Fall 2016

# Conceptual parameters necessary for modeling wettability alteration in an enhanced smart brine-chalk system

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## Recommended Citation

Albahrani, Ahmed Abdulkareem Hussein, "Conceptual parameters necessary for modeling wettability alteration in an enhanced smart brine-chalk system" (2016). *Masters Theses*. 7589.
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# CONCEPTUAL PARAMETERS NECESSARY FOR MODELING WETTABILITY ALTERATION IN AN ENHANCED SMART BRINE-CHALK SYSTEM

**BY**

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**A THESIS**

**Presented to the Faculty of the Graduate School of the**

**MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY**

**In Partial Fulfillment of the Requirements for the Degree**

**MASTER OF SCIENCE IN PETROLEUM ENGINEERING**

**2016**

**Approved by**

**Dr.Ralph Flori, Advisor**
**Dr.Shari Dunn Norman**
**Dr. Mingzhen Wei**

# ABSTRACT

Achieving higher recovery of oil from proven carbonate reserves around the world is not an easy task. One promising new method, especially for carbonate reservoirs, is the use of “Smart Water” technology, which is an injection water with carefully determined, optimal ionic composition and salinity. Recent experiments have shown good recovery results, but the mechanism of wettability alteration by this fluid are still not well understood. The goal of this study is to review the high and optimal salinity and ionic composition literature plus perform dimensional analysis of key variables in order to shed light on the physical and chemical factors of improved recovery in carbonates. This work will discuss physical and thermal principles and relationships of flow and heat distributions in the presence of the rock-fluid reaction. A series of logical connection among plenty of physical and chemical principles using Buckingham Pi theorem in the dimensionless analysis has proposed to model and find a general formula that can best fit to describe the nature of the resulting changes accompanied with heat and flow transport through a porous medium in the presence of an abundance of sulfate concentrations. The primary purpose of this work is to show the factors that can control the wettability alteration using the chalk-sulfate system using the proposed general formula and predict the likely phenomenon such as undesirable mineral deposition, diagnosing the diffusion reduction, and fingering possibility. This work will show the numerical estimation of the contact angles of wettability alteration for two crude oils, oil A and B using smart brine contains four times sulfate concentration at different temperatures 70 C$^{\circ}$, 90 C$^{\circ}$, 100 C$^{\circ}$, and 120 C$^{\circ}$ reinforced by Buckingham Pi theorem and series of proven empirical correlations used to derive the general formula of wettability alteration mechanism in carbonates.

# ACKNOWLEDGMENTS

Firstly, I would like to express my sincere gratitude to my advisor Dr. Ralph Flori for the continuous support of my Msc. Study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of investigation and writing of this thesis.

Besides my advisor, I would like to thank the rest of my thesis committee: Dr. Shari Dunn Norman, Dr. Mingzhen Wei, for their insightful comments and encouragement, but also for the hard question which incented me to widen my research from various perspectives.

Last but not the least, I would like to thank my wife for her patience and my family: my parents and to my brothers and sisters for supporting me spiritually throughout writing this thesis.

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# 1. INTRODUCTION

## 1.1 HISTORY OF CONTROLLED SALINITY WATERFLOODING

The latest studies showed that the carbonate reservoirs around the world have more than 50% of proven oil reserves. (Sheng, 2013), has stated that about 60% of remaining oil and 40 % of gas reserves are still existing in carbonate reservoirs globally. In last decades, the carbonate reservoirs have known of its 10% of primary recovery as well as its inadequate response to secondary recovery using water injection (Xie et al., 2004).

The reason why carbonate reservoirs consider not efficient is due to oil or mixed wet, various properties of rock, low permeability, and natural fractures (Cuiec, 1984). Figure 1.1 below, shows 1,507 Global EOR projects, and gas injection is the most conventional EOR Method from 18% of proper EOR Methods used in carbonate (Alvarado and Manrique, 2010).

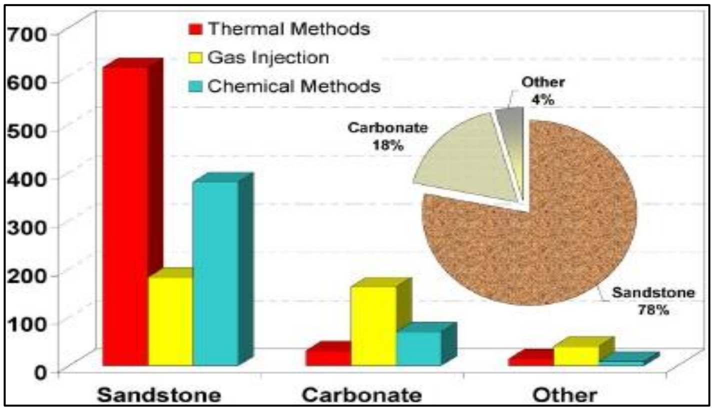


Figure 1.1. EOR methods by lithology (Alvarado and Manrique, 2010)

The little use of water flooding projects in carbonate in the world in addition to the fact of a high percentage of proven oil and the complexity nature of carbonate reservoirs has encouraged plenty of the researchers and inventors in the oil industry to find a method to improve oil recovery from the carbonate reservoirs. Series of researches have emerged to introduce a synthetic seawater as EOR fluid in water flooding to improve oil recovery.

The scientific need for a modern water modified ionically named later smart water become crucial to find a way not only to increase the sufficient income of oil production but also to help better understanding of the mechanisms that lead to wettability alteration in carbonates.

Famous petroleum researchers such as T. Austad, S. Strand, Zhang, Fathi, et al. have shared the same idea that wettability still the primary parameter that can control the efficiencies of enhanced oil recovery methods. Those researchers based on the results of their experimental works showed that doing an ionic change to the injected brines to alter the rock surface chemistry and switch the oil or mixed wet to water wet is related to major determining ions – rock interactions. Active determining ions such as $Ca^{2+}$, $Mg^{2+}$, and $SO4^{2-}$ were responsible for wettability alteration in carbonates.

The exchange interactions among ions and the rock – carboxylic group in crude oil have studied based on the thermal condition of the porous medium in the presence of gradient concentration ratios. From the reservoir point of view, the main two aspects of any enhanced oil recovery are pressure maintenance and increasing macroscopic sweep efficiency and those both can control them in water flooding project using smart water. Macroscopic efficiency or displacement efficiency depends on the fluids saturations this can control by monitoring the injection pumps pressures used in water injection surface facilities, existing of a flexible completion design. In the laboratory, using a pressure regulator in the outlet stream of the core holder chamber which can prevent the within fluids inside the core samples used to evaporate can keep the confining pressure within the pore spaces of the core in constant.

Water flooding using smart brines in which both relative permeability and capillary pressure can test considered as an inexpensive method compared with the other EOR methods; it can accomplish oil recovery in the range of 30% to 40%.The secret key is to adjust the brine concentration through increasing the effective determining ion concentration to magnitudes that compatible with acidity degree of the aged oil within the core samples. (Fathi et al., 2010), have declared that the salinity and ionic composition of injected brines have the influences on wettability alteration and the improvement of oil recovery.

Before Fathi et al., Bernard (1967) was one of the first to show that the salinity of flood water could affect oil recovery. Al Mumen (1990) investigated the effect of injected brine salinity on oil recovery using Berea Sandstone core samples; he showed an increase in oil recovery with enhancing the salinity of the injected water in the absence of clay. Jadhunandan ( 1990 ), investigated the effect of the ionic composition of injected brine on oil recovery using Berea core samples and low salinity brine; he observed improved in oil recovery and attributed that improvement to changes in rock wettability.

Although most of the research on the emerging of low salinity flooding method has focused on Sandstone reservoirs, laboratory core flooding tests, and single-well trails revealed that low salinity flooding can also be applied to carbonate reservoirs (Bagci et al , 2001, Alotaibi et al, 2009,Vledder et al, 2010, Yousef et al, 2010, 2011, 2012, 2014, Strand et al, 2006, Al-Harrasi et al, 2012, Al attar et al, 2013, Kwak et al, 2014 ). That was supported by unexpected observed oil recovery from Ekofisk field, a fractured chalk reservoir, upon injection of flooding of North seawater (Sylte et al., 1988). (Zekri et al., 2011), studied the effect of low salinity on wettability and oil recovery of carbonate and sandstone formations and concluded that low salinity could apply to carbonate rocks.

The authors above also added that the performance of low salinity depends on the carbonate type, chalky or microcrystalline limestone. Several investigations were carried out using chalk and limestone rock samples to understand the recovery mechanisms leading to the incremental oil recovery due to injection of low salinity water.

As a result of these investigation it was proposed that the wettability of the chalk rock was changing to a more water-wet condition, and this change in wettability alteration is due to the presence of potential determining ions ( PDI) and their relative concentrations in the injected water( Austad et al., 2005, RezaeiDoust et al., 2009). Austad et al., 2005, suggested $SO4^{2-}$, $Ca^{2+}$, and $Mg2^{+}$ as potential determining ions for chalk. Furthermore, these ions ($SO4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$) are proposed to be responsible for surface wettability alteration, and it is not clear if that is the case with other carbonate rocks or only chalk due to the lack of systematic investigation on surface analysis level( Evgeny, 2014 ).

(Austad et al., 2005), proposed a wettability alteration mechanism according to which sulfate ions will adsorb onto the chalk surface and lower the net positive charge to facilitate some desorption of negatively charged polar components (carboxylic material).

They further stated that the adsorption of sulfate ions onto the chalk surface is enhanced when the temperature increased from 100 $C^{\circ}$ to 120 $C^{\circ}$. They also indicated that the concentration ratio $[SO4^{2-}]/[Ca^{2+}]$ in the injected water to be a major factor. It realized from the depletion of the $SO4^{2-}$ ions in the effluent from flooding chalk cores with seawater that has a ratio of $[SO4^{2-}]{\sim}2[Ca^{2+}]$.They attributed the depletion of $SO4^{2-}$ partly to the adsorption of $SO4^{2-}$ ions on the chalk surface (Austad et al., 2005).Imbibition tests conducted on modified carbonate rocks with stearic acid saturated initially with formation brine accompany with an imbibition process with fluids containing $Mg^{2+}$ or $SO4^{2-}$, at the same concentration as the injected seawater, showed that the highest oil recovery obtained when $Mg^{2+}$ is present in the imbibing fluids, which ruled out the above suggested mechanism(Karoussi and Hamouda,2008).

Further core flooding tests performed using combination of different injection rates, temperature, crude oil types, core plugs and compositions of the injected brine, revealed that the incremental oil recovery with the aid of sulfate ions cannot be explained just by the rock wettability alteration, and injection of brine rich in sulfate ions may lead to additional oil recovery even under completely water-wet conditions. Not only this, but crude oil composition type was found to play a dominant role in the effect of brine composition on the incremental recovery in addition to the injection rate (Zahid, 2012).

Core flooding experiments in carbonates based on advanced ion management principle has achieved the best quality regarding oil recovery compared with carbonates with formation water; advanced ion management purpose is to improve oil recovery by adding or removing ions to the injected brines.

One of the biggest challenges that might face the core flooding project in carbonates is the reverse reactions between brine and Anhydrite or Gypsum (Taber and Martin, 1983). Although that challenge, that belief gradually decayed when an attractive amount of oil has recovered from a fractured chalk reservoir of Ekofisc field in north sea (Sylte et al., 1988; Hallenbeck et al., 1991).

The published important papers related to spontaneous imbibition and laboratory measurements has conducted at the University of Stavanger by Austad and his co - workers. The main aim of those researchers is to find a way to improve the imbibition processes accompany with adding different sulfate concentrations to seawater within chalk cores in addition to using different crude oil have aged at different ages to establish an oil - wet case.

Although the majority of core flooding test have carried out on chalk, a logical proof has been reached using spontaneous imbibition experiments on limestone and fractured limestone.Not only chalk was the raw sample of spontaneous imbibition experiments but also limestone had used as well. Ligthelm (2009), has estimated the oil recovery in about 17% of OOIP  of complete recovery using core samples of limestone from the middle east. However, Hogenson et al. (2005) observed that even using sulfate in different concentrations as well as adjusted crude oils has no impact on oil recovery for an unfractured limestone.

The topic of using different brines in various salinity has also encouraged plenty of the researchers to examine the improvement of oil recovery in carbonates using low salinity brines. (Yousef et al. 2010) has observed a real improvement in oil recovery on carbonate cores from the middle east around 18-19% OOIP.

In conclusion, water flooding using modified injection brines can give accredited additional oil recovery from carbonate reservoirs regardless the type of carbonate rock by adjusting the ionic composition of brines within valid ranges of salinity. The proven experimental results, as well as the great effort in series of investigation works, encourage the researchers increasingly to seek deeply about the unknown and unproven aspects that need interpretation about wettability mechanisms in carbonates.

## 1.2 WETTABILITY ALTERATION INTERPRETATION

Carbonate rocks such as chalk, limestone, dolomite have positive charge wet surfaces to oil. The reason why carbonate rocks have considered as oil wet rocks is the basic structure of the carbonates which positively charged. On the other hand, oil has found to be acidic or negative charge in its nature. The opposite polarity between oil and the surface of the rock leads to attraction the free acidic carboxylic group of crude oil towards the carbonate surface. The carboxylic group (-COOH) has ends that can bond in heavy products of crude oil like asphaltene and resin (Speight, 1999), while the other end will interact with the rock to establish oil wet areas throughout the exposed pores opened to the flow.

In any carbonate rock, if the only wetting phase is the formation water so, the rock will have wet areas to water which is in the broad salty base. In water flooding experiments, the rock will age with different types of crude oil for a long times might exceed 7 weeks and no less than 4 weeks (This work will focus on 8 weeks and 4 weeks aging times of two types of crude oil A and B) in order to force the rock surface to be oil wet which will be necessary later in study the spontaneous imbibition phenomenon with different types of imbibing brines. Specifically, aging the rock with oils for a long time will create a severe oil - rock bond that can ensure the majority of pores have interacted oil-wet surface areas to ensure that the aging process has conducted successfully in carbonate cores an accurate measuring of the acidity of the crude oil after aging must do.

The acidity will give an indicator about how much the free ends of the carboxylic group suspended in the crude oil. The more the carboxylic group within the porous medium the more acidity after oil aging process and then the success result of getting an oil wet rock.The magnitude of the crude oil acidity has a scientific term called acid number which will discuss in next sections in details which are specifically a tool to predict the severity bonding of oil - rock system.(Fathi et al., 2011), has showed that the chemical properties of the carboxylic substances such as the acidity of the crude oil have a sharp importance especially in synthetic seawater to behave as wettability modifier. One of the facts about carbonate rocks are its tendency to be water wet at high ranges of temperatures compared to small ranges of temperatures (Rao, 1996). Aging the cores with oils for long times will be enough to establish a coated film of the heavier fractions of crude oil regarding carboxylic group around the pore spaces of the core.

The difficulty of oil wet rock to give a smooth flow and ease recovery depends on how much the acidity and how long the aging has done for the core. The importance of temperature on the wet pores surfaces areas chemically is to reduce the acidity or the acid number by decarboxylation operation as well as reduce the intermolecular forces for the heavier series in the crude oil to ensure better sweep efficiency. The distinct process of decarboxylation can observe on calcite (Shimoyama and Johns,1972).

The noticeable effect of brine composition used in carbonate on wettability was great with sulfate.Sulfate is the dominant active ion that can control the initial wettability of the rock.The influence of sulfate affected by the concentration of $Ca^{2+}$ in the formation water especially with the combination of high temperature; those two factors will limit the number of aqueous sulfates to lowerest value and will lead to more precipitation of anhydrite CaSO4(s).The anhydrite reaction is the exothermic reaction in which any rising of temperature will shift it to endothermic; the shifting to endothermic means reduce the presence of sulfate in the aqueous solution and then affect the sweep efficiency.(Shariatpanahi et al., 2011), have mentioned that sulfate as the most active ion will be the top active ion of preventing adsorption of carboxylic material onto the rock surface, which will increase the water wetness within the core.

(Zhang et al.,2007), has explained the mechanism of wettability alteration in carbonate. Figure 1.2, shows the proposed chemical mechanisms for wettability modification on chalk surface especially in a double layer in which the different ions will replace and fill with along the surface of the chalk. The operation starts with the negatively charged carboxylic group (-COOH), the component containing in crude oil, will affix on carbonate surface which positively charged. The attraction of sulfate ions onto the chalk surface will help to eliminate the carboxylic group in the crude oil away from the calcite surface and enhance the recovery. Sulfate play the main role in any replacement reaction to and from the chalk surface. $Ca^{2+}$ will reinforce the wettability alteration as well through creating a separating barrier between calcite and the carboxylic group; $Mg^{+2}$ will do the same job as $Ca^{2+}$ when the temperature exceeds 90 C°.

(Zhang et al.,2007), has suggested that at high temperatures, dissolution/precipitation chemical reactions might happen as well, which will impact surface chemistry significantly. At 90C° and above, based on Le Chatelier's principle in reversible reactions, $Ca^{2+}$ will be replaced by $Mg^{+2}$ and for calcite reaction the release of $Ca^{2+}$ in aqueous solution will lead to shifting the dissolution reaction of calcite which is exothermic to endothermic due to the unbalance concentrations of product and reactors towards the opposite side of calcite dissolution reaction and encourage more deposition of calcite instantly. For that reason, $Ca^{2+}$ and $Mg^{+2}$ both can enhance the recovery but to a point less than of sulfate. The following reaction, indicates the ion exchange process on the surface (Rezaei Doust et al., 2009):

$$RCOO\text{-}Ca\text{-}CaCO_3(s) + M^{2+} + SO_4^{2-} = M\text{-}CaCO_3(s) + RCOO\text{-}Ca^{2+} + SO_4^{2-}$$

Where: RCOO- the carboxylate ion which an ion with negative charge represents the conjugate base of a carboxylic acid., R is the radical chemical group that contains a carbon or hydrogen atom that will be attached to the rest of the molecule, M is calcium or magnesium.

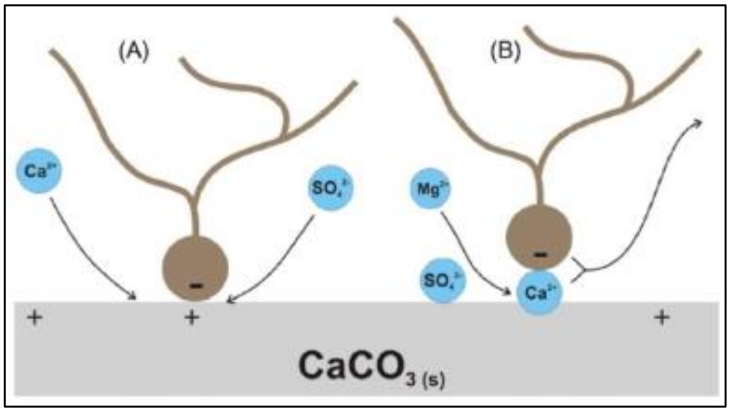


Figure 1.2. Proposed chemical mechanism for wettability alteration of chalk (Zhang et al., 2007)

When the carboxylic group release from the carbonate; the carbonate surface becomes water-wet. Rezaei Doust et al. (2009), summarized that the composition of injected brine has to contain sulfate in addition to either calcium or magnesium or both for carbonate wettability alteration, and high temperature (> 90℃) is necessary. In carbonate reservoirs, the carboxylic material that found in the heavier parts of crude oil adsorbs on the surface of the rock and turns it into oil-wet over time.The mechanism of wettability alteration during chemically tuned waterflooding seems to be adsorption of ca tions in the water and desorption of negatively charged carboxylic group on the rock surface, which alters the rock toward water-wetness (Standnes and Austad, 2000). Yu et al. (2007), has shown that the contact angles varied from mixed-wet to water-wet as the temperature increased from 20℃ to 130℃ by using of seawater with four times of sulfate.

The magnitude of how much carboxylic group will adsorb onto the chalk surface depends on the extent of the intermolecular forces between this group and the injected brine as well as this group with the surface of the chalk. These intermolecular forces represented by interfacial tension which is the measure of the interacted forces between the immiscible liquids at the interface; the interfacial tension affected by temperature directly. The rising of temperature within the core will lead to decrease the interfacial tension ( This work will focus on showing the impact of interfacial tension lowering on determining the contact angles of wettability alteration on chalk ).

Figure 1.3 below, shows a typical behavior of interfacial tension versus temperature. Increasing temperature leads to an apparent reduction in interfacial tension values.

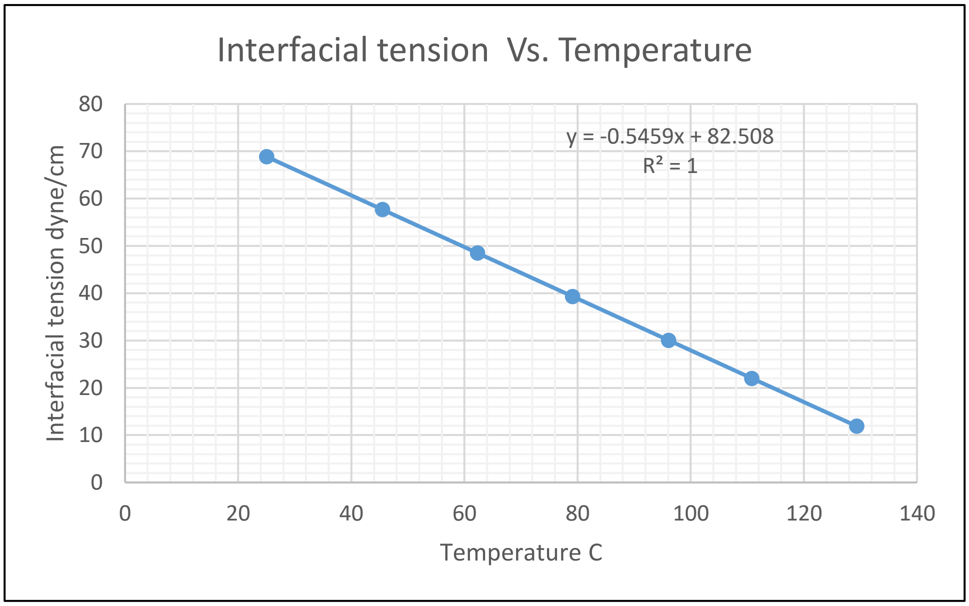


Figure 1.3. Typical behavior of Interfacial tension versus Temperature

The interfacial tension also has found to be affected by the amount of the impurities added to the injected brine. Since this work will show the adjusting of the injected brine by adding double values of concentration of sulfate, so a significant reduction in interfacial tensions will observe. Figure 1.4, shows the typical attitude of interfacial tension versus the concentration of injected brine.

