott evaluation the cores act neutral to oil-wet after oil (RES40-0.35) flooding.
3. Ion chromatographic analysis show that the cores were oil-wet: $WI = 0.201$(oil-wet) at 50 ^{0}C , $WI = 0.225$ (oil-wet) at 90 ^{0}C
4. The water-wetness of a core flooded with RES40-0.35 in one direction for about 17 pore volumes is less than a core flooded with RES40 in both directions for 1.5 pore volumes.

Suggestions

1. It is known that acidic components effect the wettability alteration, but exactly what kind of components effect is not studied. More works on that, might improve "smart water" efficiency.
2. Mathematical modeling of the wettability alteration by "smart water" might simplify the introduction of "smart water" to the oil industry.

3. The same experiments can be carried out on reservoir cores to compare with outcrop cores.
4. The same experiments can also be carried out with different acid number values, to see a relation between AN in crude oil and total pore volumes required to reach full adsorption.

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Appendix A

Raw Data

Table A.1: AN measurements during flooding core T1 at 50 ^{0}C

T1									
Sample nr	Test#1	Test#2	Test#3	Test#4	AN	Stdev	Stdev(%)	PV	Adsorption
1	0.38	0.35	0.36		0.36	0.02	4%	0.2	0 %
2	0.21	0.21	0.27		0.23	0.03	14%	0.3	34 %
3	0.12	0.14	0.12		0.13	0.01	8%	0.5	64 %
5	0.11	0.06	0.06		0.08	0.03	34%	0.9	77 %
7	0.06	0.06	0.06		0.06	0.00	0%	1.2	82 %
9	0.06	0.06	0.06		0.06	0.00	0%	1.5	82 %
11	0.06	0.06	0.06		0.06	0.00	0%	1.9	82 %
13	0.09	0.09			0.09	0.00	5%	2.2	74 %
15	0.07	0.10	0.09	0.07	0.08	0.02	18%	2.6	76 %
17	0.08	0.09			0.09	0.01	10%	2.9	75 %
19	0.21	0.12	0.09		0.14	0.06	41%	3.3	60 %
21	0.23	0.21	0.19		0.21	0.02	10%	3.6	39 %
23	0.21	0.21			0.21	0.00	1%	3.9	40 %
25	0.21	0.24	0.23		0.23	0.02	7%	4.3	34 %
27	0.36	0.36	0.21		0.31	0.08	27%	4.6	12 %
29	0.22	0.26	0.22		0.23	0.02	8%	5.0	33 %
31	0.27	0.24	0.30		0.27	0.03	11%	5.3	23 %
33	0.30	0.27	0.24		0.27	0.03	11%	5.7	23 %
36	0.27	0.27	0.26		0.27	0.01	2%	6.2	23 %
40	0.33	0.27	0.34		0.31	0.03	11%	6.9	10 %
44	0.29	0.27	0.27		0.28	0.02	5%	7.5	21 %
48	0.32	0.26	0.29		0.29	0.03	11%	8.2	17 %
52	0.37	0.35	0.29		0.33	0.04	12%	8.9	5 %
60	0.33	0.27	0.44		0.35	0.09	25%	10.3	0 %
68	0.34	0.34	0.34		0.34	0.00	0%	11.7	3 %
76	0.34	0.34	0.34		0.34	0.00	0%	13.0	3 %
80	0.29	0.33	0.29		0.30	0.02	6%	13.7	13 %
81	0.38	0.38	0.35	0.28	0.35	0.05	14%	13.9	0 %
82	0.35	0.36	0.34		0.35	0.01	3%	14.1	1 %
84	0.32	0.32			0.32	0.00	1%	14.4	8 %
86	0.35	0.32			0.34	0.02	6%	14.7	4 %
88	0.32	0.35			0.33	0.02	5%	15.1	4 %
93	0.35	0.40	0.30		0.35	0.05	14%	15.9	0 %
97	0.30	0.29	0.30		0.30	0.01	2%	16.6	15 %

Table A.2: AN measurements during flooding core T2 at 90 ^{0}C

T2									
Sample nr	Test#1	Test#2	Test#3	Test#4	AN	Stdev	Stdev(%)	PV	Adsorption
1	0.33	0.33			0.33	0.00	1%	0.17	6 %
2	0.15	0.15	0.15		0.15	0.00	0%	0.35	58 %
3	0	0	0		0.00	0.00	0%	0.52	100 %
4	0	0	0		0.00	0.00	0%	0.69	100 %
5	0	0			0.00	0.00	0%	0.87	100 %
7	0	0			0.00	0.00	0%	1.21	100 %
9	0	0			0.00	0.00	0%	1.56	100 %
11	0.06	0.06			0.06	0.00	1%	1.91	83 %
13	0.15	0.12			0.13	0.02	16%	2.25	62 %
15	0.19	0.16	0.15		0.17	0.02	11%	2.6	53 %
17	0.17	0.16			0.16	0.00	3%	2.95	54 %
19	0.17	0.15			0.16	0.01	9%	3.3	53 %
21	0.18	0.18			0.18	0.00	1%	3.64	49 %
23	0.18	0.24			0.21	0.04	20%	3.99	40 %
27	0.15	0.15	0.15		0.15	0.00	1%	4.68	56 %
29	0.15	0.16	0.15		0.15	0.01	4%	5.03	57 %
31	0.18	0.16			0.17	0.01	7%	5.38	52 %
33	0.3	0.15			0.22	0.11	48%	5.72	36 %
35	0.2	0.21			0.21	0.00	2%	6.07	41 %
37	0.23	0.2			0.22	0.02	8%	6.42	38 %
39	0.22	0.23			0.23	0.01	3%	6.76	35 %
41	0.22	0.23			0.23	0.01	5%	7.11	35 %
43	0.23	0.24			0.23	0.01	4%	7.46	33 %
45	0.23	0.29	0.34		0.29	0.06	19%	7.8	18 %
50	0.34	0.31			0.33	0.03	8%	8.67	7 %
55	0.26	0.33	0.32		0.30	0.04	13%	9.54	14 %
60	0.26	0.25	0.49		0.33	0.14	42%	10.4	5 %
65	0.37	0.34			0.36	0.01	4%	11.3	0 %
70	0.34	0.37			0.36	0.02	5%	12.1	0 %
75	0.43	0.34	0.35		0.38	0.05	13%	13	0 %
85	0.34	0.31	0.38		0.35	0.04	11%	14.7	1 %
86	0.38	0.4			0.39	0.02	4%	14.9	0 %
89	0.31	0.36			0.34	0.03	9%	15.4	4 %
90	0.42	0.39	0.38		0.40	0.02	4%	15.6	0 %
95	0.3	0.35			0.32	0.03	11%	16.5	8 %
105	0.38	0.28	0.36		0.34	0.05	15%	18.2	3 %

Table A.3: AN measurements during flooding core T4 at 130 ^{0}C

T4									
Sample nr	Test#1	Test#2	Test#3	Test#4	AN	Stdev	Stdev(%)	PV	Adsorption
1	0.33	0.41	0.28	0.27	0.32	0.06	20%	0.25	8 %
6	0.13	0.1	0.08		0.10	0.02	24%	0.53	71 %
8	0.04	0.04			0.04	0.00	10%	0.58	89 %
10	0.05	0.04			0.04	0.00	5%	0.73	87 %
12	0.04	0.04			0.04	0.00	10%	0.93	89 %
14	0.05	0.1			0.08	0.03	39%	0.98	79 %
16	0.04	0.04			0.04	0.00	0%	1.16	90 %
20	0.09	0.12	0.07		0.10	0.03	27%	1.41	72 %
24	0.08	0.15	0.18		0.14	0.05	37%	1.72	60 %
28	0.37	0.21	0.22		0.27	0.09	33%	1.94	24 %
32	0.21	0.18	0.2		0.20	0.01	7%	2.18	43 %
36	0.25	0.23			0.24	0.01	3%	2.39	32 %
40	0.29	0.19	0.25		0.24	0.05	20%	2.65	31 %
44	0.26	0.21	0.24		0.24	0.03	11%	2.99	32 %
48	0.26				0.26		0%	3.24	26 %
52	0.29	0.3			0.30	0.01	2%	3.65	15 %
56	0.28	0.35			0.31	0.05	15%	3.91	11 %
60	0.26	0.29	0.32		0.29	0.03	10%	4.20	18 %
64	0.31	0.27	0.28		0.29	0.02	7%	4.56	18 %
68	0.25	0.27	0.24		0.25	0.02	6%	4.84	29 %
72	0.26	0.2	0.22		0.22	0.03	13%	5.11	36 %
76	0.35	0.29	0.27		0.30	0.04	12%	5.35	14 %
84	0.26	0.24	0.29	0.32	0.28	0.03	12%	5.76	21 %
101	0.43	0.42	0.35		0.40	0.05	12%	6.20	0 %
105	0.4	0.35	0.32		0.35	0.04	12%	6.78	0 %
111	0.4	0.34	0.34		0.36	0.04	11%	7.59	0 %
120	0.35	0.35	0.35		0.35	0.01	1%	8.98	0 %
130	0.35	0.39			0.37	0.03	8%	10.36	0 %
140	0.31	0.36	0.33		0.33	0.02	7%	11.83	5 %
141	0.26	0.29			0.27	0.02	6%	12	21 %
143	0.33				0.33		0%	12.3	6 %
144	0.26	0.35	0.29		0.30	0.05	16%	12.5	15 %
145	0.33				0.33		0%	12.7	6 %
149	0.33	0.44	0.36		0.38	0.06	15%	13.4	0 %
153	0.27	0.37	0.58		0.41	0.16	39%	14.1	0 %
157	0.24	0.27			0.26	0.02	10%	14.7	26 %