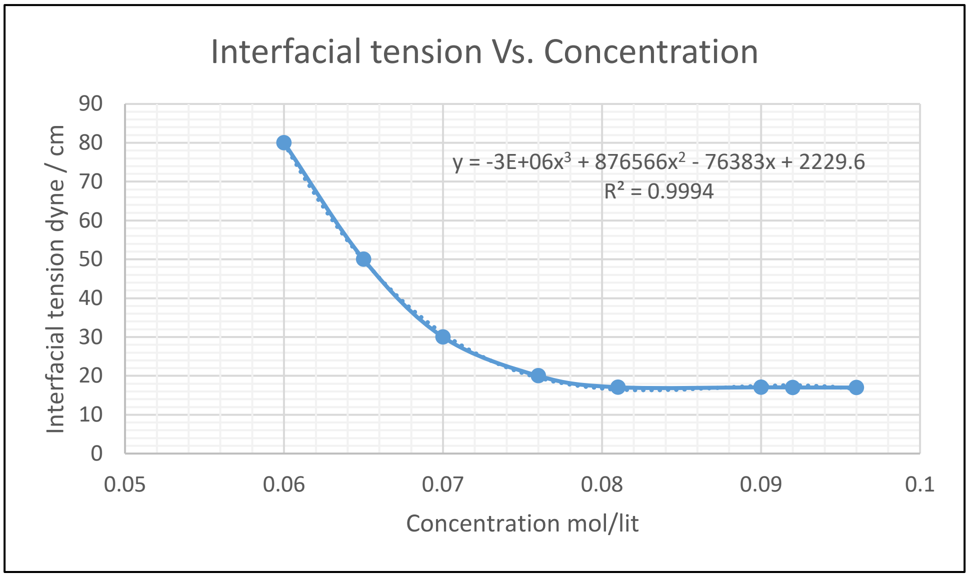


Figure 1.4. Typical behavior of Interfacial tension vs. Brine concentration

Frankly, it is easy to observe that after the system switches to water wet, the value of interfacial tension will be the same approximately in around value of 17 dyne/cm, and this is logic since the system reached its equilibrium average temperature at the end of the imbibition period. As it has know that the quality of any crude oil will be detected based on its API extensive that the lower values of it mean an excellent indicator of the amount parts of dissolved gas in the crude oil as well as an index to the quantity of the heavier suspended compounds in crude oil.

The decreasing of the dense phase with increasing temperature leads to reduce the interfacial tension or, in other words, the crude oil with high quality (High API) has straight reduction tendency of interfacial tension with increasing temperature. Figure 1.5, shows the typical behavior of interfacial tension vs. API degree of crude oil at different ranges of temperatures.

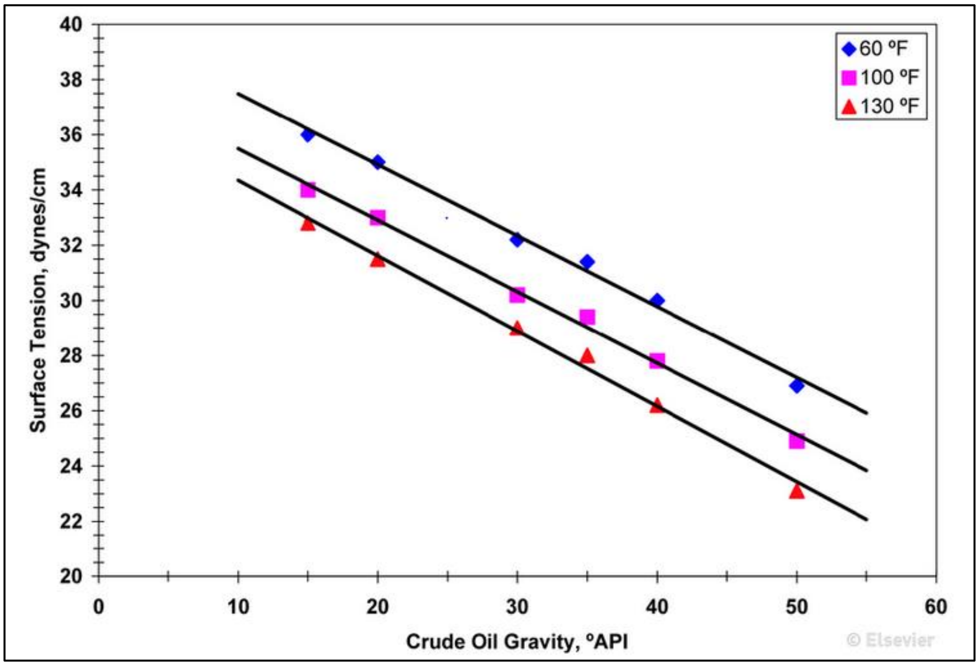


Figure 1.5. Typical behavior of Interfacial tension vs. API degree at various temperatures (Baker, O. and Swerdloff, W. 1956)

From the graph above, it is easy to notice that the values of interfacial tensions will decrease with increasing the temperatures from 60 F° up to 130 F° in addition to the increasing of API degree of the crude oil used. The crude oil with API 50° has interfacial tensions values of 27 dyne/cm, 25 dyne/cm, 23 dyne/cm at 60F°, 100F°, and 130F°respectively which mean the same crude oil can have different values of low interfacial tensions during the rising of its temperature.

## 1.3 WETTABILITY DETERMINATION

The relationship between interfacial tension and the contact angle in any carbonate rock is intimate relationship in way each parameter will detect the other, and this will be applicable according to the following equation:

$$\cos\theta_{ow} = \frac{(\sigma_{os} - \sigma_{ws})}{\sigma_{ow}} \qquad (1)$$

Where: $\theta_{ow}$ is the contact angle dimensionless, $\sigma_{os}$ is the interfacial tension between crude oil and the solid surface in unit of dyne/cm , $\sigma_{ws}$ is the interfacial between brine and the solid surface in unit of dyne/cm , $\sigma_{ow}$ is the interfacial tension between two immiscible liquids ( crude oil and brine ) in unit of dyne/cm .

The basis that on it equ.1 based is the principle of forces equilibrium throughout the interface of two immiscible liquids ( crude oil and brine) and the resultant force of the liquids forces along the surface of the solid. Figure 1.6, shows the interfacial forces distribution around and along a droplet of water surrounded by oil:

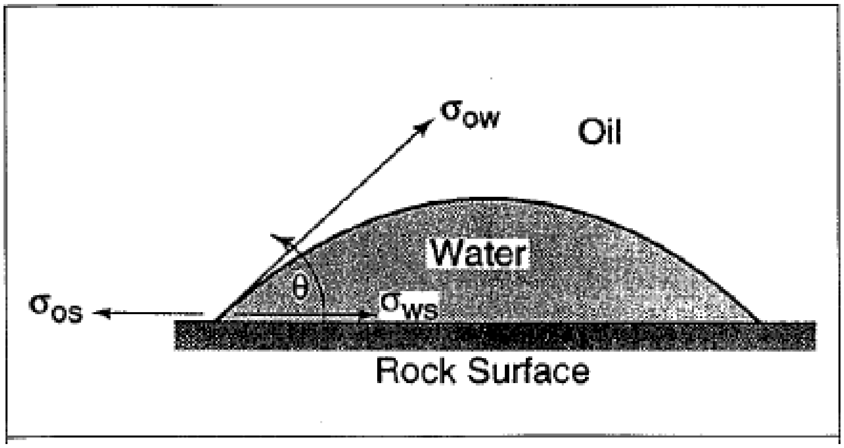


Figure 1.6. Interfacial forces at an interface between two immiscible fluids and a solid (Ayers, 2001)

According to on the estimated contact angles, the wettability can detect. The following ranges are the typical for finding the wettability in carbonates:

Water wet: 0° < θ < 70°

Intermediate or mixed wet: 70°< θ < 110°

Oil wet: 110°< θ < 180°

Neutral wet: θ = 90°

In Figure 1.7 on the left side, if $\theta = 0^\circ$, we have strong water wet and 100% grains coated with water completely, and the oil will be free to move and produce ,but if we have $\theta = 180^\circ$ Figure 1.7 on the right side, we have strong oil wet and 100% grains coated with oil entirely and water will be free to move and produce .

At ($\theta = 0^\circ$), the reservoir will produce oil in the smoothly way and ultimate economic rates of production but in the case ($\theta = 180^\circ$), the reservoir will not produce more oil except water, and this is not okay for petroleum engineering considerations.

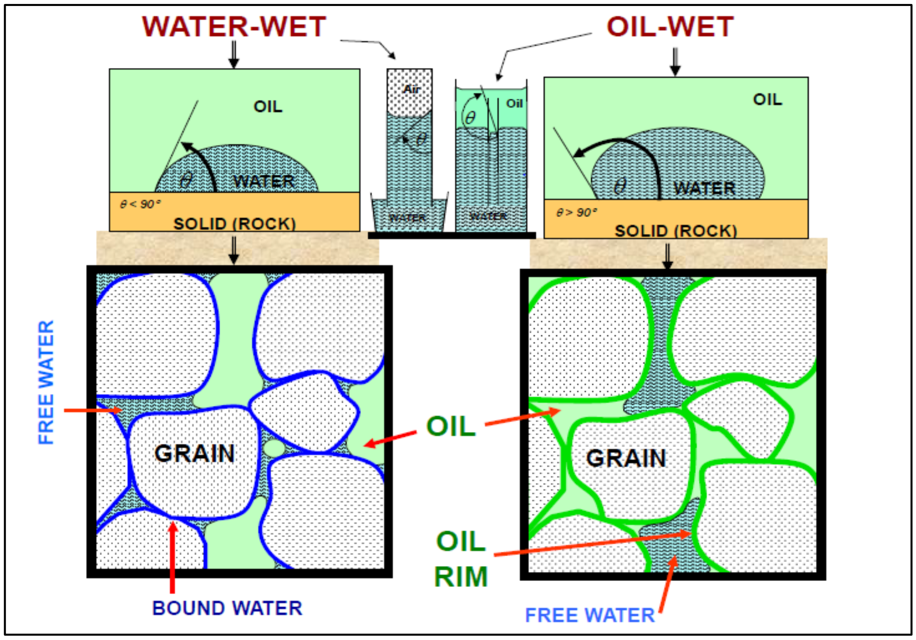


Figure 1.7. Wettability differentiation in Rock (Ayers, 2001)

## 1.4 OBJECTIVE OF THIS WORK

The fact of that the light compounds series of crude oil will penetrate deeply into the rock surface on consequence the free existing heavier compounds coated and restricted the flow path leads to high interfacial tension between oil and solid ($\sigma_{os}$) whereas; the heavier compounds such as the carboxylic group like asphalt, wax, and risen will create a thick viscous film coated the interior wet areas surfaces of the pore spaces. Establishing a general formula of wettability alteration to show a logic connection among main parameters that control the wettability alteration mechanism is the aim of this work. The main reasons that encourage to introduce a proven numerical formula to describe and find the key parameters related to wettability alteration in carbonates is the fact that there is a possibility to get enormous production of heavier compounds represented accurately in an abundant amount of viscous carboxylic materials and the fact of high-temperature relationship with interfacial forces, viscosities, and dissolution/precipitation reactions on chalk. To easy production of the heavier crude oil compounds through switching the wettability alteration and monitoring the change of contact angles with other physical and chemical principles related to the porous medium properties and the fluid flow constrictors required using adjusted synthetic brines with systematic thermal condition in order to improve the displacement efficiency by reducing the oil remaining saturation along the direction of the flow of the imbibing brine , reducing the interfacial tension between oil and brine , and achieve best mobility of oil .

# 2. EXAMPLE PROJECT: EKOFISK OIL FIELD

Ekofisk oil field is one of the biggest oil fields in the North Sea and was the first oil discovery after 200 exploration wells have drilled. Figure 2.1, shows a geographical map of Ekofisk field in the North Sea; it is located in the block 2/4 of the Norwegian section about of 320 km away from the southwestern part of Stavanger. This field has been discovered in 1969 by Phillips Petroleum Company and started to its first production in 1971 from four subsea wells.This field is offshore, and the platform type used with it is the kind of jackup.

The Oil production in Ekofisk has planned to continue until at least 2050.The main Ekofisk reservoirs consist of Cod, Ekofisk, West Ekofisk, Tor, Albuskjell, Eldfisk, Edda and Embla oil fields.The Ekofisk terminal is a large complex of platforms and structures that have built; those platforms have connected to a massive connection manifold or a transportation hub that can connect with other adjacent fields such as Valhall, Hod, Gyda, Ula, Statfjord, Heimdal, Tommeliten and Gullfaks.The whole unification section consists of 29 offshore platforms in which the oil produced transferred through the Norpipe oil flowline to the Teesside Refinery in England while the naturally produced gas has moved using the Norpipe gas pipeline to Emden in Germany.

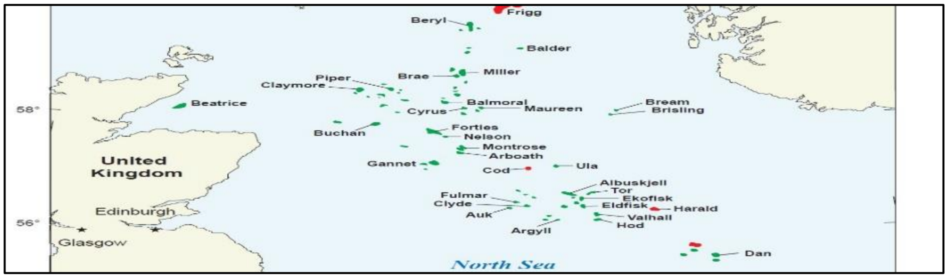
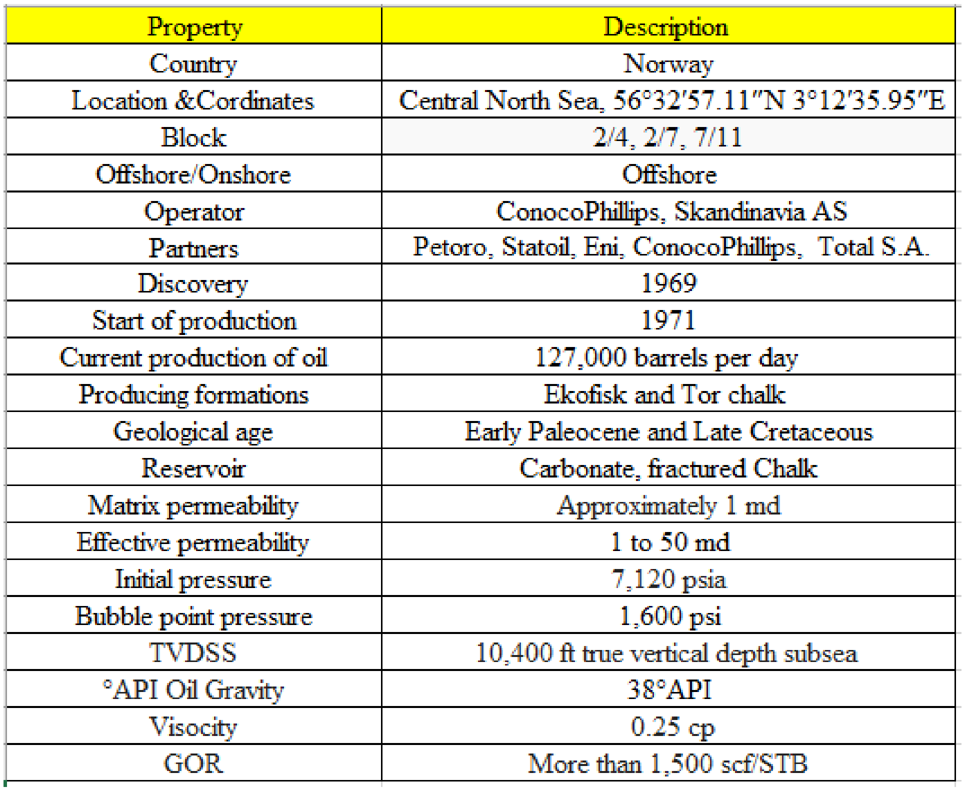


Figure 2.1. Geographical map of Ekofisk oil field location in the North Sea (Gautier, D.L.,2013)

The whole descriptive information related to Ekofisk field shown in Table 2.1 below, Which contains the overall characteristic information of Ekofisk field:

Table 2.1. The overall characteristic information of Ekofisk field



| Property | Description |
|---|---|
| Country | Norway |
| Location &Cordinates | Central North Sea, 56°32′57.11″N 3°12′35.95″E |
| Block | 2/4, 2/7, 7/11 |
| Offshore/Onshore | Offshore |
| Operator | ConocoPhillips, Skandinavia AS |
| Partners | Petoro, Statoil, Eni, ConocoPhillips, Total S.A. |
| Discovery | 1969 |
| Start of production | 1971 |
| Current production of oil | 127,000 barrels per day |
| Producing formations | Ekofisk and Tor chalk |
| Geological age | Early Paleocene and Late Cretaceous |
| Reservoir | Carbonate, fractured Chalk |
| Matrix permeability | Approximately 1 md |
| Effective permeability | 1 to 50 md |
| Initial pressure | 7,120 psia |
| Bubble point pressure | 1,600 psi |
| TVDSS | 10,400 ft true vertical depth subsea |
| °API Oil Gravity | 38°API |
| Visocity | 0.25 cp |
| GOR | More than 1,500 scf/STB |

## 2.1 WATER INJECTION PILOT PROJECTS OF EKOFISK FIELD

As it has mentioned before, the oil productivity from Ekofisk has started in June 1971, and the production reached its maximum value of 350,000 bbl/day from the total productivity of 30 oil producers and eight gas injectors. Figure 2.2, shows the overall distribution of 143 oil producers and 40 water injectors of Ekofisk field in 2013.

A list of laboratory tests results revealed that the water flooding using water imbibition on low permeability chalk samples were preferable in Tor formation. The first water flooding project in chalk reservoir of Tor formation of Ekofisk field started in 1981, and the obtained results were highly desirable later in 1983. The massive project of water injection performed in 1987 using 30 water injection platforms and with entire water injection capacity of 375,000 bbl/day.

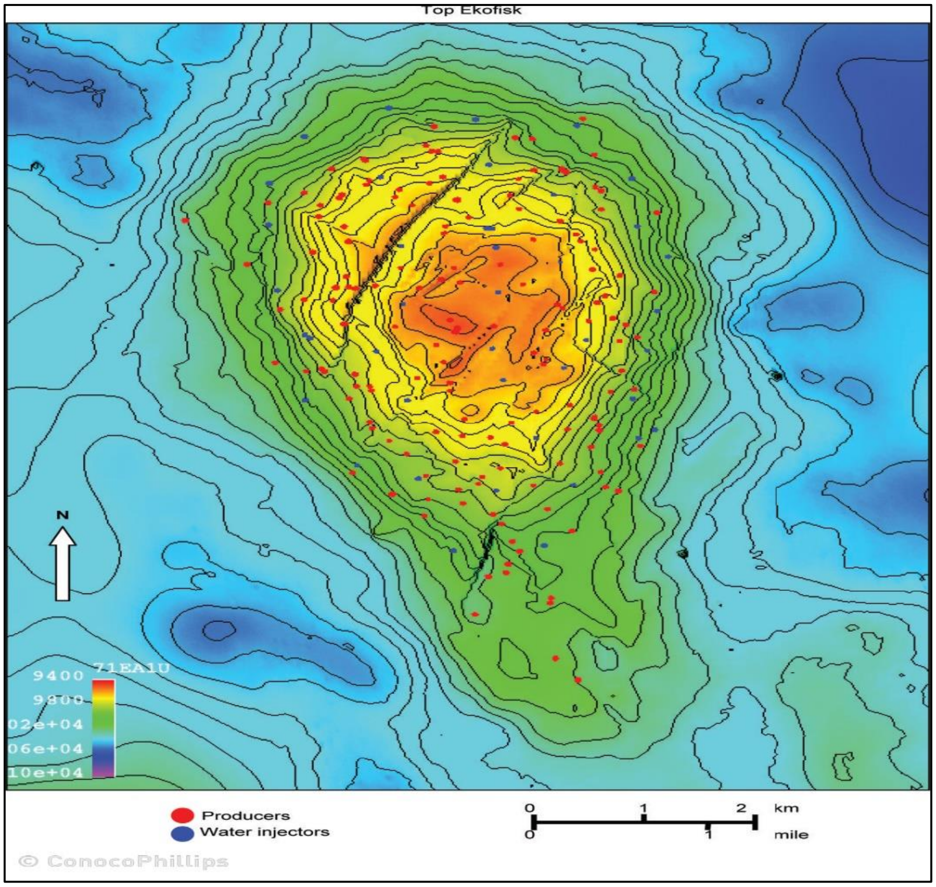


Figure 2.2. Distribution of oil producers and water injectors of Ekofisk field (Glendasmith, 2013)

Much successful water injection project has conducted in lower Ekofisk in the period extended between 1985 - 1987. On the other hand, for upper Ekofisk formation, the water flooding results showed negative attitude firstly but, after six months of sidetracked coring from the wells and replay the test, the results were different and positive which can support the idea of the possibility of doing the water flooding successfully in upper Ekofisk formation. The first production data history of Ekofisk showed that the field has produced about 17%-18% of OOIP. But, nowadays, the recovery has jumped to 50% of OOIP and for 40 years because of applying the improved oil recovery methods frequently especially water flooding.