Table A.4: Results from spontaneous imbibition, T1 @ 50 C

T1					
	Time				
Day	Hour	Min	Real Time (days)	Produced Oil (mL)	Oil Recovery
0	11	30	0	0	0%
0	13	30	0.083333	0	0%
0	15	30	0.166667	0	0%
1	10	0	0.9375	0.4	1%
1	13	15	1.072917	0.4	1%
2	11	45	2.010417	0.6	2%
3	10	0	2.9375	0.8	3%
4	9	30	3.916667	0.8	3%
5	12	0	5.020833	0.8	3%
7	11	15	6.989583	0.8	3%

Table A.5: Results from spontaneous imbibition, T2 @ 90 C

T2					
	Time				
Day	Hour	Min	Real Time (days)	Produced Oil (mL)	Oil Recovery
0	14	0	0	0	0%
1	17		1.125	0.4	1%
3	8	30	2.770833	0.7	2%
4	10	30	3.854167	0.8	2%
5	10		4.833333	0.85	3%
8	15		8.041667	0.95	3%
10	11		9.875	0.95	3%
12	12		11.91667	0.95	3%

Table A.6: Results from spontaneous imbibition, T4 @ 130 C

T4					
Time					
Day	Hour	Min	Real Time (days)	Produced Oil (mL)	Oil Recovery
0	16	0	0	0	0%
0	18	30	0.104	0.8	2.3%
1	10	0	0.75	2.4	7%
1	13	30	0.89	2.5	7.3%
2	16	10	2	3.05	8.9%
3	12	30	2.85	3.35	9.8%
4	9	10	3.71	3.4	10%

Table A.7: Results from Ion-chromatography flooding and testing, T1

Sample #	Empty W	Full W	V effl.	PV effl	C-SO4		C-Tracer		$\int \delta C * PV$
1	8.52	10.61	2.05	0.1					0
2	8.52	10.48	1.92	0.1	0.001	0%	0	0%	0
3	9.05	11.08	1.99	0.2				0%	0
4	8.92	10.97	2.01	0.2	0.001	0%	0	0%	0
5	8.43	10.48	2.01	0.3				0%	0
6	9.56	11.61	2.01	0.3	0.002	0%	0	0%	0
7	9.16	11.21	2.01	0.4				0%	0
8	8.45	10.48	1.99	0.5	0.002	0%	0	0%	0
9	8.97	11.01	2.00	0.5				0%	0
10	9.02	11.06	2.00	0.6	0.002	0%	0	0%	0
11	9.14	11.16	1.98	0.6				0%	0
12	8.5	10.52	1.98	0.7	0.002	0%	0	0%	0
13	9.56	11.56	1.96	0.7				0%	0
14	9.06	11.09	1.99	0.8	0.001	0%	0.0002	0%	0.000285
15	9.06	11.1	2.00	0.8				0%	0
16	8.39	10.42	1.99	0.9	0.003	0%	0.0027	1%	0.01028
17	8.44	10.47	1.99	1.0				0%	0
18	9.03	11.04	1.97	1.0	0.03	4%	0.0538	22%	0.02617
19	9.56	11.6	2.00	1.1				0%	0
20	9.13	11.16	1.99	1.1	0.306	46%	0.1808	74%	0.02146
21	8.49	10.53	2.00	1.2				0%	0
22	9.02	11.06	2.00	1.2	0.591	88%	0.2372	97%	0.00537
23	9.1	11.13	1.99	1.3				0%	0
24	9.17	11.2	1.99	1.4	0.654	98%	0.2196	90%	0.00037
25	8.51	10.55	2.00	1.4				0%	0
26	8.41	10.44	1.99	1.5	0.616	92%	0.2396	98%	0.0005
27	8.48	10.52	2.00	1.5				0%	0
28	9.04	11.07	1.99	1.6	0.659	98%	0.2407	99%	0.0006
29	8.5	10.55	2.01	1.6				0%	0
30	9.04	11.08	2.00	1.7	0.667	99%	0.2445	100%	0
31	9.05	11.1	2.01	1.8				0%	0
32	9.13	11.17	2.00	1.8	0.681	100%	0.2403	99%	0
33	9.14	11.18	2.00	1.9				0%	0
34	8.43	10.48	2.01	1.9	0.665	99%	0.2395	98%	0
35	8.52	10.54	1.98	2.0				0%	0
36	9.04	11.05	1.97	2.0	0.68	100%	0.2374	97%	0
37	8.54	10.53	1.95	2.1				0%	0
38	8.5	10.52	1.98	2.1	0.708	100%	0.2421	99%	0
39	8.46	10.5	2.00	2.2				0%	0
40	9.11	11.14	1.99	2.3	0.664	99%	0.234	96%	0
41	8.97	11	1.99	2.3				0%	0
42	9.03	11.07	2.00	2.4	0.717	100%	0.2407	99%	0
43	9.06	11.09	1.99	2.4				0%	0
44	8.53	10.56	1.99	2.5	0.694	100%	0.2462	100%	0