## 2.2 SUBSIDENCE PROBLEM IN EKOFISK FIELD

The biggest problem that obstacle the productivity in Ekofisk field was the seabed subsidences. It has noticed that a severe decline in the overall complex of the platforms where the platforms' tanks were immersed partly in seawater. The geologists showed that the Excessive production of both oil and gas from the field had led to minimizing the confining pressure within the porous media and create an axial compaction. For that reasons finding a way that can achieve pressure maintenance for the entire reservoir as well as enhance the productivity is the best solution in reservoir point of view. The positive results obtained from the first water injection pilot projects, the abundant of seawater that compatible with the formation easily, the cheapness of water injection project compared with other EOR methods, and many reservoirs and design considerations has encouraged to use water injection to maintain the pressure and achieve the peak production rates. In 1987, Phillips company held an agreement with its partners to use a new water injection to improve oil recovery and maintain the reservoir pressures. To the late of 1990's Phillips company has injected the biggest appropriate amount of water of 900,000 bbl/day into the reservoir. Nowadays, that rate has reduced to 500,000 bbl/day. In addition to the use of water injection in highest rate, Phillips was enabled to fix the damages of all the immersed platforms by lifting the legs of jack-up platforms up to 6 meters, installed new extension structures, and reinforced the platforms' tanks with double protective metal layers so as to it can be ready for hight rate water injection.

The following equation will show the importance of existing pore pressure maintenance during water injection to keep the fractures open as possible and achieving high conductivity and then high permeability in maner will meet the criteria of getting improved oil production:

$$\sigma_e = \sigma - \alpha(P_p) \tag{2.1}$$

Where: $\sigma_e$ Effective stress, $\sigma$ External stress, $\alpha$ Engineering factor (0-1), $P_p$ Pore pressure

The success of water injection project especially in chalk formation has canceled the wrong belief about the applicability of water imbibition to improve the oil recovery. This Stig S. Kvendesh said.“ water injection had a reasonable effect.” and he stated that “ it maximize pressure gradually in the reservoir and today we are controlling subsidence with water injection.” But his comment just was pessimistic when he declared that” Some thought at the time it wasn’t possible to produce from a chalk reservoir at all” about the possibility of getting oil recovery from chalk reservoir, the Phillips’ spokesman in Norway shared the wrong belief when he said “ When it comes to water injection it was normal in sandstone. But it hadn’t been done with chalk.” All those opinions have changed after getting the positive results from the previous pilot projects and became confident especially after many modifications have done to the Terminal of Ekofisk as well as achieving best production rates. The searching of any Experimental pieces of evidence by experiments and simulators will eliminate the wrong beliefs about the applicability of using water injection in chalk reservoir of Ekofisk field. This work will be a tool to distinguish the facts that can judge the wettability alteration during water imbibition phenomenon and give a logical interpretation of the main key parameters leading to improve oil recovery in carbonates.

# 3. QUANTITIVE AND QUALITIVE DESCRIPTION OF WETTABILITY ALTERATION IN CARBONATES

The best way to describe the wettability is to study the physical phenomenon accompany with the direction of increasing in wetting phase. The concentration of sulfate will diffuse along the positively charged sites on the rock surface and the concentration gradient of the active determining ion throughout the path of flow depends upon the pore spaces geometry of the porous medium, the packing complexity of the rock grains, the type of the porosity of the core, the kind of the permeability, the interfacial forces within the system, the thermal condition of the porous medium, the imbibing brine density, the ambient temperature, the properties of the crude oil, the type of the carbonate rock used, and the final flow impedance generated while imbibition process. This work will focus on the wettability alteration mechanism from the quantitive point of view. As previously mentioned, the wettability of the rock can detect using the contact angles. The contact angles determination will discuss in next sections with taking in the consideration all the reasonable physical and the chemical factors accompany with the capillary tendency of the modified wetting brine.

For a gradual comprehensive understanding of the methodology of wettability alteration distinguishing, it will be better to illustrate the initial steps of the logic procedures of determining the contact angles task to start with the introduction to the main conceptual phenomenon that is permanent to occur in any carbonate- smart brine interaction.

The thorough understanding of diffusivity, mobility of the wetting phase, the viscosity ratio between the two immiscible liquids, and crude oil acidity- sulfate concentration relationship will facilitate the difficulties of understanding the wettability alteration mechanism.

The wettability alteration in carbonates is not an easy task. The motivation of finding a way to detect the contact angles of wettability alteration increased when no coordinated numerical study has carried out that consider all the possible water-rock interactions simultaneously before this work.

This work successfully reached its purposes when the suggested general formula of wettability alteration estimation (which will derive in next sections) has accurately calculated the gradual adjustments and then the corresponding contact angles of the rock-smart brine interactions. The chalk cores aged with oil for a long time to force the core to accept oil as the new wetting phase; the first model created shows a value of contact angles around 89°-90°which means changing from strong oil wet to neutral wet. The following reaction will explain that tendency:

$$R - COO - H \leftrightarrow RCOO^{-} + H^{+}$$

Where: RCOOH: is the carboxylic acid.

RCOO - : is the carboxylate ion which will be free after the increasing of sulfate affinity onto the chalk surface. $H^{+}$ is the proton and the cause of the acidity of the solute.

At high temperature, the reversal reaction above will release more carboxylic groups as free compounds to produce and more protons ( $H^{+}$ ) will leave the system which will cause a reduction of PH of the solute. The increasing of temperature means more alkalinity of the system, and for this reason, the system will be at a precise moment in neutral PH and as a consequence the contact angles is approximately 90°. (Hirasaki and Zhang, 2004), have mentioned that the carbonate rock surface still in its positive charged even in an existing of neutral PH brine. The following equations will show the inverse relationship between acidic scale or power of the hydrogen PH and basic level or the power of hydroxide POH:

$$\mathrm{POH}=14-\mathrm{PH} \tag{3.1}$$

$$\mathrm{PH}=-\log[\mathrm{H}^{+}] \tag{3.2}$$

$$\mathrm{POH}=-\log[\mathrm{OH}^{-}] \tag{3.3}$$

$$[\mathrm{H}]^{+}*[\mathrm{OH}^{-}]=10^{-14} \tag{3.4}$$

When $[H^+]$ which is the concentration of hydrogen decrease, the concentration of hydroxide $[OH^-]$ will increase causes an increase in POH and then reduction of PH, and for this reason, the solute will be neutral.

## 3.1 SPONTANEOUCE IMBIBITION

Spontaneous imbibition is the process of increasing of saturation of wetting phase in the rock with decreasing the nonwetting phase saturation. It is self-process that doesn’t require any pressure difference across the core; it causes due to the differential change of the adhesion forces generated at the interface of two immiscible liquids within the porous medium as well as due to the increasing of the interfacial capillary property in addition to the decreasing of the interfacial tension between the two immiscible phases. Figure 3.1, shows the ideal behavior of the drainage and imbibition processes in oil wet carbonate rock:

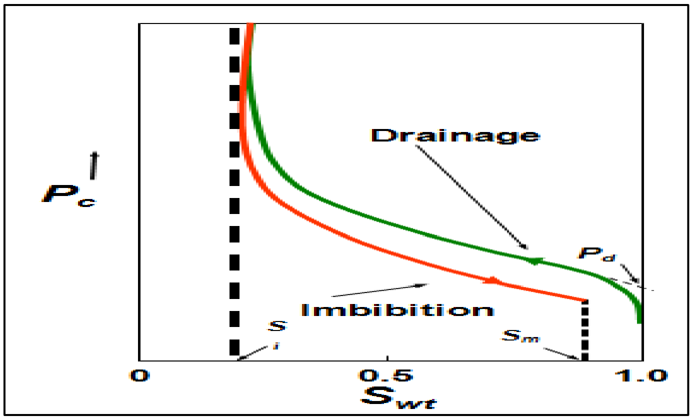


Figure 3.1. The typical response of drainage and imbibition processes in carbonate

Where :

Si is the irreducible wetting phase(water) saturation, Sm*:* 1 - Residual nonwetting phase (oil) saturation, Pd: the displacement pressure, which is the pressure necessary to force the non-wetting liquid to enter the large pores of the rock, $P_c$ is the capillary pressure, and $S_{wt}$ is the water saturation.

At wetting phase (water) saturation equal 1, the non-wetting phase (oil) require a $P_d$ pressure to force oil to accumulate gradually in the large pore spaces of the carbonate core. The accumulation of oil as non-wetting phase inside the core will mimic the oil migration to the source rock.This process called drainage in which the non-wetting phase will increase and then its mobility will increase while the wetting phase will decrease to its irreducible saturation ($S_i$). The leaving of nonwetting phase from the pore spaces by the displacement of wetting phase called imbibition in which the wetting phase will increase and then its mobility will improve but on the other hand, the nonwetting phase will decrease to its lowerest saturation ($S_m$) and this process simulate the water flooding or water drive mechanism from the injector to the reservoir.

## 3.2 CHROMATOGRAPHY TEST

The chromatography is an intelligence way to distinguish between two mixtures or solvents. The meaning of this terminology is the color writing which is the easiest manner that the chemists or biologists can use to test the liquids mixing degrees. The primary role of the chromatography will appear after using two immiscible liquids one is nonactive with the surface that needed to know its nature or its surface chemistry and the other liquid is the joker liquid that the chromatography test has done to examine its effect, i.e., the liquid the target that is necessary to know its influence on wettability alteration for example.One of the important properties of the secondary fluid in the chromatography test are:

Should be a nonactive compound, easy to observe it depending on color especially in the effluent, has not any effect on the diffusivity of the primary fluid needed to test its effectiveness, and has consistent results representations on curves in addition to explicit offset separating with the essential curve of the main fluid in case of estimating the area of wetting.

## 3.3 CHROMATOGRAPHY MECHANISM

The fact is that in general, the majority of brines used in wettability alteration tests look as homogenous substances. But in reality, it consisted of many ions and cations; the precise way to distinguish them is to use chromatography test.

The chromatography had invented by the Russian botanist scientist M.S. Tswett in 1903. In summary, with chromatography, it will be easy to separate the substances as organic and inorganic materials so that it can be easily analyzed and studied. By analyzing the compounds, it will be clear to figure out what makes up that compound. The chromatography mechanism depends on the differential trip of the solutes of the mobile phase through the static phase. Depending on the affinity degree of the solutes with the mobile phase and the time that will spend that solutes in the mobile phase, it can quickly to detect the solutes that prefer the static phase to flow through.

At the time that the solutes will flow through the static phase, it will be gradual and separated in a way that can easily to distinguish them and to study them. In another word the mobile phase will carry all the compounds that have the possibility to pass through the static phase. The affinity of those solutes is different from compound to the other; some of those compounds will adsorb onto the surface that contains the static phase while the other compound still moving with the mobile phase. The relative distance of those compound along the static phase is very useful to distinguish how those adsorbed materials will behave onto the rock surface and will give an indicator about the relative diffusion of the modified solutes of the smart brine used.

## 3.4 AREA BETWEEN CURVES OF CHROMATOGRAPHY TEST

In this work the main active determining ions or the main solutes are $Ca^{+2}$, $Mg^{+2}$, and $So_4^{-2}$ which represent the mobile phases. On contrast, $SCN^-$ is the static phase. This work will focus on Sulfate response curve, so to detect the area between it and the curve of $SCN^-$; it required the equation of each curve and then applying the below formula:

$$\text{Area} = \int_{x_i}^{x_f} \left|\left(f(x)\right) - \left(g(x)\right)\right| . dx \tag{3.5}$$

Where: Area: is the area between two curves, $x_i$: is the initial intersection point between two curves, $x_f$: is the final intersection point between two curves. F(x): is the function of $SCN^-$ curve regarding x, g(x): is the function of Sulfate curve regarding x. Engauge Digitizer version 9.3 has used to digitize the upper left light green curve of $C/C_O$ SCN. $SW_ONaCl\text{-}4So_4$ (SWK#5) as shown in Figure 3.2 below:

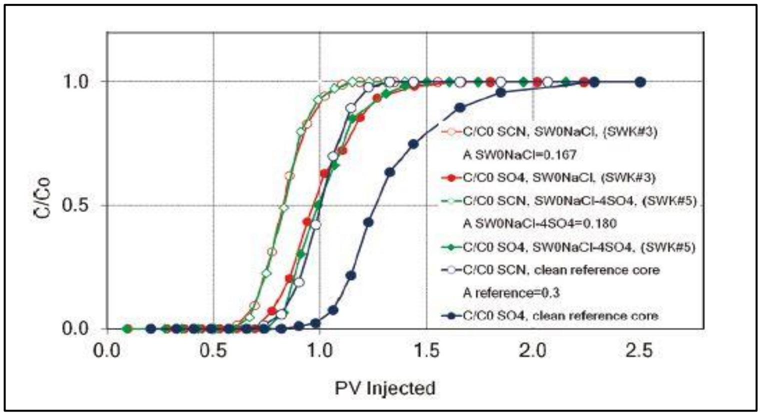


Figure 3.2. The chromatography wettability analysis at 90 $c^{\circ}$ of different synthetic brines with $SCN^-$ ( Fathi et al., 2011)

Figure 3.3, shows both the digitized C/$C_O$ SCN. $SW_O$NaCl-4$So_4$ (SWK#5) curve and its corresponding curve which has drawn in Excel:

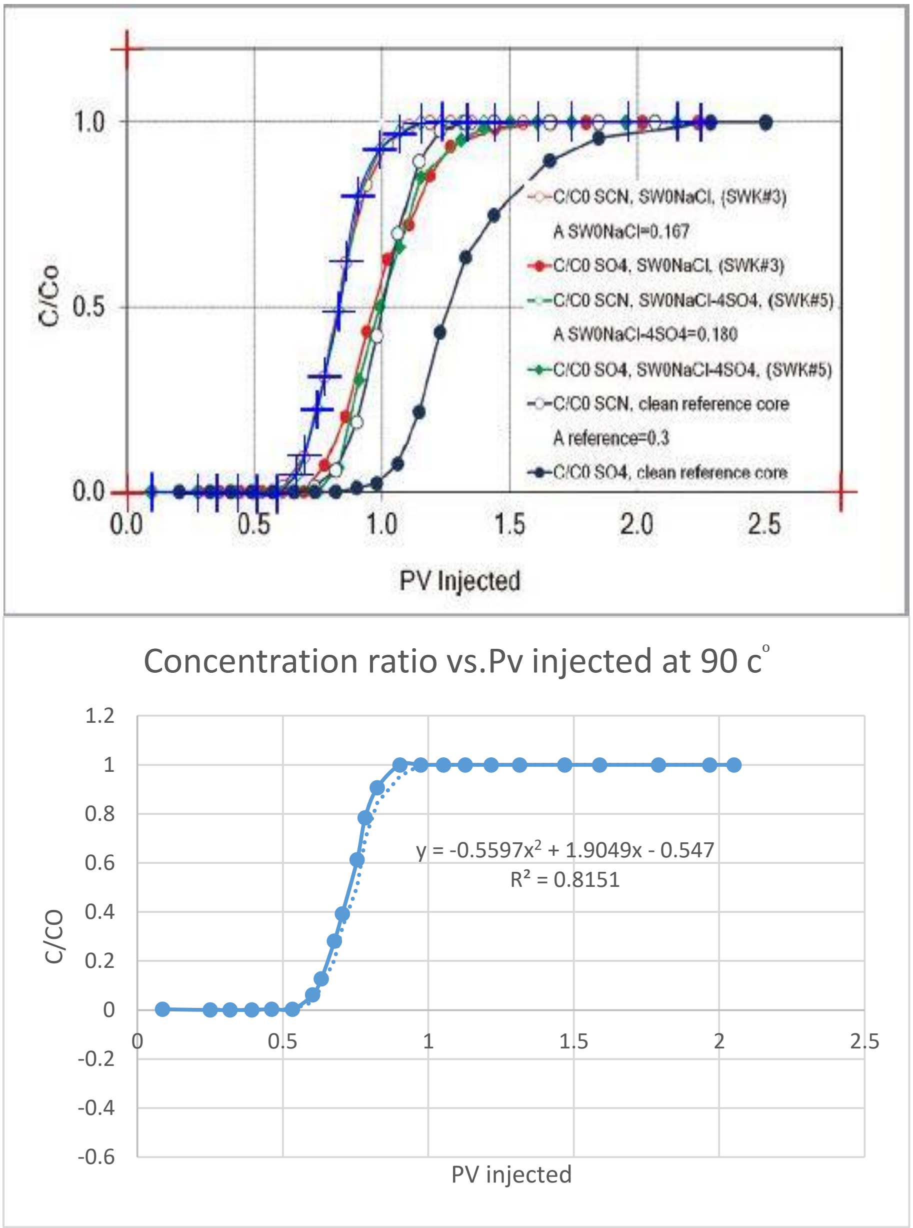


Figure 3.3. Digitized C/$C_O$ SCN. $SW_O$NaCl-4$So_4$ (SWK#5) curve and Excel curve.

F(x) is corresponding to F(PV)= $C/C_O$ and the $SCN^-$ equation is:

$$F(PV)= C/C_O = -0.5597\ PV^2+1.9049\ PV-0.547 \qquad (3.6)$$

In the same procedure, Figure 3.4 shows the digitized $C/C_O$ So4. $SW_O$NaCl $4So_4$ (SWK#5) bold green curve and the Excel curve:

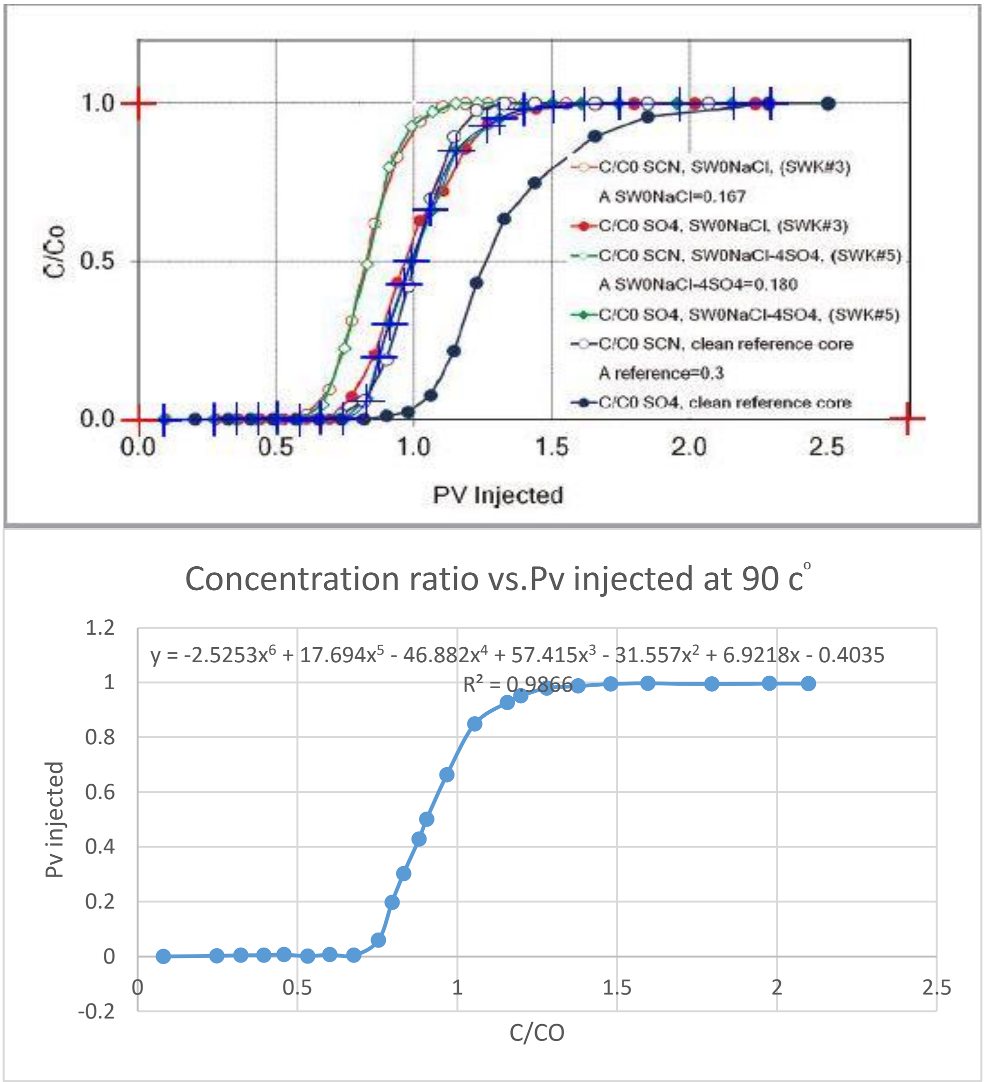


Figure 3.4. The digitized $C/C_O$ So4. (SWK#5) and Excel curve

g(x) is corresponding to g(pv)= $C/C_O$ and the $So_4$ equation is :

$$g(PV)= C/C_O = -2.5253PV^6 + 17.694PV^5 - 46.882PV^4 + 57.415PV^3 - 31.557PV^2+6.9218PV-0.4035 \quad (3.7)$$

Recal the area between curves formula:

$$\text{Area} = \int_{x_i}^{x_f} \left| \left(f(x)\right) - \left(g(x)\right) \right| . dx$$

The Figure 3.5 below shows the both curves of $SCN^-$ (Blue) and $So_4^{-2}$( Orange) drawn in Excel to show the intersection points Xi and $X_f$ which are equivalent to $PV_i$ and $PV_f$:

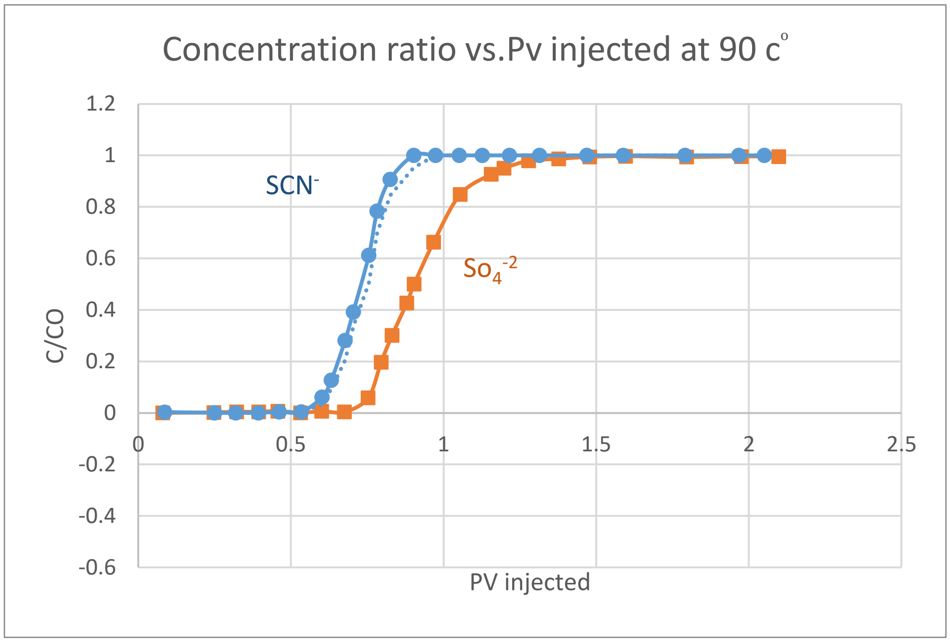


Figure 3.5. The intersection points between $SCN^-$ and $So_4^{-2}$ curves

From the above Figure, the $PV_i$ is 0.53488 and $PV_f$ are 1.37791. After the substitution of f(PV) and g(PV) curves' equations and by using the online WolframAlpha calculator for computational knowledge engine, the area between the $SCN^-$ and $So_4^{-2}$ curves is 0.171524 and this represents the area at which the synthetic brine ( $SW_ONaCl-4So_4$) will wet the surface of chalk, and it refers as $A_{wet.}$ Figure 3.6, shows both curves of digitized $C/C_O$ So4.clean reference core and the Excel curve:

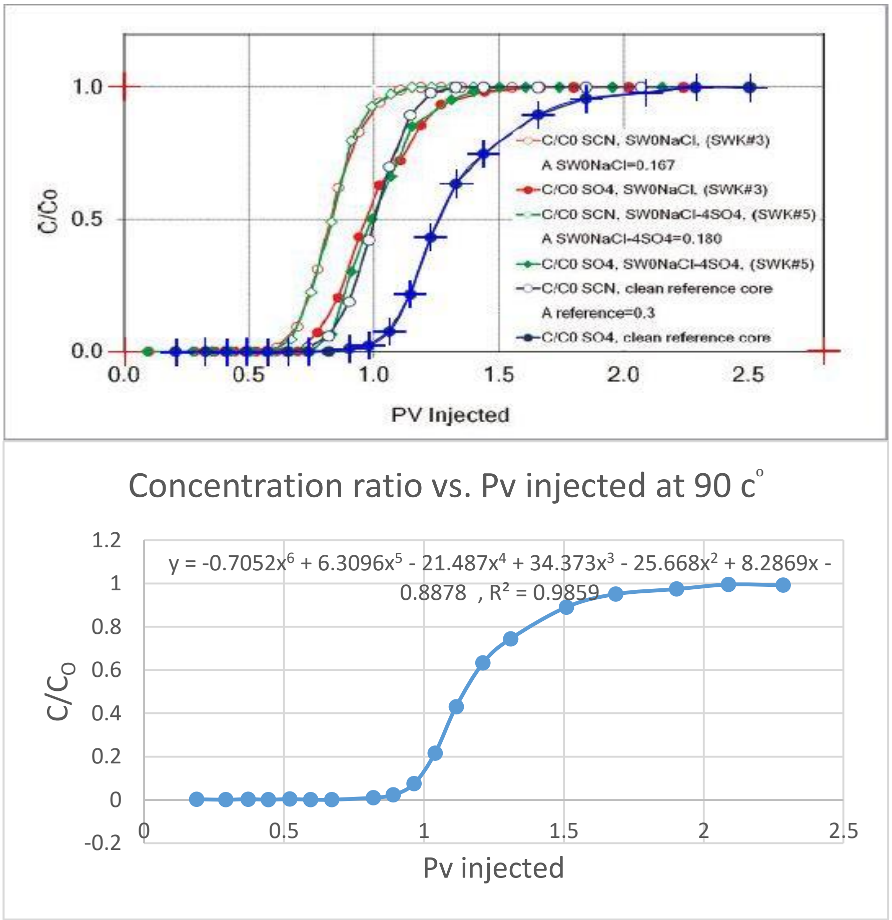


Figure 3.6. The digitized $C/C_O$ So4.clean reference core and the Excel curve

Figure 3.7, shows the intersection points between $C/C_O$ So4.clean reference core curve and $C/C_O$ SCN. $SW_O$NaCl-4$So_4$ (SWK#5) curve:

From the figure below, the $PV_i$ is 0.53205 and $PV_f$ are 1.96795.F(PV), and g(PV) are as following:

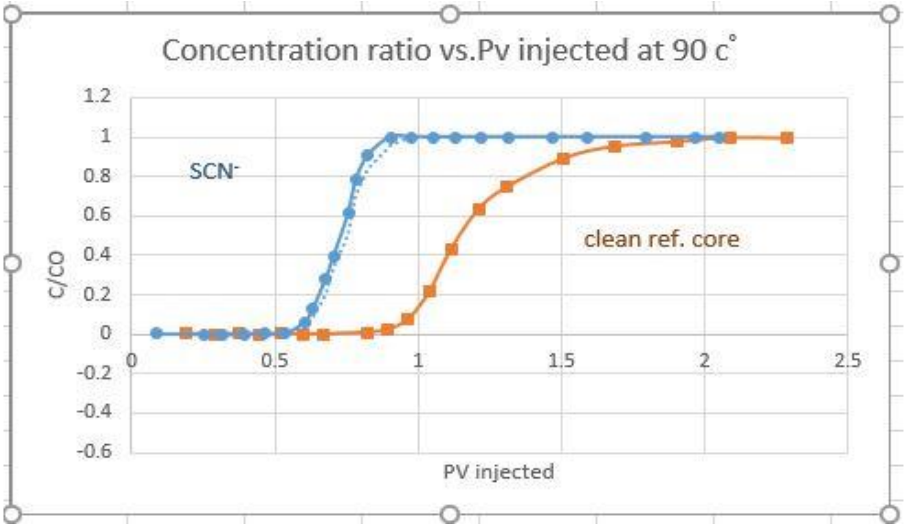


Figure 3.7. The intersection points between clean core and SCN$^-$ curves

F(PV)= C/C$_O$ = -0.5597 PV$^2$+1.9049 PV-0.547 (3.8)

G(PV)= C/C$_O$ = -0.7052PV$^6$ + 6.3096PV$^5$ - 21.487PV$^4$ + 34.373PV$^3$ - 25.668PV$^2$ + 8.2869PV - 0.8878 (3.9)

Recal the area between curve formula :

$$\text{Area} = \int_{x_i}^{x_f} \left|\left(f(x)\right) - \left(g(x)\right)\right| . dx$$

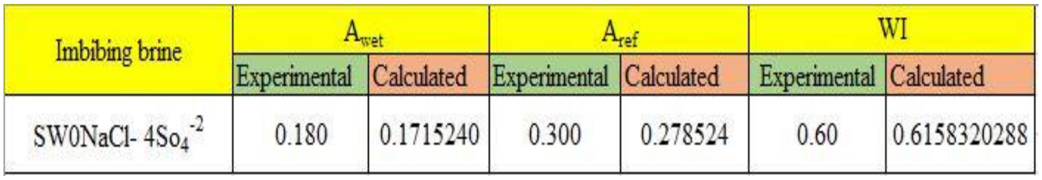
By using the online WolframAlpha calculator, the area between the SCN$^-$ and So4.clean reference core curves is 0.278524, and this is A$_{ref}$.

From the value of area of wet (A$_{wet}$) and the area of reference (A$_{ref}$), wettability index (WI) can quickly calculate as following:

$$WI = \frac{Awet}{Aref} \qquad (3.10)$$

The value of WI is 0.6158320288 which is very close to WI = 0.60 that has estimated experimentally by Fathi et al. WI = 0.6 > 0.5 means the smart water has succeeded to alter the wettability of the chalk from oil wet to nearly strong water wet and meant the sulfate has diffused onto the chalk surface due to its affinity and then increased the water wet sites on chalk surface.Table 3.1, show the comparisons between the experimental and calculated parameters of chromatography test on chalk with four times sulfate:

Table 3.1. Experimental and Calculated values on chromatography test

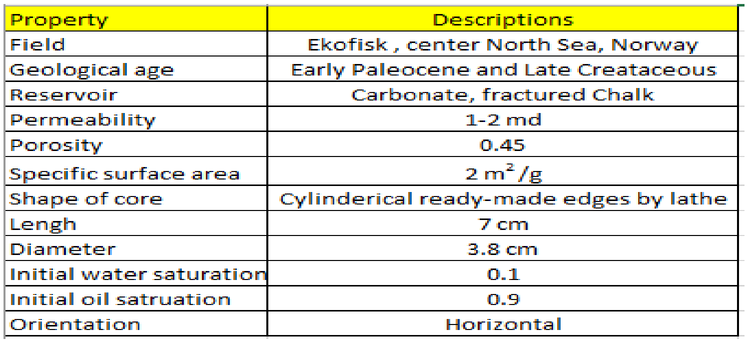


| Imbibing brine | $A_{wet}$ | | $A_{ref}$ | | WI | |
|---|---|---|---|---|---|---|
| | Experimental | Calculated | Experimental | Calculated | Experimental | Calculated |
| SW0NaCl- $4So_4^{-2}$ | 0.180 | 0.1715240 | 0.300 | 0.278524 | 0.60 | 0.6158320288 |

## 3.5 THE BRINES AND CRUDE OILS USED IN MODELING

To formulate the relationship between the adjusted brine and the wettability alteration requires knowing the flow and fluids properties. Since the porous medium will be the theater of all the events, this work will use the specific parameters available of the outcrop chalk of Ekofisk field and a series of typical values of specific heat and other constants that no longer change regardless the type of brine used. Table 3.2 below contains the major petrophysical properties available of the chalk used:

Table 3.2. Petrophysical and initial conditions of Ekofisk chalk



| Property | Descriptions |
|---|---|
| Field | Ekofisk , center North Sea, Norway |
| Geological age | Early Paleocene and Late Createaceous |
| Reservoir | Carbonate, fractured Chalk |
| Permeability | 1-2 md |
| Porosity | 0.45 |
| Specific surface area | 2 $m^2/g$ |
| Shape of core | Cylinderical ready-made edges by lathe |
| Lengh | 7 cm |
| Diameter | 3.8 cm |
| Initial water saturation | 0.1 |
| Initial oil satruation | 0.9 |
| Orientation | Horizontal |

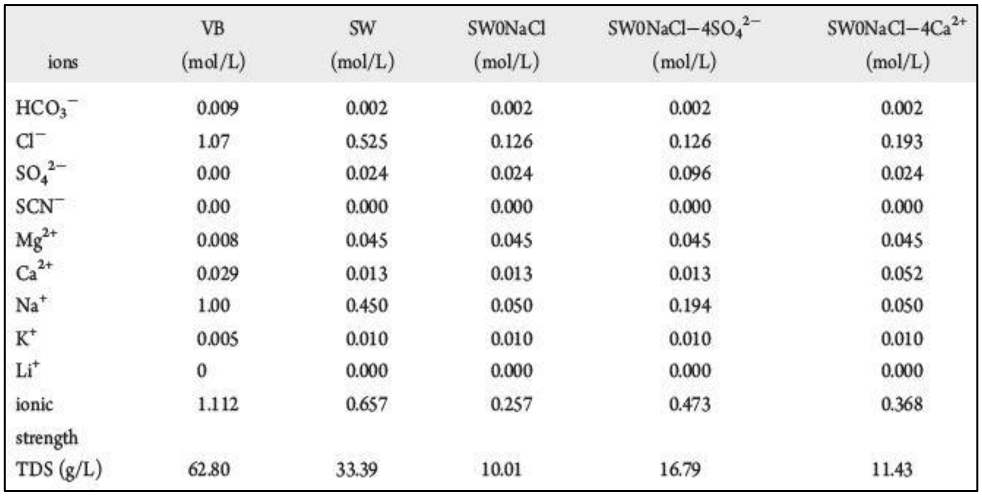
The fact of rock-brine-oil interactions has observed experimentally. The proposed determining ions which are $Ca^{+2}$, $Mg^{+2}$ and $So_4^{-2}$ will interact with the surface of the chalk depending on its affinity which entirely depends on the relative diffusivities and will interact with the carboxylic material as well. The temperature effect has studied in ranges of 70 c°, 90 c°, 100 c°, and 120 c°.

The crude oils used were classified to type A crude oil and class B crude oil; the brines used differently as well which are industrial formation water (VB) which is similar to Valhall field formation water, synthetic seawater (SW) used as the base displacing brine, modified brines which have made from synthetic seawater by adjusting the composition and the salinity which are: SW0NaCl, SW depleted in NaCl, SW0NaCl- $4So_4^{-2}$, and SW0NaCl-4 $Ca^{+2}$.

All the interactions among the suggested brine and the crude oils used in this work have happened in and around ionic layer called the double layer in which two beds of opposite charges ( anions, cations ) will exist and interact on the surface of the chalk.The magnitudes of the interfacial forces accompany to the series of the brines - crude oils interactions will lead to unity value of the confining pressure which is the pressure generated by the ionic reactions between two layers of the opposite charges through the unit area of the rock surface.

The disjoining forces created, will be perpendicular to the unit area of the reaction surface. In other words, the confining pressure accurately can define as the pressure difference between the overall wetting phase pressure and the interfacial pressure of the same phase along the surface of the membrane of the interface. Table 3.3, shows the specific brines used in the imbibition and chromatography tests:

Table 3.3. The typical brines used on chalk ( Fathi et al., 2011)



| ions | VB (mol/L) | SW (mol/L) | SW0NaCl (mol/L) | SW0NaCl−4$SO_4^{2-}$ (mol/L) | SW0NaCl−4$Ca^{2+}$ (mol/L) |
|---|---|---|---|---|---|
| $HCO_3^-$ | 0.009 | 0.002 | 0.002 | 0.002 | 0.002 |
| $Cl^-$ | 1.07 | 0.525 | 0.126 | 0.126 | 0.193 |
| $SO_4^{2-}$ | 0.00 | 0.024 | 0.024 | 0.096 | 0.024 |
| $SCN^-$ | 0.00 | 0.000 | 0.000 | 0.000 | 0.000 |
| $Mg^{2+}$ | 0.008 | 0.045 | 0.045 | 0.045 | 0.045 |
| $Ca^{2+}$ | 0.029 | 0.013 | 0.013 | 0.013 | 0.052 |
| $Na^+$ | 1.00 | 0.450 | 0.050 | 0.194 | 0.050 |
| $K^+$ | 0.005 | 0.010 | 0.010 | 0.010 | 0.010 |
| $Li^+$ | 0 | 0.000 | 0.000 | 0.000 | 0.000 |
| ionic strength | 1.112 | 0.657 | 0.257 | 0.473 | 0.368 |
| TDS (g/L) | 62.80 | 33.39 | 10.01 | 16.79 | 11.43 |

As mentioned before, two types of crude oils ( type A and type B ) will utilize in this work, but the method of preparing them is as following:

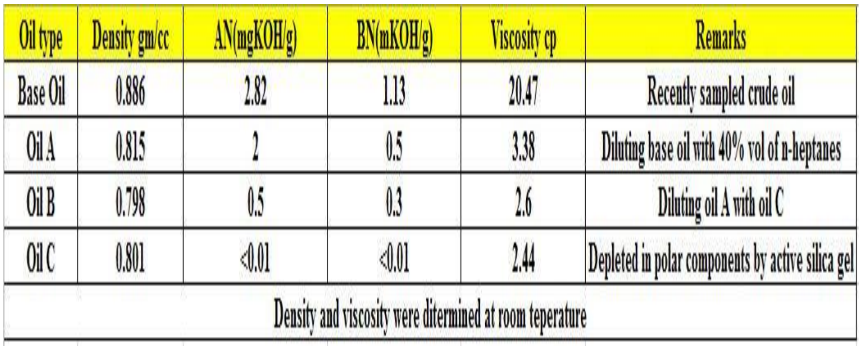
Oil A: It has prepared by diluting a base crude oil has acidic stability with 4% volume of Heptane.

Oil C: It represents the non - polar compounds oil which has prepared by adding 10% weight of silica gel for the first three days to oil A mentioned above and then adding more 10% weight of silica gel to it for two days in order to get an oil that has adsorbed its polar components to silica gel .

Oil B: It has prepared by adding oil A to oil C.

All the crude oils made above have filtered with millipores filters and centrifuged and left for three days to test the deposition possibility of the undesirable substances. The tests show that there is no deposition materials have deposited. Table 3.4, lists the types of crude oils used with chalk:

Table 3.4. Typical crude oils used with chalk ( Fathi et al., 2011)



| Oil type | Density gm/cc | AN(mgKOH/g) | BN(mKOH/g) | Viscosity cp | Remarks |
|---|---|---|---|---|---|
| Base Oil | 0.886 | 2.82 | 1.13 | 20.47 | Recently sampled crude oil |
| Oil A | 0.815 | 2 | 0.5 | 3.38 | Diluting base oil with 40% vol of n-heptanes |
| Oil B | 0.798 | 0.5 | 0.3 | 2.6 | Diluting oil A with oil C |
| Oil C | 0.801 | <0.01 | <0.01 | 2.44 | Depleted in polar components by active silica gel |
| Density and viscosity were ditermined at room teperature | | | | | |

## 3.6 COREFLOODING APPARATUS AND PROCEDURE

Figure 3.8 below, shows the measuring device used to do the core flooding tests using chalk core samples. The temperature of the measurements kept constant using an oven. Dead crude oils A and B as well as the brines all have held inside floating pistons cells in which the pistons will move by driven hydraulic fluid which is water in a stabilized pressure rate. Pumps #1 and #2 are positive piston displacement pumps have connected to deliver brines to the core used. The device has many bypasses and converters that can give a flexibility design to divert the direction of the fluids used. Each core plug used has put inside a core holder in a horizontal orientation in a way that enables the lines made the pressure supplier to get a constant confining pressure inside the core.

The outlet and the inlet of the core have both attached with a pressure gauge to measure the pressure difference across the core used in addition to using back pressure regulator to prevent the liquids inside the core to evaporate as well as to keep the productivity of the core at fixed rate. Regarding the chalk core samples used, it has cleaned using solvents and then dried so as to series of routine measurements can do to measure the permeability and the porosity.

The core used will saturate with the base brine and then centrifuged to prepare it to initial water saturation calculations. Crude oils A and B, both has saturated inside the core used through long aging times eight weeks for oil A and four weeks for oil B at temperature 70 c$^{\circ}$, 90 c$^{\circ}$ for oil B and 100 c$^{\circ}$, 120 c$^{\circ}$ for oil A.The oil aging is to get chalk core samples in oil wet wettability to be ready for imbibition process. During the oil aging times, the oils permeabilities will study and monitor at initial water saturation. The device has many transducers necessary to prevent any differences in pressures while switching from brine to another during the water flooding. In addition to the transducers, the device has many control valves and transformers that can keep the water flooding go in the smoothly way. All those controllers have connected to each other within pneumatic suppliers.

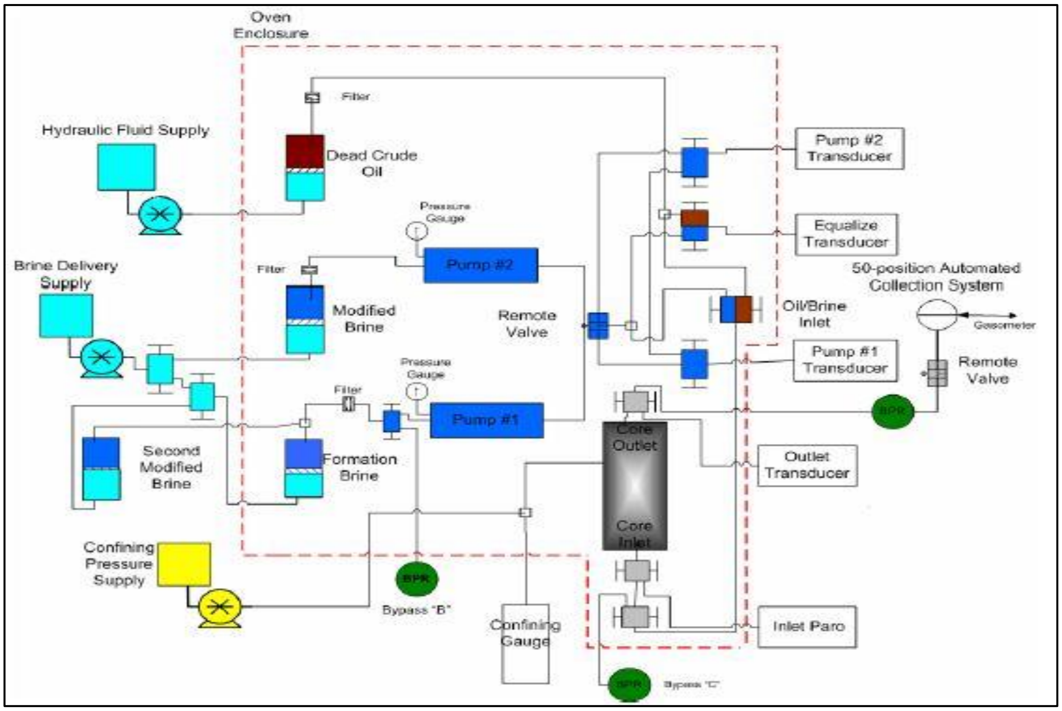


Figure 3.8. The typical core flooding apparatus

# 4. PREFACE ABOUT HEAT AND THERMAL SYSTEMS

Previously, it has mentioned the importance of temperature on the expediting of the chemical responses of active solutes of the artificial seawaters on wettability alteration. The thermal changes that happen within the porous medium and its effect on the values of interfacial forces also its effect on the viscosities and the densities of the flowing fluids will discuss conceptually through an introduction to the major concepts that can occur inside the porous medium.

The effect of temperature on oil recovery in regardless the type of crude oil used showed a unique response of sulfate when it was spiking to four times concentration compared with the other types of brines used. Figure 4.1, illustrates the relationship of oil recovery versus time during the imbibition process using different brines and crude oils at 70 $c^{\circ}$, 90 $c^{\circ}$, 100 $c^{\circ}$, and 120 $c^{\circ}$. It is easy to recognize the explicit offset between $4So_4^{-2}$ brine curve and the other brines curves. The explicit offset of $4So_4^{-2}$ brine curve which is giving a unique oil recovery is due to the decrease in the impedance forces represented in the interfacial forces between the crude oil- rock surface, the crude oil – brine used as well as due to the decrease of the flowing crude oil – brine viscosities and densities.