Table A.8: Results from Ion-chromatography flooding and testing, T2

Sample #	Empty W	Full W	V effl.	PV effl	C-SO4		C-Tracer		$\int \delta C * PV$
45	9	11.01	1.97	0.1					0
46	9.01	11.06	2.01	0.1	0.012	0.018	0	0	0
47	9.04	11.03	1.95	0.2					0
48	8.44	10.46	1.98	0.2	0.003	0.004	0	0	0
49	9.12	11.17	2.01	0.3					0
50	9.06	11.1	2.00	0.3	0	0	0	0	0
51	8.54	10.58	2.00	0.4					0
52	8.51	10.55	2.00	0.5	0.008	0.012	0	0	0
53	8.95	11	2.01	0.5					0
54	8.59	10.63	2.00	0.6	0.002	0.002	0	0	0
55	8.93	10.96	1.99	0.6					0
56	8.91	10.98	2.03	0.7	0.002	0.004	0	0	0
57	9.55	11.61	2.02	0.7					0
58	8.88	10.93	2.01	0.8	0.021	0.031	0	0	0.00237
59	9.04	11.07	1.99	0.8					0
60	9.03	11.08	2.01	0.9	0.038	0.057	0.0308	0.12941	0.0165
61	8.97	11.03	2.02	1.0					0
62	9.04	11.1	2.02	1.0	0.219	0.327	0.1289	0.5416	0.0238
63	8.48	10.53	2.01	1.1					0
64	8.57	10.63	2.02	1.1	0.418	0.623	0.1966	0.82605	0.0165
65	8.57	10.62	2.01	1.2					0
66	8.51	10.57	2.02	1.2	0.579	0.864	0.2262	0.95042	0.0085
67	8.43	10.51	2.04	1.3					0
68	9.04	11.1	2.02	1.4	0.619	0.924	0.2346	0.98571	0.0039
69	8.49	10.54	2.01	1.4					0
70	9.01	11.08	2.03	1.5	0.666	0.994	0.2384	1	0.00224
71	9.14	11.21	2.03	1.5					0
72	9.11	11.15	2.00	1.6	0.648	0.967	0.2457	1	0
73	8.47	10.52	2.01	1.7					0
74	8.87	10.93	2.02	1.7	0.669	0.998	0.2396	1	0
75	8.5	10.55	2.01	1.8					0
76	9.07	11.11	2.00	1.8	0.657	0.981	0.2398	1	0
77	9.08	11.11	1.99	1.9					0
78	8.47	10.52	2.01	1.9	0.669	0.999	0.2436	1	0
79	9.14	11.15	1.97	2.0					0
80	8.33	10.37	2.00	2.0	0.599	0.894	0.2143	0.90042	0
81	8.98	11.04	2.02	2.1					0
82	8.51	10.53	1.98	2.2	0.683	1	0.2384	1	0
83	8.97	11.03	2.02	2.2					0
84	9.09	11.14	2.01	2.3	0.659	0.983	0.2382	1	0
85	9	11.05	2.01	2.3					0
86	9.11	11.14	1.99	2.4	0.695	1	0.2395	1	0
87	9.07	11.11	2.00	2.4					0
88	9.13	11.16	1.99	2.5	0.684	1	0.2351	0.98782	0