All those estimations of oil recovery responses have calculated depending on final core temperature in a situation that might be ambiguous to the researcher about the mechanism in which the heat exchanging between the rock and with what it has contained from implied liquids.

This work will focus on the gradual understanding of temperature changes as well as the immediate changes occurred in the quantities of the entered/departed materials based on the thermal point of view. In addition to making a logical connection to those changes with the properties of the porous medium that can effect on the flow as a consequence a possibility to have a precise analysis of the flow work path of crude oil – brine inside the system. For the figure mentioned below, the top left is for 70 c°; top right is for 90 c°, bottom left is for 100 c°, and finally the bottom right is for 120 c°.

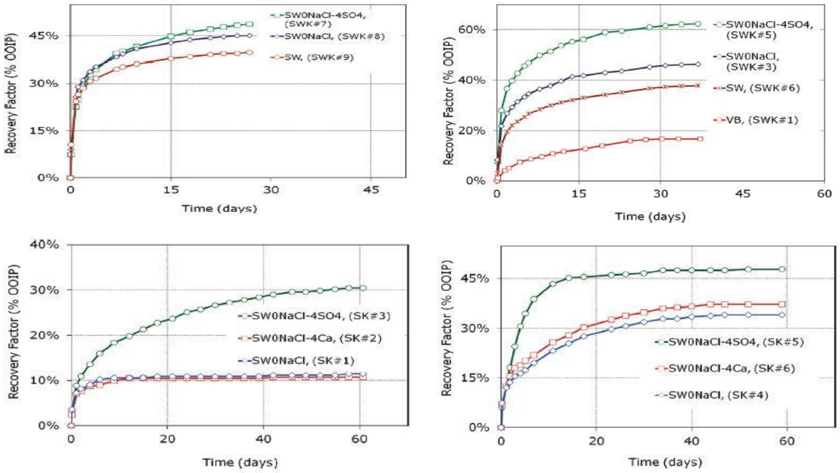


Figure 4.1. Oil Recovery vs. Time on spontaneous imbibition

## 4.1 THE HEAT

The heat is a form of energy that caused by work or transfer of matter. The energy transfer happens from the hotter body (source) to the colder body (destination).In most energy transfer situation, the substance might change to another phase depends on the relationship between the system and its surroundings as well as depends on how the heat transfer. The heat transfers in one or a combination known methodology which is conduction that happens between the solids, convection that occurs within the liquid especially that it has a mixture solutes, radiation that happens to remote materials, and the combination of those. Heat is not a state function which means it depends on the path at which the system will reach to its current situation. In this study, the core has isolated by Teflon except for the cross-sectional inlet and outlet sides of the core; this means the heat will transfer and will lose to and from the core in the same direction of the fluids flow.

Any rheological property such as the consistency of the flowing fluid especially if the fluid is heavy crude oil will deform with heat, so it is not in its continuous state. The deformation and the release of the heavy carboxylic group in the crude oil depend on the interfacial bonds among the molecules of the crude oil. The thermal cracking of any liquid means breaking the bonds between the molecules and since the carboxylic group nature is a multi - branch compound that can attract onto the surface of the chalk by the head while the another end is a series of the free branches, so the importance of existing of active ions in the presence of heat will facilitate the breaking of that attraction physically by heat and chemically by anions. The unit of heat is J which means Joule, and heat can acquire or lose from and into bodies and depend on the sign of the heat. It will be easy to know if it is negative that the heat has departed from the system to the surrounding but if it is positive means the heat has acquired from the surrounding to the system.

## 4.2 THE SYSTEM AND THE SURROUNDINGS

The system is the part of the space that within it many physical and chemical changes occur or it is the part of the material that in the case study.In this work, the system term refers to the all the instantaneous masses of the fluids within the porous medium that in touch directly with the temperature changes.The porous medium that includes the system in this work will be the control volume in thermodynamic point of view.Whereas, the surroundings refer to the atmosphere or the part that surrounds the system where the energy or work will transfer and exerted.In this work, the surroundings are the ambient laboratory temperature and pressure which are 25 $C^{\circ}$ and 14.7 psi.

## 4.3 THE TYPES OF THERMODYNAMIC SYSTEMS

After knowing the meaning of system and the surroundings, it is necessary to understand the thermodynamic systems which are first, open system in which the system will allow exchanging the material and the energy between the system and its surroundings. This type is the kind that exists in this work where the masses will transfer outside the system in the presence of fluids flow and heat energies changes. Secondly, closed system which is the system that allows only to energy to exchanging between the system and its surroundings as heat or work. Finally,  the isolated system in which the system will not allow to exchanging the energy nor the material from or to the surroundings.

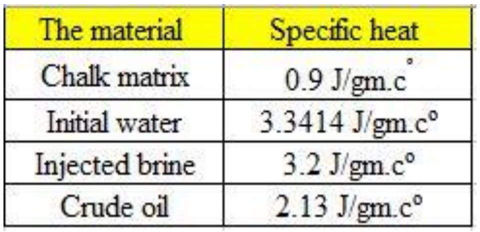
This work will study the changes in some extensive properties which are the properties that depend on the quantity of the material such as mass, volume, specific heat. In all those extensive properties, the overall summation is equivalent to the sum of the individual values of it. In addition to the extensive properties, this work will study the intensive properties which are the interfacial tension, temperature, density, and pressure that don’t depend on the quantity of the material which means that it have its individual value.

The fact that Fathi et al. have reached in an imbibition and chromatography tests is the stability of recovery at the measuring specified temperature. In more specific meaning, they examined the core flooding results at the final temperature of the imbibition, for this reason, it is possible to consider the system has acted under an isothermal and an isobaric process in which the final temperature and confining pressure have kept constants.

## 4.4 HEAT CAPACITY AND SPECIFIC HEAT

This work will use the specific heat as an extensive valuable property that can detect the acquired and lost heat energy within the porous medium and then study the applicability to get a stable heat system. Heat capacity defines as the heat energy required in Joule to raise the temperature of a mass of material to one-degree Celsius. The unit of heat capacity is J / Cº. The specific heat is the heat capacity needed to one gram of the material or the heat energy required to raise the temperature of one gram of the material one degree Celsius. The unit of specific heat is J / Cº.gm. Table 4.1, shows the typical values of specific heat used in this work's calculations:

Table 4.1. The standard specific heats used in calculations



| The material | Specific heat |
|---|---|
| Chalk matrix | 0.9 J/gm.c° |
| Initial water | 3.3414 J/gm.c° |
| Injected brine | 3.2 J/gm.c° |
| Crude oil | 2.13 J/gm.c° |

## 4.5 HEAT CONSERVATION IN SYSTEM

This work furthermore the experimental work have studied the impact of final equilibrium temperature at the end of the imbibition process at which the mechanical and thermal stability of the system have reached a point that describes the maximum effort of water flooding using smart brine can do to improve oil recovery. It is crucial to know when does the system will be at consistent behavior regardless the rate of production of oil from the core reached. The interfacial forces reduction stability and the maximum affinity of the active determining ions under final average temperature and fixed confining pressure lead to consider the system as at its moderate heat. When the system reached to its moderate heat, means there is no way to add or remove heat between system /the surroundings.

# 5. THE EXPERIMENTAL RELATIONSHIPS RELATED TO THE POROUS MEDIUM AND THE FLOW PROPERTIES

The logical relationship between the physical and chemical concepts accompany to fluids flow requires an in-depth understanding of the way that both can work together.This work will focus on the primary variables of the porous medium based on scientifically proven principles to build a solid foundation of a formula that can describe and contains the key parameters of wettability alteration in carbonates.

## 5.1 SPECIFIC SURFACE AREA DEFINITION

The specific surface area defines as the total exposed surface areas to the wetting phase of the porous medium per the mass unit of the particles that contain the wetting sites; it has unit $m^2/g$.The increasing of the number of the interior surface areas of any granular system leads to increase the possibility of getting more wettability sites. This factor has used in Kozeny–Carman equation ( will discuss later); it is a vital element from which it will be easy to know at least how much the anticipated adsorption between the wetting phase and the sites of the rock surface will interact.The increase of specific surface area especially in a high-level granularity core means the increase of the pace of wettability alteration and then increasing the oil productivity from the core.

## 5.2 THE TORTUOSITY

One of the vital parameters of the porous medium is the tortuosity which shows the way that the grains of the porous medium have geometrically packed. The tortuosity of any porous medium means that medium has many interconnected twisted paths of the flow, so it is necessary to include toruosity in porosity- permeability calculation and that what Kozeny-Carman have done. The tortuosity will show how much the porous medium will enhance the diffusion of the wetting phase in the presence of non-wetting phase.

The concentration gradient of the active solutes flowing in the pore spaces depends on the degree of the tortuosity of the porous medium, the more tortuosity means, the more complexity of the solutes to reach deeply to the specific surface wet areas.This work has implied the effect of tortuosity as a crucial factor that will detect the degree of diffusivity between oil and brine in the presence of active determining ions.

## 5.3 KOZENY-CARMAN EQUATION

One of the great relationships that can relate porosity with the permeability of the porous medium under dynamic conditions of the flow is a Kozeny-Carman equation in which the only laminar flow has accepted to be the dominant flow regime. This work is compatible with Darcy law in accordance to the homogeneity and unity of the core used regarding unique permeability and porosity in addition to the flow has considered laminar. In other words, Kozeny-Carman concept is valid since it comes with the majority assumptions of Darcy law, below is Kozeny-Carman equation:

$$\mathrm{K} = \frac{\text{Ø}^3}{\text{ß} * \mathrm{T}^2 * \mathrm{S}^2} \qquad (5.1)$$

Where: K is the permeability in md, Ø is the porosity, ß is the shape factor between 1.7 – 3, T is the tortuosity, and finally S is the specific surface area $m^2/g$.

In this work, the Kozney- Carman parameters are: K is 2 md, Ø is 0.45, S is 2 $m^2/g$, ß is 3, T calculated is 0.06161878772.

## 5.4 STOKES-EINSTEIN EQUATION

The principle of this equation is to describe the diffusion of the suspended solutes in the liquid-solid interface reaction at a uniform temperature based on the relative diffusivity between two polar solutes that have different affinity onto the solid in the presence of relative dynamic viscosities ratio between them at the absolute individual temperature of each solute as the following:

$$\frac{D_O}{D_b} = \frac{T_b}{T_o} * \frac{\mu_b}{\mu_o} \tag{5.2}$$

Where: $D_o$ is the diffusivity of oil, $D_b$ is the diffusivity of brine, $T_b$ is the absolute temperate of brine, $T_o$ is the absolute temperature of the oil, $\mu_b$ is the dynamic viscosity of brine, $\mu_o$ is the dynamic viscosity of the oil.

$\frac{D_O}{D_b}$ refers to the diffusivity ratio $D_{ratio}$ in this work as well as $\frac{\mu_b}{\mu_o}$ refers to dynamic viscosity ratio $\mu_{ratio}$.

Because of the diffused oil and brine have viscosities and densities at a uniform temperature which is the average equilibrium temperature of the system, it is important to derive the $D_{ratio}$ the formula to match the ambient temperature $T_{avg}$ as the following:

$$T_{avg} = \frac{T_i + T_f}{2} \tag{5.3}$$

$$T_{avg} = \frac{T_f}{2}\left(1 + \frac{T_i}{T_f}\right) \tag{5.4}$$

$$D_{ratio} = \frac{T_i}{T_f} * \frac{\mu_b}{\mu_o} \tag{5.5}$$

$$\frac{T_i}{T_f} = \frac{D_{ratio}}{(\mu_b/\mu_o)} \tag{5.6}$$

$$T_{avg} = \frac{T_f}{2}\left(\frac{D_{ratio}}{(\mu_b/\mu_o)} + 1\right) \tag{5.7}$$

$$\left(\frac{D_{ratio}}{(\mu_b/\mu_o)}\right) = \frac{2T_{avg}}{T_f} - 1 = x \tag{5.8}$$

$$D_{ratio=x*\left(\frac{\mu_b}{\mu_o}\right)} \tag{5.9}$$

$$\log D_{ratio=\log(\mu_b/\mu_o)+\log x} \tag{5.10}$$

$$\log_{10} D_{ratio=-y} \tag{5.11}$$

$$D_{ratio=10^{-y}} \tag{5.12}$$

In general, the calculated viscosities will decrease with increasing temperature, but the decreasing rate of brine viscosity less than the declining rate of oil viscosity in a manner keeps the viscosity ratio increase. Beside the viscosity ratio increasing, the $\mathrm{D_{ratio}}$ Will continue to decrease which lead to lower the contact angles. The shrinking of contact angles means the wettability alteration at the $T_{avg}$ has improved from oil wet to water wet. The increasing of viscosity ratio means the water viscosity is still greater than oil viscosity which is so perfect to achieve active macroscopic sweep efficiency with best oil recovery and no fingering problem possibility.

## 5.5 HALL COMPRESSIBILITY EQUATION

The carbonate reservoir in Ekofisk field has known with its high compaction that led to subsidence problem especially in chalk. One of the reasons that need to study during water flooding is the formation compressibility; the injection of 900,000 bbl/day of seawater into the reservoir in order to maintain the reservoir pressure and achieving good oil production rates requires implying the compressibility of the injected brine that will keep the disjoining pressure in constant to prevent compaction from occurring. (Hall, 1953) has proposed the following equation of compressibility:

$$\mathrm{C_{f=}}\left({}^{1.782}/_{\emptyset^{0.438}}\right)*10^{-6} \tag{5.13}$$

Where: $C_f$ is the formation compressibility ($Psi^{-1}$), Ø is the porosity.

## 5.6 OIL WET AREA AND ACID NUMBER

The oil wet area can quickly detect by subtracting $A_{wet}$ that has calculated from 1 as following:

$$\mathrm{A_{oil\ wet=1-A_{wet}}} \tag{5.14}$$

The importance of $A_{oil}$ will discuss in next section but it is in specific will play the main role to detect the factor of detecting the quality of wettability (H). The factor H will increase as the product $A_{oil\ wet}$ and $E_d$ and then this Will lead to interpreting the effectiveness of the candidate wet sites at the end of the imbibition test to the concentration effect of the active solute used in the spontaneous imbibition process. While the acid number (AN) is the measurement of the acidity that can be detected by the quantity of milligrams of KOH necessary to equivalent the amounts of acids in one gram of crude oil used. The acid number plays a primary role in wettability alteration experiments where its value always necessary to detect how much carboxylic group that exist in the crude oil used. Figure 5.1, shows the relationship of different acids number values on oil recovery with time:

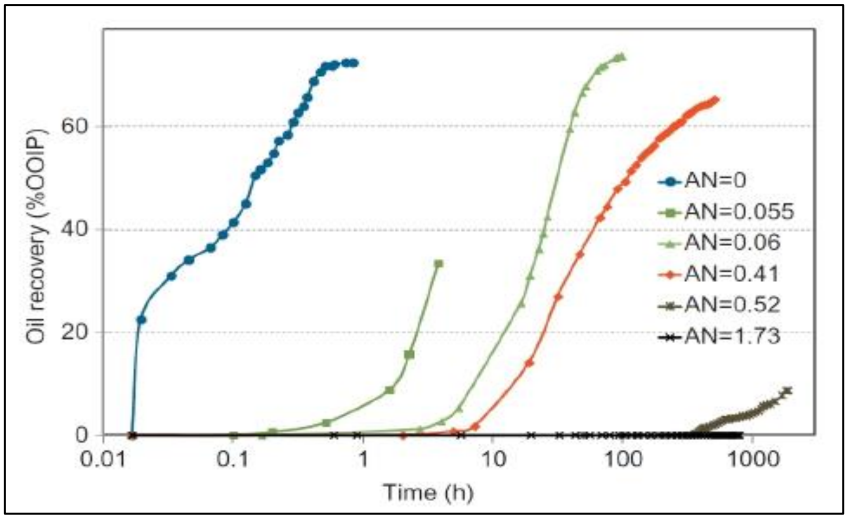


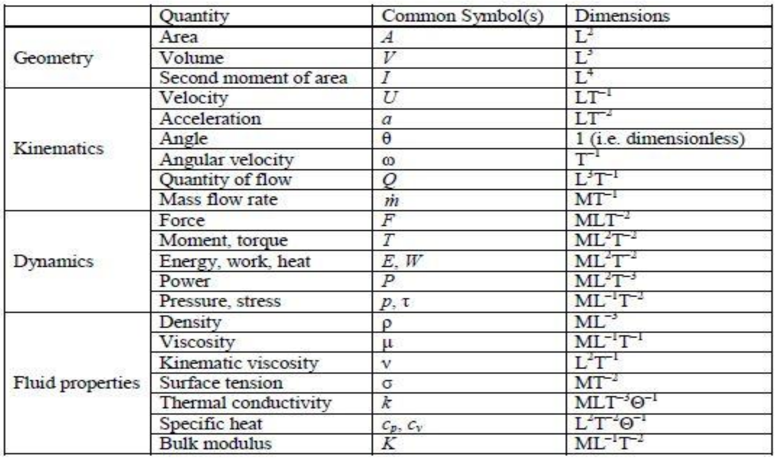
Figure 5.1. The acid numbers differences with oil recovery (Standnes and Austad, 2000)

It can conclude from the above figure that when the acid number increase, the time required of finishing the complete imbibition will be longer for the same oil recovery target. In other words, the lower the acidity of crude oils used the best rate of oil recovery can obtain and the shortest time of imbibition will take.

# 6. BUCKINGHAM PI THEOREM IN DIMENSIONLESS ANALYSIS

The main purpose of Buckingham Pi theorem is to find a formula with less independent variables to use it in modeling by reducing the number of the experimental measurements. Using sets of dimensionless groups that created according to the logic physical connection of proven concepts in addition to using sets of repeated parameters derived basically to its major units can finally lead to establishing a formula. The number of dimensionless group equations depends on how many candidate variables have selected to match the physical behavior of the model that needs to generate its governing equation. Table 6.1, shows the physical parameters and its units based on MLT (Mass, Length, Time) system:

Table 6.1. The major physical quantities and its dimensions



| | Quantity | Common Symbol(s) | Dimensions |
|---|---|---|---|
| Geometry | Area | $A$ | $L^2$ |
| | Volume | $V$ | $L^3$ |
| | Second moment of area | $I$ | $L^4$ |
| Kinematics | Velocity | $U$ | $LT^{-1}$ |
| | Acceleration | $a$ | $LT^{-2}$ |
| | Angle | $\theta$ | 1 (i.e. dimensionless) |
| | Angular velocity | $\omega$ | $T^{-1}$ |
| | Quantity of flow | $Q$ | $L^3T^{-1}$ |
| | Mass flow rate | $\dot{m}$ | $MT^{-1}$ |
| Dynamics | Force | $F$ | $MLT^{-2}$ |
| | Moment, torque | $T$ | $ML^2T^{-2}$ |
| | Energy, work, heat | $E$, $W$ | $ML^2T^{-2}$ |
| | Power | $P$ | $ML^2T^{-3}$ |
| | Pressure, stress | $p$, $\tau$ | $ML^{-1}T^{-2}$ |
| Fluid properties | Density | $\rho$ | $ML^{-3}$ |
| | Viscosity | $\mu$ | $ML^{-1}T^{-1}$ |
| | Kinematic viscosity | $\nu$ | $L^2T^{-1}$ |
| | Surface tension | $\sigma$ | $MT^{-2}$ |
| | Thermal conductivity | $k$ | $MLT^{-3}\Theta^{-1}$ |
| | Specific heat | $c_p$, $c_v$ | $L^2T^{-2}\Theta^{-1}$ |
| | Bulk modulus | $K$ | $ML^{-1}T^{-2}$ |

## 6.1 FIRST ATTEMPT OF MODELLING WETTABILITY ALTERATION IN CARBONATES

The first attempt was to find the first formula that can relate the determining ion (the sulfate) concentration ( C ) based on the heat transferred gradient (Q/L) that will change along the path of the flow of the injected pore volume of brine ( PV) in the presence of the interfacial forces (σ) and the acidity (AN). The following is the procedure that used to derive the model formula using Buckingham Pi theorem:

$$\mathrm{C} = \mathrm{f}\left(\frac{\mathrm{Q}}{\mathrm{L}} \cdot \mathrm{AN} \cdot \mathrm{PV} \cdot \sigma\right) \tag{6.1}$$

$$0 = \mathrm{f}\left(\frac{\mathrm{Q}}{\mathrm{L}} \cdot \mathrm{AN} \cdot \mathrm{C} \cdot \mathrm{PV} \cdot \sigma\right) \tag{6.2}$$

$$\mathrm{M} = 5\,, \mathrm{N} = 3\,, \left(\frac{\mathrm{Q}}{\mathrm{L}} \cdot \mathrm{AN} \cdot \sigma\right) \tag{6.3}$$

$$\pi_{1=\mathrm{M}^0\cdot \mathrm{L}^0\cdot \mathrm{T}^0=} \left(\frac{\mathrm{Q}}{\mathrm{L}}\right)^{a_1} \cdot \mathrm{AN}^{b_1} \cdot \sigma^{c_1} \cdot \mathrm{C} \tag{6.4}$$

$$\mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = (\mathrm{M.L.T}^{-2})^{a_1}.(\mathrm{M}^0.\mathrm{L}^0.\mathrm{T}^0)^{b_1}.(\mathrm{T}^{-2}.\mathrm{M})^{c_1}.\mathrm{L}^3 \tag{6.5}$$

$$\mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = \mathrm{M}^{a_1+c_1}.\mathrm{L}^{a_1-3}.\mathrm{T}^{-2a_1-2c_1} \tag{6.6}$$

$$0 = a_1 + c_1 \quad , \quad 0 = a_1 - 3, \quad 0 = -2_{a_1} - 2c_1 \tag{6.7}$$

$$\gg\ a_1 = 3\,, c_1 = -3\ ,\ \pi_1 = \frac{\left(\frac{\mathrm{Q}}{\mathrm{L}}\right)^3.\mathrm{AN.C}}{\sigma^3} \tag{6.8}$$

$$\pi_2 = \mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = \left(\frac{\mathrm{Q}}{\mathrm{L}}\right)^{a_2}.\mathrm{AN}^{b_2}.\sigma^{c_2}.\mathrm{PV} \tag{6.9}$$

$$\mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = (\mathrm{M.L.T}^{-2})^{a_2}.(\mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0)^{b_2}.(\mathrm{M.T}^{-2})^{c_2}.\mathrm{L}^3 \tag{6.10}$$

$$\mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = \mathrm{M}^{a_2+c_2}.\mathrm{L}^{a_2+3}.\mathrm{T}^{-2a_2-2c_2} \tag{6.11}$$

$$0 = a_2 + c_2 \quad , \quad 0 = a_2 + 3, \quad 0 = -2a_2 - 2c_2 \tag{6.12}$$

$$\gg\ a_2 = -3\,,\ c_2 = 3\ ,\ \pi_2 = \frac{\mathrm{AN}.\sigma^3.\mathrm{PV}}{\left(\frac{\mathrm{Q}}{\mathrm{L}}\right)^3} \tag{6.13}$$

$$\mathrm{f}(\pi_1\,, \pi_2) = 0 \quad \rightarrow \quad \pi_1 = \mathrm{f}\pi_2 \tag{6.14}$$

$$\mathrm{C} = \left(\frac{\sigma\,.\mathrm{L}}{\mathrm{Q}}\right)^6.\mathrm{PV} \tag{6.15}$$

Equ.6.15 refers to the formula that has gotten from the first attempt model, below the second attempt:

$$\mathrm{C} = \mathrm{f}\left(\frac{\mathrm{Q}}{\mathrm{L}} \cdot \mathrm{AN} \cdot \mathrm{PV} \cdot \sigma\right) \tag{6.16}$$

$$0 = \mathrm{f}\left(\frac{\mathrm{Q}}{\mathrm{L}} \cdot \mathrm{AN} \cdot \mathrm{C} \cdot \mathrm{PV} \cdot \sigma\right) \tag{6.17}$$

$$\mathrm{M} = 5, \mathrm{N} = 3, \left(\frac{\mathrm{Q}}{\mathrm{L}}\ , \mathrm{PV}, \sigma\ \right) \tag{6.18}$$

$$\pi_1 = \mathrm{M}^0 \cdot \mathrm{L}^0 \cdot \mathrm{T}^0 = (\mathrm{M.L.T}^{-2})^{a_1}.(\mathrm{L}^3)^{b_1}.(\mathrm{M.T}^{-2})^{c_1}.\mathrm{quantity}.\mathrm{C} \tag{6.19}$$

The quantity means the number of moles used which it has assumed to one mole for simplification purposes:

$$\pi_1 = M^0 \cdot L^0 \cdot T^0 = (M.L.T^{-2})^{a_1}.(L^3)^{b_1}.(M.T^{-2})^{c_1}.L^{-3} \qquad (6.20)$$

$$\pi_1 = M^0 \cdot L^0 \cdot T^0 = M^{a_1+c_1}.L^{a_1+b_1-3}.T^{a_1-c_1} \qquad (6.21)$$

$$a_1 + c_1 = 0\ , \quad \gg \quad a_1 = -c_1\ , \quad 0 = a_1 + b_1 - 3\ , \quad 0 = -2a_1 - 2c_1 \qquad (6.22)$$

For $a_1$ , $c_1$ : +ve $a_1$ means -ve $c_1$ : $1 \geq a_1 \geq 0$ , $[0\ ,1]$

$$0 \geq c_1 \geq -1\ , [0\ ,-1]$$

Let's assume $a_1 = 0.5$ , $c_1 = -0.5$ so, $b_1 = 0.83$ (6.23)

Therefore, $\pi_1 = \left(\frac{Q}{L}\right)^{0.5}.(PV)^{0.83}.(\sigma)^{-0.5}.C$ (6.24)

$$\pi_2 = M^0 \cdot L^0 \cdot T^0 = \left(\frac{Q}{L}\right)^{a_2}.(PV)^{b_2}.(\sigma)^{c_2}.AN \qquad (6.25)$$

$$M^0 \cdot L^0 \cdot T^0 = (M.L.T^{-2})^{a_2}.(L^3)^{b_2}.(M.T^{-2})^{c_2} \qquad (6.26)$$

The acid number AN has assumed to be 1 = $M^0 \cdot L^0 \cdot T^0$ for simplification purposes :

$$M^0 \cdot L^0 \cdot T^0 = M^{a_2+c_2}.L^{a_2+3b_2}.T^{-2a_2-2c_2} \qquad (6.27)$$

Using the same assumptions of $a_1$=0.5 , $c_1$ = -0.5 , therefore, b = - 1/6 (6.28)

$$\pi_2 = \left(\frac{Q}{L}\right)^{0.5}.(PV)^{-1/6}.(\sigma)^{-0.5}.AN \qquad (6.29)$$

$$f(\pi_1, \pi_2) = 0 \ \rightarrow \ \pi_1 = f(\pi_2) \qquad (6.30)$$

$$\left(\frac{Q}{L}\right)^{0.5}.PV^{0.83}.\sigma^{-0.5}.C = \left(\frac{Q}{L}\right)^{0.5}.PV^{-1/6}.\sigma^{-0.5}.AN \qquad (6.31)$$

Multiply by $\left(\frac{1}{\left(\frac{Q}{L}\right)^{0.5}.PV^{0.83}.\sigma^{-0.5}}\right)$ in both sides and solve for C:

$$C = PV^{-0.83-1/6}.AN \qquad (6.32)$$

Equ.6.32, refers to the final formula of the second attempt model which logically and dimensionally better that the Equ. 6.15; the conclusions are:

For high AN crude oil, it is necessary to minimize the injected pore volume of brine but make it with a high concentration of Sulfate. On the other hand, for low AN crude oil; it is necessary to take the opportunity to use a high rate of injected pore volume with low salinity or low concentration of sulfate to get the better-improved amount of oil from the core.Moreover, by combining Equ. 6.15 and Equ. 6.32 yield:

$$\mathrm{C} = \left(\frac{\sigma}{\mathrm{Q}/\mathrm{L}}\right)^3 . \sqrt[2]{\mathrm{AN}} \tag{6.33}$$

From specific heat formula: $Q = C_P.M.\Delta T$ (6.34)

Then: $\mathrm{C} = \left(\frac{\sigma}{\frac{\mathrm{C_P.M.\Delta T}}{\mathrm{L}}}\right)^3 . \sqrt[2]{\mathrm{AN}}$ , the quantities $\mathrm{C_P}, \mathrm{M}$, and $\mathrm{L}$ considered constants, then:

$$\mathrm{C} = \mathrm{constant}.\left(\frac{\sigma^3}{\Delta \mathrm{T}^3}\right). \sqrt[2]{\mathrm{AN}} \tag{6.35}$$

The conclusion that has written about the formula above is : if the magnitude of heat transferred is tiny, this means a film of sulfate ions will be created onto the rock surface in which the interfacial tension between injected brine and the rock is still in high and not breaking in a way that can ensure the more oil to produce regardless the type of crude oil used.

More modification has added to the formula above to spread its logical cycle of use; the first modification is to imply the following equation known before:

$$\cos \theta_{\mathrm{ow}} = \left(\frac{\sigma_{\mathrm{os}} - \sigma_{\mathrm{ws}}}{\sigma_{\mathrm{ow}}}\right) \tag{6.36}$$

A new assumption has proposed that the value of the numerator ($\sigma_{\mathrm{os}} - \sigma_{\mathrm{ws}}$ ) is approximately constant so that the contact angle will be affected by the interfacial forces between the injected brine and crude oil used in the experiment. By solving the equation above for $\sigma_{ow}$ and cubic the both sides yield:

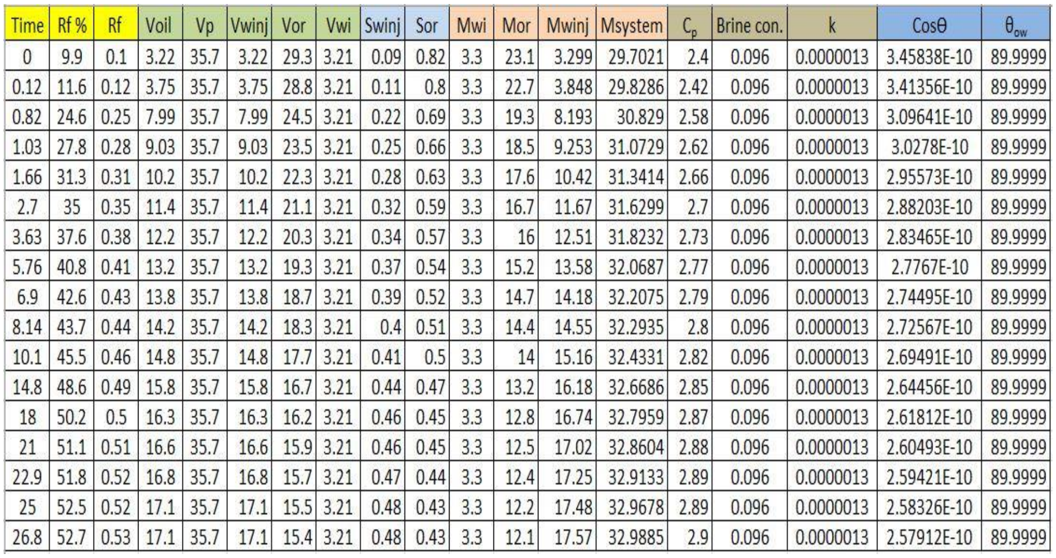
$$\mathrm{C} = \mathrm{Constant}\,.\,(\sigma_{\mathrm{os}} - \sigma_{\mathrm{ws}})^3\,.\,\frac{\sqrt[2]{\mathrm{AN}}}{(\cos \theta_{\mathrm{ow}})^3.(\Delta \mathrm{T})^3} \tag{6.37}$$

$$\mathrm{K} = \mathrm{Constant}\,.\,(\sigma_{\mathrm{os}} - \sigma_{\mathrm{ws}})^3 \tag{6.38}$$

$$\mathrm{C} = \mathrm{K}.\frac{\sqrt[2]{\mathrm{AN}}}{(\cos \theta_{\mathrm{ow}}\,.\Delta \mathrm{T})^3} \tag{6.39}$$

The equ. 6.39 has used to model the wettability alteration on chalk using sulfate as active determining ion but the contact angles estimated were unified and about $89^{\circ}$ - $90^{\circ}$ which means that the surface of rock has improved from oil wet to neutral.Table 6.2, Excel sheet shows the calculations made using the equ. 6.39:

Table 6.2. The first model calculations by Buckingham Pi theorem



| Time | Rf % | Rf | Voil | Vp | Vwinj | Vor | Vwi | Swinj | Sor | Mwi | Mor | Mwinj | Msystem | $C_p$ | Brine con. | k | Cosθ | $\theta_{ow}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 9.9 | 0.1 | 3.22 | 35.7 | 3.22 | 29.3 | 3.21 | 0.09 | 0.82 | 3.3 | 23.1 | 3.299 | 29.7021 | 2.4 | 0.096 | 0.0000013 | 3.45838E-10 | 89.9999 |
| 0.12 | 11.6 | 0.12 | 3.75 | 35.7 | 3.75 | 28.8 | 3.21 | 0.11 | 0.8 | 3.3 | 22.7 | 3.848 | 29.8286 | 2.42 | 0.096 | 0.0000013 | 3.41356E-10 | 89.9999 |
| 0.82 | 24.6 | 0.25 | 7.99 | 35.7 | 7.99 | 24.5 | 3.21 | 0.22 | 0.69 | 3.3 | 19.3 | 8.193 | 30.829 | 2.58 | 0.096 | 0.0000013 | 3.09641E-10 | 89.9999 |
| 1.03 | 27.8 | 0.28 | 9.03 | 35.7 | 9.03 | 23.5 | 3.21 | 0.25 | 0.66 | 3.3 | 18.5 | 9.253 | 31.0729 | 2.62 | 0.096 | 0.0000013 | 3.0278E-10 | 89.9999 |
| 1.66 | 31.3 | 0.31 | 10.2 | 35.7 | 10.2 | 22.3 | 3.21 | 0.28 | 0.63 | 3.3 | 17.6 | 10.42 | 31.3414 | 2.66 | 0.096 | 0.0000013 | 2.95573E-10 | 89.9999 |
| 2.7 | 35 | 0.35 | 11.4 | 35.7 | 11.4 | 21.1 | 3.21 | 0.32 | 0.59 | 3.3 | 16.7 | 11.67 | 31.6299 | 2.7 | 0.096 | 0.0000013 | 2.88203E-10 | 89.9999 |
| 3.63 | 37.6 | 0.38 | 12.2 | 35.7 | 12.2 | 20.3 | 3.21 | 0.34 | 0.57 | 3.3 | 16 | 12.51 | 31.8232 | 2.73 | 0.096 | 0.0000013 | 2.83465E-10 | 89.9999 |
| 5.76 | 40.8 | 0.41 | 13.2 | 35.7 | 13.2 | 19.3 | 3.21 | 0.37 | 0.54 | 3.3 | 15.2 | 13.58 | 32.0687 | 2.77 | 0.096 | 0.0000013 | 2.7767E-10 | 89.9999 |
| 6.9 | 42.6 | 0.43 | 13.8 | 35.7 | 13.8 | 18.7 | 3.21 | 0.39 | 0.52 | 3.3 | 14.7 | 14.18 | 32.2075 | 2.79 | 0.096 | 0.0000013 | 2.74495E-10 | 89.9999 |
| 8.14 | 43.7 | 0.44 | 14.2 | 35.7 | 14.2 | 18.3 | 3.21 | 0.4 | 0.51 | 3.3 | 14.4 | 14.55 | 32.2935 | 2.8 | 0.096 | 0.0000013 | 2.72567E-10 | 89.9999 |
| 10.1 | 45.5 | 0.46 | 14.8 | 35.7 | 14.8 | 17.7 | 3.21 | 0.41 | 0.5 | 3.3 | 14 | 15.16 | 32.4331 | 2.82 | 0.096 | 0.0000013 | 2.69491E-10 | 89.9999 |
| 14.8 | 48.6 | 0.49 | 15.8 | 35.7 | 15.8 | 16.7 | 3.21 | 0.44 | 0.47 | 3.3 | 13.2 | 16.18 | 32.6686 | 2.85 | 0.096 | 0.0000013 | 2.64456E-10 | 89.9999 |
| 18 | 50.2 | 0.5 | 16.3 | 35.7 | 16.3 | 16.2 | 3.21 | 0.46 | 0.45 | 3.3 | 12.8 | 16.74 | 32.7959 | 2.87 | 0.096 | 0.0000013 | 2.61812E-10 | 89.9999 |
| 21 | 51.1 | 0.51 | 16.6 | 35.7 | 16.6 | 15.9 | 3.21 | 0.46 | 0.45 | 3.3 | 12.5 | 17.02 | 32.8604 | 2.88 | 0.096 | 0.0000013 | 2.60493E-10 | 89.9999 |
| 22.9 | 51.8 | 0.52 | 16.8 | 35.7 | 16.8 | 15.7 | 3.21 | 0.47 | 0.44 | 3.3 | 12.4 | 17.25 | 32.9133 | 2.89 | 0.096 | 0.0000013 | 2.59421E-10 | 89.9999 |
| 25 | 52.5 | 0.52 | 17.1 | 35.7 | 17.1 | 15.5 | 3.21 | 0.48 | 0.43 | 3.3 | 12.2 | 17.48 | 32.9678 | 2.89 | 0.096 | 0.0000013 | 2.58326E-10 | 89.9999 |
| 26.8 | 52.7 | 0.53 | 17.1 | 35.7 | 17.1 | 15.4 | 3.21 | 0.48 | 0.43 | 3.3 | 12.1 | 17.57 | 32.9885 | 2.9 | 0.096 | 0.0000013 | 2.57912E-10 | 89.9999 |

The pink columns have created after digitizing the oil recovery vs. time of imbibition process at 70 $C^{\circ}$, the rest columns have created as following:

Bulk volume $V_{b}$: $$V_b = \frac{\pi.D^2.L}{4} = \frac{7\pi.(3.8)^2}{4} = 79.38\ \text{cc} \qquad (6.40)$$

Pore volume $P_{v}$: $$P_v = \emptyset.V_b = 0.45 * 79.38 = 35.721\ \text{cc} \qquad (6.41)$$

Origin oil in place Voil init. : $$V_{\text{oil init.}} = S_{oi} * V_p = 0.91 * 35.721 = 32.506\ \text{cc} \qquad (6.42)$$

Oil produced volume $V_{oil}$: $$V_{oil} = R_f * V_{\text{oil init.}} \qquad (6.43)$$

Oil remaining volume $V_{or}$: $$V_{or} = V_{\text{oil init.}} - V_{oil} \qquad (6.44)$$

Initial water volume $V_{wi}$: $$V_{wi} = S_{wi} * V_p = 0.09 * 35.721 = 3.2149\ \text{cc} \qquad (6.45)$$

Brine injected volume $V_{winj.}$ : $V_{winj.} = V_p - V_{or} - V_{wi}$ (6.46)

Injected water saturation $S_{winj.}$ : $S_{winj.} = \frac{V_{winj.}}{V_p}$ (6.47

Oil remaining saturation $S_{or}$: $S_{or} = \frac{V_{or}}{V_p}$ (6.48)

Initial water mass $M_{wi}$: $M_{wi} = 1.025 * V_{wi}$ (6.49)

Remaining oil mass $M_{or}$: $M_{or} = 0.789 * V_{or}$ (6.50)

Injected water mass $M_{winj.}$ : $M_{winj} = 1.025 * V_{winj}$ (6.51)

Mass of system $M_{system}$: $M_{system} = M_{wi} + M_{or} + M_{winj}$ (6.52)

System specific heat $C_p$: $C_p = \left(\frac{(2.13*M_{or})+3.3414(M_{winj}+M_{wi})}{M_{system}}\right)$, from calorimetry priciple

Rock type constant K: $K = \left(\frac{L}{C_p.M_{system}}\right)^3.(\sigma_{os} - \sigma_{ws})^3.10^{-21}$ (6.53)

$\cos\theta_{ow}$: $\cos\theta_{ow} = \frac{K^{0.33}.\sqrt[2]{AN}}{C^{0.33}.\Delta T}$ (6.54)

Contact angle $\theta_{ow}$: $\theta_{ow} = DEGREES(ACOS(\cos\theta_{OW})) = \cos^{-1}(\cos\theta_{ow})$ (6.55)

It can see from the Excell sheet mentioned above that the contact angles 89° refer to the neutral wet condition. For that reason, it is mandatory to do some modifications to the created equation to get water wet condition.

## 6.2 THE GENERAL WETTABILITY ALTERATION FORMULA APPROACH

The limitations of the first model derivation lead to get neutral wettability instead of getting water wet of the estimation of instantaneous contact angles. Regardless, those limitations, the equation can use as the basis for formulating a general equation of wettability alteration mechanism.

The fist model has neglected the following factors: The formation compressibility, oil wet area, Crude oil – brine viscosity ratio changes, diffusivity ratio of crude oil – brine system, the porous medium geometrical factor, and properties such as tortuosity, permeability, porosity, flow impedance, constrictivity of capillary tubes of the porous medium, active ion molecular weight, brine density, heat conservation and average temperature and finally the macroscopic sweep efficiency changes per unit length.

Implying all factors above lead to get the water wet conditions for brine – oil B system at 70 C°, 90 C° with AN 0.5 and for brine – oil A system at 100 C°, 120 C° with AN 2 successfully.Starting of digitizing the oil recovery vs. time response of spontaneous imbibition of the specified temperatures above then complete the saturation-volume-mass calculation of the flowing components within the porous medium.

It is important to know what is the meaning of constrictivity which is the ratio of the diffused solute diameter to the pore space diameter. It is one of the important considerations of diffusion transportation in the entire path of the porous medium. It is also important to know the term flow impedance which means the porous medium resistance to flow due to the capillary geometry of the porous medium.Below the steps of calculation of flow impedance of the chalk used:

Using Hagen-Poisulle's equation to determine the capillary tube pore size:

$$\mathrm{K} = 12.7 * 10^{6} * \mathrm{r}^{2} \tag{6.56}$$

K is the permeability in Darcy, r: is the capillary tube pore size in Cm.

$$0.002 = 12.7 * 10^{6} * \mathrm{r}^{2}$$

$$\mathrm{r} = 0.000031622 \text{ cm}$$

$$\mathrm{P_V} = \pi * \mathrm{r}^{2} * \mathrm{L}$$

$$35.721 = 7\pi \mathrm{r}^{2}$$

$$\mathrm{r} = 1.624335349 \text{ cm}$$

$$\text{The No. of capillary tubes} = \frac{1.624335349}{0.000031622} = 51367.25537 \text{ tube} \tag{6.57}$$

$$\text{Flow impedance(FI)} = \text{No. of capillary tubes} * \text{Constrictivity} \tag{6.58}$$

Since it is hard for this work to estimate the diffused solute diameter because this problem needs a microscopic analysis for that reason, it is easy to deduce the magnitude of flow impedance based on the known parameters of the general formula of wettability alteration.

The idea is for any chalk if the flow impedance is high means the concentration of the active solute will face difficulty to reach the farthest portions of the chalk surface or in other words, it will affect the degree of solute diffusion onto the rock surface and then will change the wettability index.The following is the general formula of wettability alteration in chalk:

$$\theta_{ow} = \cos^{-1}\left[\frac{C*FI*C_p*M_{sys}*\Delta T*(\sigma_{os}-\sigma_{ws})*AN}{10^{-7}*H*\rho_B*P_v*D_{ratio}}\right] \tag{6.59}$$

The wettability detector factor $H = \frac{E_d*A_{oil}}{L*T_r*\mu_w*{C_f}^2}$ (6.60)

$T_r$ is the tortuosity, $\mu_w$ is the solute molecular weight, $C_f$ is the formation compressibility, $A_{oil}$ is the oil wet area, $E_d$ is the displacement efficiency, L is the core length.

$$Q_{sys} = C_p * M_{sys} * \Delta T = Q_{injected} = Q_{or} + Q_{wi} + Q_{produced} \tag{6.61}$$

$Q_{injected}$ , $Q_{or}$ , $Q_{wi}$ , $Q_{produced}$ are the heat energy of injected brine, remaining oil, initial water, oil produced respectively. $C_p$ is the specific heat at constant pressure, $Q_{sys}$ is the conservative heat energy of the system, $M_{sys}$ is the overall mass of the system, $\Delta T$ is the average temperature.

$$E_d = \frac{(S_{oi}-S_{or})}{S_{oi}} \tag{6.62}$$

$$\rho_b = -4 * 10^{-6}T^2 - 4 * 10^{-5}T + 0.9997 \tag{6.63}$$

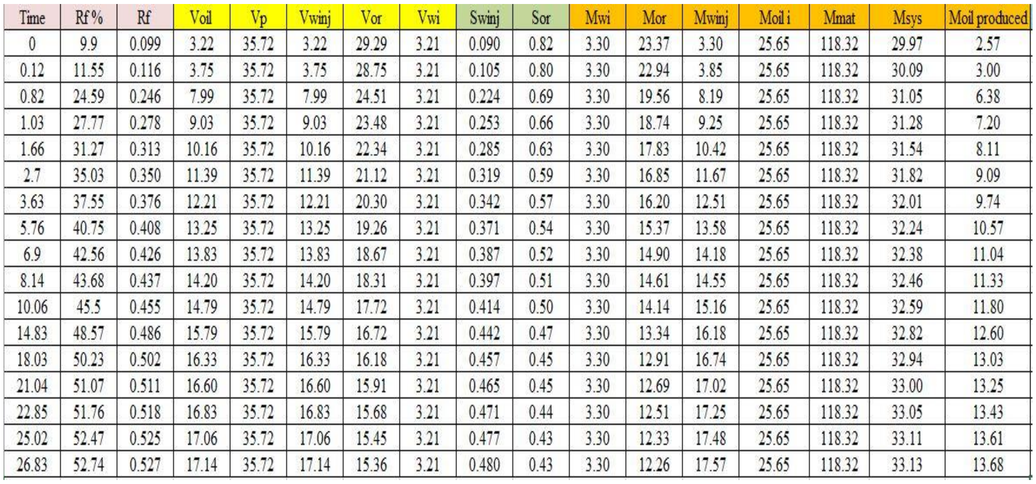
$$\mu_b = -0.412 \ln T + 2.1982 \tag{6.64}$$

$$\mu_o = 7.077e^{-0.022T} \tag{6.65}$$

Where $\rho_b$ is the brine density in gm/cc , T is the average temperature in $C^{\circ}$ , $\mu_b$ is the brine viscosity in cp, $\mu_o$ is the oil viscosity in cp.

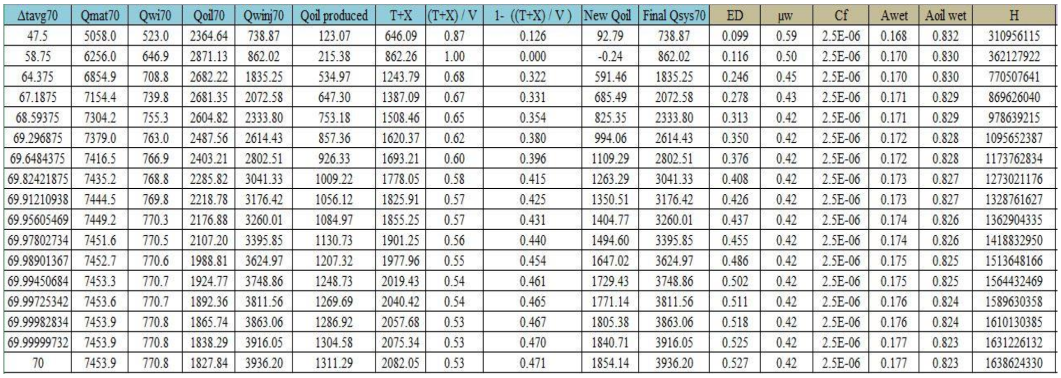
Table 6.3, Table 6.4 , and Table 6.5 below show all the calculations using the general formula for oil B , AN = 0.5 at 70 C°, oil viscosity 2.6 cp:

Table 6.3. Part 1 calculations of Oil B, AN=0.5 at T= 70 C°



| Time | Rf % | Rf | Voil | Vp | Vwinj | Vor | Vwi | Swinj | Sor | Mwi | Mor | Mwinj | Moil i | Mmat | Msys | Moil produced |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 9.9 | 0.099 | 3.22 | 35.72 | 3.22 | 29.29 | 3.21 | 0.090 | 0.82 | 3.30 | 23.37 | 3.30 | 25.65 | 118.32 | 29.97 | 2.57 |
| 0.12 | 11.55 | 0.116 | 3.75 | 35.72 | 3.75 | 28.75 | 3.21 | 0.105 | 0.80 | 3.30 | 22.94 | 3.85 | 25.65 | 118.32 | 30.09 | 3.00 |
| 0.82 | 24.59 | 0.246 | 7.99 | 35.72 | 7.99 | 24.51 | 3.21 | 0.224 | 0.69 | 3.30 | 19.56 | 8.19 | 25.65 | 118.32 | 31.05 | 6.38 |
| 1.03 | 27.77 | 0.278 | 9.03 | 35.72 | 9.03 | 23.48 | 3.21 | 0.253 | 0.66 | 3.30 | 18.74 | 9.25 | 25.65 | 118.32 | 31.28 | 7.20 |
| 1.66 | 31.27 | 0.313 | 10.16 | 35.72 | 10.16 | 22.34 | 3.21 | 0.285 | 0.63 | 3.30 | 17.83 | 10.42 | 25.65 | 118.32 | 31.54 | 8.11 |
| 2.7 | 35.03 | 0.350 | 11.39 | 35.72 | 11.39 | 21.12 | 3.21 | 0.319 | 0.59 | 3.30 | 16.85 | 11.67 | 25.65 | 118.32 | 31.82 | 9.09 |
| 3.63 | 37.55 | 0.376 | 12.21 | 35.72 | 12.21 | 20.30 | 3.21 | 0.342 | 0.57 | 3.30 | 16.20 | 12.51 | 25.65 | 118.32 | 32.01 | 9.74 |
| 5.76 | 40.75 | 0.408 | 13.25 | 35.72 | 13.25 | 19.26 | 3.21 | 0.371 | 0.54 | 3.30 | 15.37 | 13.58 | 25.65 | 118.32 | 32.24 | 10.57 |
| 6.9 | 42.56 | 0.426 | 13.83 | 35.72 | 13.83 | 18.67 | 3.21 | 0.387 | 0.52 | 3.30 | 14.90 | 14.18 | 25.65 | 118.32 | 32.38 | 11.04 |
| 8.14 | 43.68 | 0.437 | 14.20 | 35.72 | 14.20 | 18.31 | 3.21 | 0.397 | 0.51 | 3.30 | 14.61 | 14.55 | 25.65 | 118.32 | 32.46 | 11.33 |
| 10.06 | 45.5 | 0.455 | 14.79 | 35.72 | 14.79 | 17.72 | 3.21 | 0.414 | 0.50 | 3.30 | 14.14 | 15.16 | 25.65 | 118.32 | 32.59 | 11.80 |
| 14.83 | 48.57 | 0.486 | 15.79 | 35.72 | 15.79 | 16.72 | 3.21 | 0.442 | 0.47 | 3.30 | 13.34 | 16.18 | 25.65 | 118.32 | 32.82 | 12.60 |
| 18.03 | 50.23 | 0.502 | 16.33 | 35.72 | 16.33 | 16.18 | 3.21 | 0.457 | 0.45 | 3.30 | 12.91 | 16.74 | 25.65 | 118.32 | 32.94 | 13.03 |
| 21.04 | 51.07 | 0.511 | 16.60 | 35.72 | 16.60 | 15.91 | 3.21 | 0.465 | 0.45 | 3.30 | 12.69 | 17.02 | 25.65 | 118.32 | 33.00 | 13.25 |
| 22.85 | 51.76 | 0.518 | 16.83 | 35.72 | 16.83 | 15.68 | 3.21 | 0.471 | 0.44 | 3.30 | 12.51 | 17.25 | 25.65 | 118.32 | 33.05 | 13.43 |
| 25.02 | 52.47 | 0.525 | 17.06 | 35.72 | 17.06 | 15.45 | 3.21 | 0.477 | 0.43 | 3.30 | 12.33 | 17.48 | 25.65 | 118.32 | 33.11 | 13.61 |
| 26.83 | 52.74 | 0.527 | 17.14 | 35.72 | 17.14 | 15.36 | 3.21 | 0.480 | 0.43 | 3.30 | 12.26 | 17.57 | 25.65 | 118.32 | 33.13 | 13.68 |

Table 6.4. Part 2 calculations of Oil B, AN = 0.5 at T= 70 C°



| Δtavg70 | Qmat70 | Qwi70 | Qoil70 | Qwinj70 | Qoil produced | T+X | (T+X) / V | 1- ((T+X) / V ) | New Qoil | Final Qsys70 | ED | µw | Cf | Awet | Aoil wet | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 47.5 | 5058.0 | 523.0 | 2364.64 | 738.87 | 123.07 | 646.09 | 0.87 | 0.126 | 92.79 | 738.87 | 0.099 | 0.59 | 2.5E-06 | 0.168 | 0.832 | 310956115 |
| 58.75 | 6256.0 | 646.9 | 2871.13 | 862.02 | 215.38 | 862.26 | 1.00 | 0.000 | -0.24 | 862.02 | 0.116 | 0.50 | 2.5E-06 | 0.170 | 0.830 | 362127922 |
| 64.375 | 6854.9 | 708.8 | 2682.22 | 1835.25 | 534.97 | 1243.79 | 0.68 | 0.322 | 591.46 | 1835.25 | 0.246 | 0.45 | 2.5E-06 | 0.170 | 0.830 | 770507641 |
| 67.1875 | 7154.4 | 739.8 | 2681.35 | 2072.58 | 647.30 | 1387.09 | 0.67 | 0.331 | 685.49 | 2072.58 | 0.278 | 0.43 | 2.5E-06 | 0.171 | 0.829 | 869626040 |
| 68.59375 | 7304.2 | 755.3 | 2604.82 | 2333.80 | 753.18 | 1508.46 | 0.65 | 0.354 | 825.35 | 2333.80 | 0.313 | 0.42 | 2.5E-06 | 0.171 | 0.829 | 978639215 |
| 69.296875 | 7379.0 | 763.0 | 2487.56 | 2614.43 | 857.36 | 1620.37 | 0.62 | 0.380 | 994.06 | 2614.43 | 0.350 | 0.42 | 2.5E-06 | 0.172 | 0.828 | 1095652387 |
| 69.6484375 | 7416.5 | 766.9 | 2403.21 | 2802.51 | 926.33 | 1693.21 | 0.60 | 0.396 | 1109.29 | 2802.51 | 0.376 | 0.42 | 2.5E-06 | 0.172 | 0.828 | 1173762834 |
| 69.82421875 | 7435.2 | 768.8 | 2285.82 | 3041.33 | 1009.22 | 1778.05 | 0.58 | 0.415 | 1263.29 | 3041.33 | 0.408 | 0.42 | 2.5E-06 | 0.173 | 0.827 | 1273021176 |
| 69.91210938 | 7444.5 | 769.8 | 2218.78 | 3176.42 | 1056.12 | 1825.91 | 0.57 | 0.425 | 1350.51 | 3176.42 | 0.426 | 0.42 | 2.5E-06 | 0.173 | 0.827 | 1328761627 |
| 69.95605469 | 7449.2 | 770.3 | 2176.88 | 3260.01 | 1084.97 | 1855.25 | 0.57 | 0.431 | 1404.77 | 3260.01 | 0.437 | 0.42 | 2.5E-06 | 0.174 | 0.826 | 1362904335 |
| 69.97802734 | 7451.6 | 770.5 | 2107.20 | 3395.85 | 1130.73 | 1901.25 | 0.56 | 0.440 | 1494.60 | 3395.85 | 0.455 | 0.42 | 2.5E-06 | 0.174 | 0.826 | 1418832950 |
| 69.98901367 | 7452.7 | 770.6 | 1988.81 | 3624.97 | 1207.32 | 1977.96 | 0.55 | 0.454 | 1647.02 | 3624.97 | 0.486 | 0.42 | 2.5E-06 | 0.175 | 0.825 | 1513648166 |
| 69.99450684 | 7453.3 | 770.7 | 1924.77 | 3748.86 | 1248.73 | 2019.43 | 0.54 | 0.461 | 1729.43 | 3748.86 | 0.502 | 0.42 | 2.5E-06 | 0.175 | 0.825 | 1564432469 |
| 69.99725342 | 7453.6 | 770.7 | 1892.36 | 3811.56 | 1269.69 | 2040.42 | 0.54 | 0.465 | 1771.14 | 3811.56 | 0.511 | 0.42 | 2.5E-06 | 0.176 | 0.824 | 1589630358 |
| 69.99982834 | 7453.9 | 770.8 | 1865.74 | 3863.06 | 1286.92 | 2057.68 | 0.53 | 0.467 | 1805.38 | 3863.06 | 0.518 | 0.42 | 2.5E-06 | 0.176 | 0.824 | 1610130385 |
| 69.99999732 | 7453.9 | 770.8 | 1838.29 | 3916.05 | 1304.58 | 2075.34 | 0.53 | 0.470 | 1840.71 | 3916.05 | 0.525 | 0.42 | 2.5E-06 | 0.177 | 0.823 | 1631226132 |
| 70 | 7453.9 | 770.8 | 1827.84 | 3936.20 | 1311.29 | 2082.05 | 0.53 | 0.471 | 1854.14 | 3936.20 | 0.527 | 0.42 | 2.5E-06 | 0.177 | 0.823 | 1638624330 |

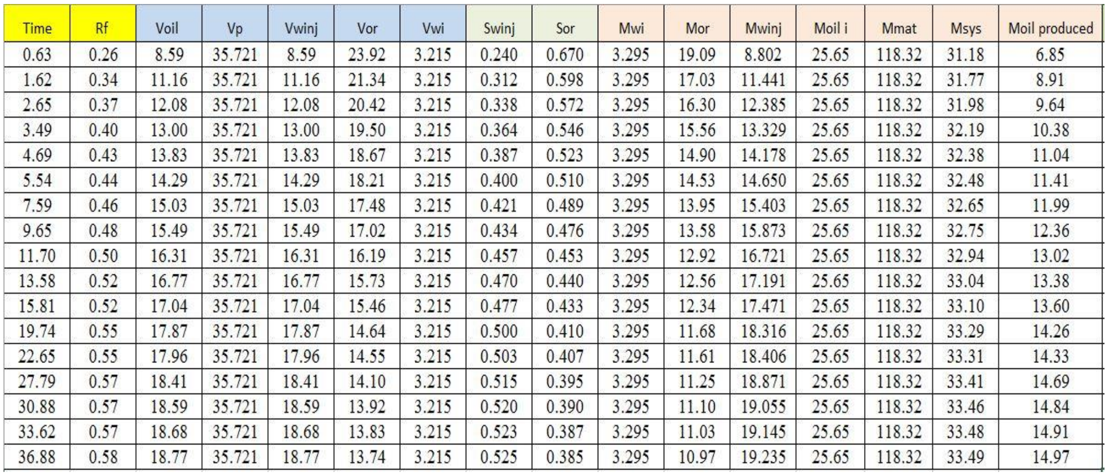
Table 6.5. Part 3 calculations of Oil B, AN = 0.5 at T = 70 C°

| ρbrine | µbrine | µOil | X | µbrine/µOil | LogX | Log(µbrine/µOil) | Y | 10^-Y(Dratio) | θow70 | Cosθ | Interfacial tension σow | Rf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.9888 | 0.608 | 2.49 | 2.800 | 0.244 | 0.44715803 | -0.612 | -0.165 | 0.684 | 77.32 | 0.219 | 55.59 | 0.099 |
| 0.9835 | 0.520 | 1.94 | 1.474 | 0.268 | 0.16840443 | -0.573 | -0.404 | 0.394 | 67.47 | 0.383 | 31.84 | 0.116 |
| 0.9805 | 0.482 | 1.72 | 1.191 | 0.281 | 0.07609017 | -0.551 | -0.475 | 0.335 | 63.06 | 0.453 | 26.93 | 0.246 |
| 0.9790 | 0.465 | 1.61 | 1.087 | 0.288 | 0.03638080 | -0.541 | -0.504 | 0.313 | 60.96 | 0.485 | 25.13 | 0.278 |
| 0.9781 | 0.456 | 1.56 | 1.042 | 0.292 | 0.01780956 | -0.535 | -0.518 | 0.304 | 59.93 | 0.501 | 24.35 | 0.313 |
| 0.9777 | 0.452 | 1.54 | 1.021 | 0.293 | 0.00881349 | -0.533 | -0.524 | 0.299 | 59.41 | 0.509 | 23.97 | 0.350 |
| 0.9775 | 0.450 | 1.53 | 1.010 | 0.294 | 0.00438439 | -0.531 | -0.527 | 0.297 | 59.14 | 0.513 | 23.78 | 0.376 |
| 0.9774 | 0.449 | 1.52 | 1.005 | 0.295 | 0.00218666 | -0.531 | -0.528 | 0.296 | 58.99 | 0.515 | 23.68 | 0.408 |
| 0.9774 | 0.448 | 1.52 | 1.003 | 0.295 | 0.00109195 | -0.530 | -0.529 | 0.296 | 58.91 | 0.516 | 23.62 | 0.426 |
| 0.9773 | 0.448 | 1.52 | 1.001 | 0.295 | 0.00054563 | -0.530 | -0.530 | 0.295 | 58.86 | 0.517 | 23.59 | 0.437 |
| 0.9773 | 0.448 | 1.52 | 1.001 | 0.295 | 0.00027273 | -0.530 | -0.530 | 0.295 | 58.82 | 0.518 | 23.56 | 0.455 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00013634 | -0.530 | -0.530 | 0.295 | 58.79 | 0.518 | 23.54 | 0.486 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00006817 | -0.530 | -0.530 | 0.295 | 58.77 | 0.519 | 23.53 | 0.502 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00003408 | -0.530 | -0.530 | 0.295 | 58.74 | 0.519 | 23.51 | 0.511 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00003195 | -0.530 | -0.530 | 0.295 | 58.72 | 0.519 | 23.50 | 0.518 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00000210 | -0.530 | -0.530 | 0.295 | 58.70 | 0.520 | 23.48 | 0.525 |
| 0.9773 | 0.448 | 1.52 | 1.000 | 0.295 | 0.00000003 | -0.530 | -0.530 | 0.295 | 58.68 | 0.520 | 23.47 | 0.527 |

The general formula has succeeded to obtain contact angles below $70^{\circ}$ at values about $58^{\circ}$ which means a water-wet condition at interfacial tension about 23.4 dyne/cm.In other words, all the modifications proposed have worked well together to get a smooth wettability alteration on chalk.

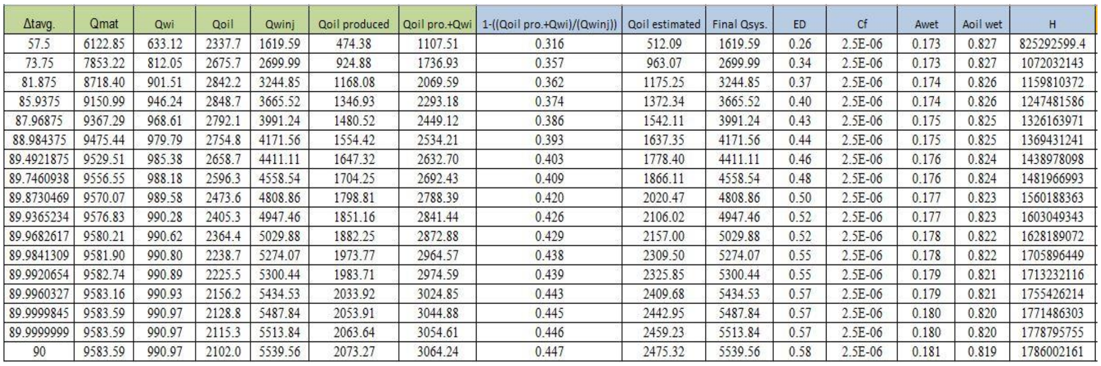
In the same procedure, Table 6.6, Table 6.7, Table 6.8 show the overall calculations of oil B with AN = 0.5 at T= 90 $C^{\circ}$:

Table 6.6. Part 1 calculations of Oil B, AN=0.5 at T=90 $C^{\circ}$



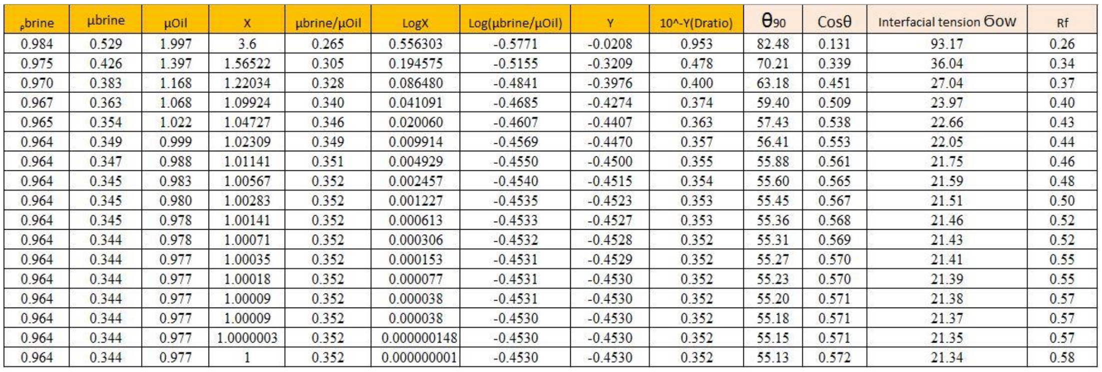
| Time | Rf | Voil | Vp | Vwinj | Vor | Vwi | Swinj | Sor | Mwi | Mor | Mwinj | Moil i | Mmat | Msys | Moil produced |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.63 | 0.26 | 8.59 | 35.721 | 8.59 | 23.92 | 3.215 | 0.240 | 0.670 | 3.295 | 19.09 | 8.802 | 25.65 | 118.32 | 31.18 | 6.85 |
| 1.62 | 0.34 | 11.16 | 35.721 | 11.16 | 21.34 | 3.215 | 0.312 | 0.598 | 3.295 | 17.03 | 11.441 | 25.65 | 118.32 | 31.77 | 8.91 |
| 2.65 | 0.37 | 12.08 | 35.721 | 12.08 | 20.42 | 3.215 | 0.338 | 0.572 | 3.295 | 16.30 | 12.385 | 25.65 | 118.32 | 31.98 | 9.64 |
| 3.49 | 0.40 | 13.00 | 35.721 | 13.00 | 19.50 | 3.215 | 0.364 | 0.546 | 3.295 | 15.56 | 13.329 | 25.65 | 118.32 | 32.19 | 10.38 |
| 4.69 | 0.43 | 13.83 | 35.721 | 13.83 | 18.67 | 3.215 | 0.387 | 0.523 | 3.295 | 14.90 | 14.178 | 25.65 | 118.32 | 32.38 | 11.04 |
| 5.54 | 0.44 | 14.29 | 35.721 | 14.29 | 18.21 | 3.215 | 0.400 | 0.510 | 3.295 | 14.53 | 14.650 | 25.65 | 118.32 | 32.48 | 11.41 |
| 7.59 | 0.46 | 15.03 | 35.721 | 15.03 | 17.48 | 3.215 | 0.421 | 0.489 | 3.295 | 13.95 | 15.403 | 25.65 | 118.32 | 32.65 | 11.99 |
| 9.65 | 0.48 | 15.49 | 35.721 | 15.49 | 17.02 | 3.215 | 0.434 | 0.476 | 3.295 | 13.58 | 15.873 | 25.65 | 118.32 | 32.75 | 12.36 |
| 11.70 | 0.50 | 16.31 | 35.721 | 16.31 | 16.19 | 3.215 | 0.457 | 0.453 | 3.295 | 12.92 | 16.721 | 25.65 | 118.32 | 32.94 | 13.02 |
| 13.58 | 0.52 | 16.77 | 35.721 | 16.77 | 15.73 | 3.215 | 0.470 | 0.440 | 3.295 | 12.56 | 17.191 | 25.65 | 118.32 | 33.04 | 13.38 |
| 15.81 | 0.52 | 17.04 | 35.721 | 17.04 | 15.46 | 3.215 | 0.477 | 0.433 | 3.295 | 12.34 | 17.471 | 25.65 | 118.32 | 33.10 | 13.60 |
| 19.74 | 0.55 | 17.87 | 35.721 | 17.87 | 14.64 | 3.215 | 0.500 | 0.410 | 3.295 | 11.68 | 18.316 | 25.65 | 118.32 | 33.29 | 14.26 |
| 22.65 | 0.55 | 17.96 | 35.721 | 17.96 | 14.55 | 3.215 | 0.503 | 0.407 | 3.295 | 11.61 | 18.406 | 25.65 | 118.32 | 33.31 | 14.33 |
| 27.79 | 0.57 | 18.41 | 35.721 | 18.41 | 14.10 | 3.215 | 0.515 | 0.395 | 3.295 | 11.25 | 18.871 | 25.65 | 118.32 | 33.41 | 14.69 |
| 30.88 | 0.57 | 18.59 | 35.721 | 18.59 | 13.92 | 3.215 | 0.520 | 0.390 | 3.295 | 11.10 | 19.055 | 25.65 | 118.32 | 33.46 | 14.84 |
| 33.62 | 0.57 | 18.68 | 35.721 | 18.68 | 13.83 | 3.215 | 0.523 | 0.387 | 3.295 | 11.03 | 19.145 | 25.65 | 118.32 | 33.48 | 14.91 |
| 36.88 | 0.58 | 18.77 | 35.721 | 18.77 | 13.74 | 3.215 | 0.525 | 0.385 | 3.295 | 10.97 | 19.235 | 25.65 | 118.32 | 33.49 | 14.97 |

Table 6.7. Part 2 calculations of Oil B, AN=0.5 at T= 90 $C^{\circ}$



| Δtavg. | Qmat | Qwi | Qoil | Qwinj | Qoil produced | Qoil pro.+Qwi | 1-((Qoil pro.+Qwi)/(Qwinj)) | Qoil estimated | Final Qsys. | ED | Cf | Awet | Aoil wet | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57.5 | 6122.85 | 633.12 | 2337.7 | 1619.59 | 474.38 | 1107.51 | 0.316 | 512.09 | 1619.59 | 0.26 | 2.5E-06 | 0.173 | 0.827 | 825292599.4 |
| 73.75 | 7853.22 | 812.05 | 2675.7 | 2699.99 | 924.88 | 1736.93 | 0.357 | 963.07 | 2699.99 | 0.34 | 2.5E-06 | 0.173 | 0.827 | 1072032143 |
| 81.875 | 8718.40 | 901.51 | 2842.2 | 3244.85 | 1168.08 | 2069.59 | 0.362 | 1175.25 | 3244.85 | 0.37 | 2.5E-06 | 0.174 | 0.826 | 1159810372 |
| 85.9375 | 9150.99 | 946.24 | 2848.7 | 3665.52 | 1346.93 | 2293.18 | 0.374 | 1372.34 | 3665.52 | 0.40 | 2.5E-06 | 0.174 | 0.826 | 1247481586 |
| 87.96875 | 9367.29 | 968.61 | 2792.1 | 3991.24 | 1480.52 | 2449.12 | 0.386 | 1542.11 | 3991.24 | 0.43 | 2.5E-06 | 0.175 | 0.825 | 1326163971 |
| 88.984375 | 9475.44 | 979.79 | 2754.8 | 4171.56 | 1554.42 | 2534.21 | 0.393 | 1637.35 | 4171.56 | 0.44 | 2.5E-06 | 0.175 | 0.825 | 1369431241 |
| 89.4921875 | 9529.51 | 985.38 | 2658.7 | 4411.11 | 1647.32 | 2632.70 | 0.403 | 1778.40 | 4411.11 | 0.46 | 2.5E-06 | 0.176 | 0.824 | 1438978098 |
| 89.7460938 | 9556.55 | 988.18 | 2596.3 | 4558.54 | 1704.25 | 2692.43 | 0.409 | 1866.11 | 4558.54 | 0.48 | 2.5E-06 | 0.176 | 0.824 | 1481966993 |
| 89.8730469 | 9570.07 | 989.58 | 2473.6 | 4808.86 | 1798.81 | 2788.39 | 0.420 | 2020.47 | 4808.86 | 0.50 | 2.5E-06 | 0.177 | 0.823 | 1560188363 |
| 89.9365234 | 9576.83 | 990.28 | 2405.3 | 4947.46 | 1851.16 | 2841.44 | 0.426 | 2106.02 | 4947.46 | 0.52 | 2.5E-06 | 0.177 | 0.823 | 1603049343 |
| 89.9682617 | 9580.21 | 990.62 | 2364.4 | 5029.88 | 1882.25 | 2872.88 | 0.429 | 2157.00 | 5029.88 | 0.52 | 2.5E-06 | 0.178 | 0.822 | 1628189072 |
| 89.9841309 | 9581.90 | 990.80 | 2238.7 | 5274.07 | 1973.77 | 2964.57 | 0.438 | 2309.50 | 5274.07 | 0.55 | 2.5E-06 | 0.178 | 0.822 | 1705896449 |
| 89.9920654 | 9582.74 | 990.89 | 2225.5 | 5300.44 | 1983.71 | 2974.59 | 0.439 | 2325.85 | 5300.44 | 0.55 | 2.5E-06 | 0.179 | 0.821 | 1713232116 |
| 89.9960327 | 9583.16 | 990.93 | 2156.2 | 5434.53 | 2033.92 | 3024.85 | 0.443 | 2409.68 | 5434.53 | 0.57 | 2.5E-06 | 0.179 | 0.821 | 1755426214 |
| 89.9999845 | 9583.59 | 990.97 | 2128.8 | 5487.84 | 2053.91 | 3044.88 | 0.445 | 2442.95 | 5487.84 | 0.57 | 2.5E-06 | 0.180 | 0.820 | 1771486303 |
| 89.9999999 | 9583.59 | 990.97 | 2115.3 | 5513.84 | 2063.64 | 3054.61 | 0.446 | 2459.23 | 5513.84 | 0.57 | 2.5E-06 | 0.180 | 0.820 | 1778795755 |
| 90 | 9583.59 | 990.97 | 2102.0 | 5539.56 | 2073.27 | 3064.24 | 0.447 | 2475.32 | 5539.56 | 0.58 | 2.5E-06 | 0.181 | 0.819 | 1786002161 |

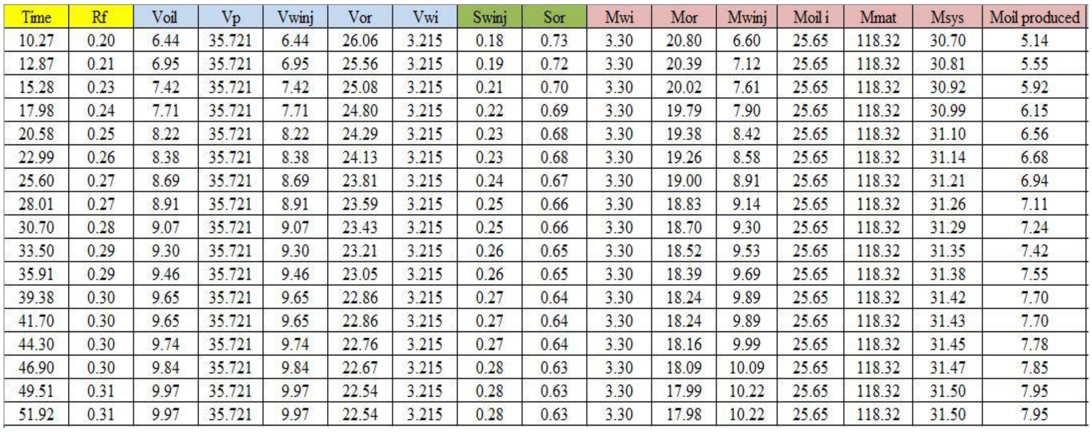
Table 6.8. Part 3 calculations of Oil B, AN=0.5, at T = 90 C°



| ρbrine | μbrine | μOil | X | μbrine/μOil | LogX | Log(μbrine/μOil) | Y | 10^-Y(Dratio) | θ90 | Cosθ | Interfacial tension Ϭow | Rf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.984 | 0.529 | 1.997 | 3.6 | 0.265 | 0.556303 | -0.5771 | -0.0208 | 0.953 | 82.48 | 0.131 | 93.17 | 0.26 |
| 0.975 | 0.426 | 1.397 | 1.56522 | 0.305 | 0.194575 | -0.5155 | -0.3209 | 0.478 | 70.21 | 0.339 | 36.04 | 0.34 |
| 0.970 | 0.383 | 1.168 | 1.22034 | 0.328 | 0.086480 | -0.4841 | -0.3976 | 0.400 | 63.18 | 0.451 | 27.04 | 0.37 |
| 0.967 | 0.363 | 1.068 | 1.09924 | 0.340 | 0.041091 | -0.4685 | -0.4274 | 0.374 | 59.40 | 0.509 | 23.97 | 0.40 |
| 0.965 | 0.354 | 1.022 | 1.04727 | 0.346 | 0.020060 | -0.4607 | -0.4407 | 0.363 | 57.43 | 0.538 | 22.66 | 0.43 |
| 0.964 | 0.349 | 0.999 | 1.02309 | 0.349 | 0.009914 | -0.4569 | -0.4470 | 0.357 | 56.41 | 0.553 | 22.05 | 0.44 |
| 0.964 | 0.347 | 0.988 | 1.01141 | 0.351 | 0.004929 | -0.4550 | -0.4500 | 0.355 | 55.88 | 0.561 | 21.75 | 0.46 |
| 0.964 | 0.345 | 0.983 | 1.00567 | 0.352 | 0.002457 | -0.4540 | -0.4515 | 0.354 | 55.60 | 0.565 | 21.59 | 0.48 |
| 0.964 | 0.345 | 0.980 | 1.00283 | 0.352 | 0.001227 | -0.4535 | -0.4523 | 0.353 | 55.45 | 0.567 | 21.51 | 0.50 |
| 0.964 | 0.345 | 0.978 | 1.00141 | 0.352 | 0.000613 | -0.4533 | -0.4527 | 0.353 | 55.36 | 0.568 | 21.46 | 0.52 |
| 0.964 | 0.344 | 0.978 | 1.00071 | 0.352 | 0.000306 | -0.4532 | -0.4528 | 0.352 | 55.31 | 0.569 | 21.43 | 0.52 |
| 0.964 | 0.344 | 0.977 | 1.00035 | 0.352 | 0.000153 | -0.4531 | -0.4529 | 0.352 | 55.27 | 0.570 | 21.41 | 0.55 |
| 0.964 | 0.344 | 0.977 | 1.00018 | 0.352 | 0.000077 | -0.4531 | -0.4530 | 0.352 | 55.23 | 0.570 | 21.39 | 0.55 |
| 0.964 | 0.344 | 0.977 | 1.00009 | 0.352 | 0.000038 | -0.4531 | -0.4530 | 0.352 | 55.20 | 0.571 | 21.38 | 0.57 |
| 0.964 | 0.344 | 0.977 | 1.00009 | 0.352 | 0.000038 | -0.4530 | -0.4530 | 0.352 | 55.18 | 0.571 | 21.37 | 0.57 |
| 0.964 | 0.344 | 0.977 | 1.0000003 | 0.352 | 0.000000148 | -0.4530 | -0.4530 | 0.352 | 55.15 | 0.571 | 21.35 | 0.57 |
| 0.964 | 0.344 | 0.977 | 1 | 0.352 | 0.000000001 | -0.4530 | -0.4530 | 0.352 | 55.13 | 0.572 | 21.34 | 0.58 |

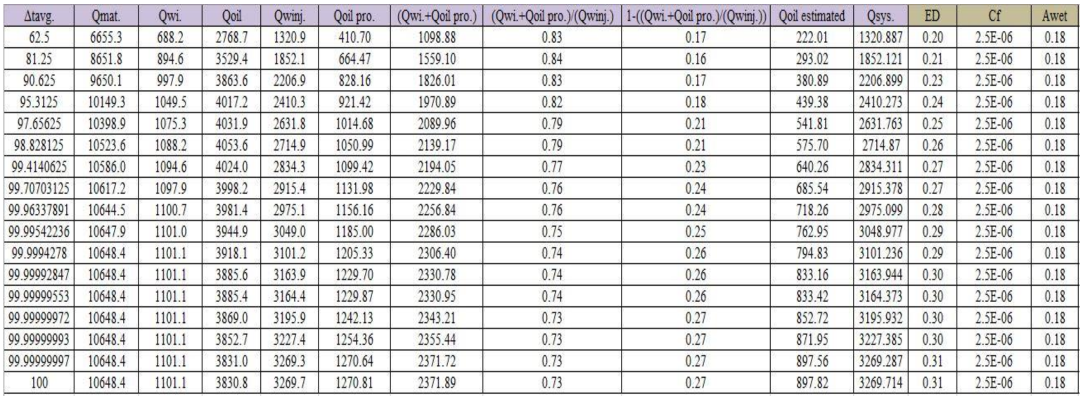
From the Tables 6.6, 6.7, and 6.8 above of Oil B, AN=0.5, at T= 90 C°, best improvements have happened to the contact angles and the interfacial tensions. When the temperature has raised from 70 C° to 90 C°, the interfacial tensions have decreased and the contact angles as well. The reason behind that is rising the temperature leads to lower the viscosities of the flowing liquids in a way that enable the diffusivity of brine to be the dominant onto the rock surface than the diffusivity of oil. In addition to the decreasing of interfacial tension and increasing of the brine-wet areas. All those factors lead to get contact angle of 55° at 90 C° lower than that one at 70 C°as well as lower interfacial tension about 21 dyne/cm. The same procedure will follow at T= 100 C°and T=120 C° of oil A, AN=2, oil viscosity 3.38 cp except for the high viscosity of this oil required double the sulfate concentration and double the lowering of flow impedance to gain more oil produced from the core.Below, Table 6.9, Table 6.10, and Table 6.11 of the total calculations that have done of Oil A, AN=2, 3.38 cp, 100 C°:

Table 6.9. Part 1 calculations of Oil A, AN=2 at T=100 C$^{\circ}$



| Time | Rf | Voil | Vp | Vwinj | Vor | Vwi | Swinj | Sor | Mwi | Mor | Mwinj | Moil i | Mmat | Msys | Moil produced |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10.27 | 0.20 | 6.44 | 35.721 | 6.44 | 26.06 | 3.215 | 0.18 | 0.73 | 3.30 | 20.80 | 6.60 | 25.65 | 118.32 | 30.70 | 5.14 |
| 12.87 | 0.21 | 6.95 | 35.721 | 6.95 | 25.56 | 3.215 | 0.19 | 0.72 | 3.30 | 20.39 | 7.12 | 25.65 | 118.32 | 30.81 | 5.55 |
| 15.28 | 0.23 | 7.42 | 35.721 | 7.42 | 25.08 | 3.215 | 0.21 | 0.70 | 3.30 | 20.02 | 7.61 | 25.65 | 118.32 | 30.92 | 5.92 |
| 17.98 | 0.24 | 7.71 | 35.721 | 7.71 | 24.80 | 3.215 | 0.22 | 0.69 | 3.30 | 19.79 | 7.90 | 25.65 | 118.32 | 30.99 | 6.15 |
| 20.58 | 0.25 | 8.22 | 35.721 | 8.22 | 24.29 | 3.215 | 0.23 | 0.68 | 3.30 | 19.38 | 8.42 | 25.65 | 118.32 | 31.10 | 6.56 |
| 22.99 | 0.26 | 8.38 | 35.721 | 8.38 | 24.13 | 3.215 | 0.23 | 0.68 | 3.30 | 19.26 | 8.58 | 25.65 | 118.32 | 31.14 | 6.68 |
| 25.60 | 0.27 | 8.69 | 35.721 | 8.69 | 23.81 | 3.215 | 0.24 | 0.67 | 3.30 | 19.00 | 8.91 | 25.65 | 118.32 | 31.21 | 6.94 |
| 28.01 | 0.27 | 8.91 | 35.721 | 8.91 | 23.59 | 3.215 | 0.25 | 0.66 | 3.30 | 18.83 | 9.14 | 25.65 | 118.32 | 31.26 | 7.11 |
| 30.70 | 0.28 | 9.07 | 35.721 | 9.07 | 23.43 | 3.215 | 0.25 | 0.66 | 3.30 | 18.70 | 9.30 | 25.65 | 118.32 | 31.29 | 7.24 |
| 33.50 | 0.29 | 9.30 | 35.721 | 9.30 | 23.21 | 3.215 | 0.26 | 0.65 | 3.30 | 18.52 | 9.53 | 25.65 | 118.32 | 31.35 | 7.42 |
| 35.91 | 0.29 | 9.46 | 35.721 | 9.46 | 23.05 | 3.215 | 0.26 | 0.65 | 3.30 | 18.39 | 9.69 | 25.65 | 118.32 | 31.38 | 7.55 |
| 39.38 | 0.30 | 9.65 | 35.721 | 9.65 | 22.86 | 3.215 | 0.27 | 0.64 | 3.30 | 18.24 | 9.89 | 25.65 | 118.32 | 31.42 | 7.70 |
| 41.70 | 0.30 | 9.65 | 35.721 | 9.65 | 22.86 | 3.215 | 0.27 | 0.64 | 3.30 | 18.24 | 9.89 | 25.65 | 118.32 | 31.43 | 7.70 |
| 44.30 | 0.30 | 9.74 | 35.721 | 9.74 | 22.76 | 3.215 | 0.27 | 0.64 | 3.30 | 18.16 | 9.99 | 25.65 | 118.32 | 31.45 | 7.78 |
| 46.90 | 0.30 | 9.84 | 35.721 | 9.84 | 22.67 | 3.215 | 0.28 | 0.63 | 3.30 | 18.09 | 10.09 | 25.65 | 118.32 | 31.47 | 7.85 |
| 49.51 | 0.31 | 9.97 | 35.721 | 9.97 | 22.54 | 3.215 | 0.28 | 0.63 | 3.30 | 17.99 | 10.22 | 25.65 | 118.32 | 31.50 | 7.95 |
| 51.92 | 0.31 | 9.97 | 35.721 | 9.97 | 22.54 | 3.215 | 0.28 | 0.63 | 3.30 | 17.98 | 10.22 | 25.65 | 118.32 | 31.50 | 7.95 |

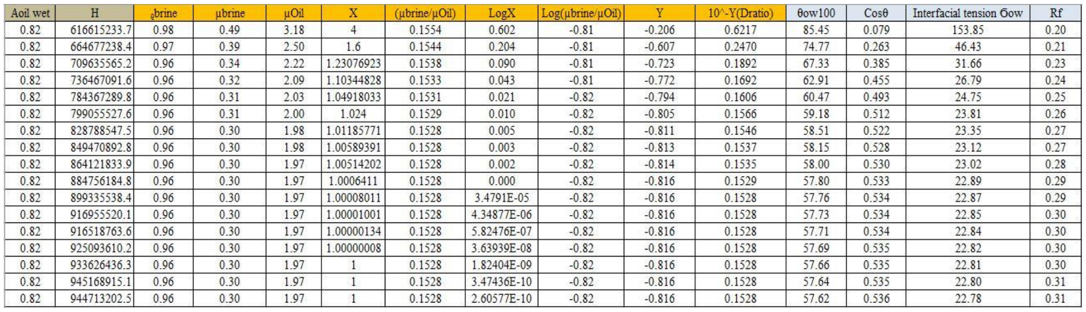
Table 6.10. Part 2 calculations of Oil A, AN=2, T=100 C$^{\circ}$



| Δtavg. | Qmat. | Qwi. | Qoil | Qwinj. | Qoil pro. | (Qwi.+Qoil pro.) | (Qwi.+Qoil pro.)/(Qwinj.) | 1-((Qwi.+Qoil pro.)/(Qwinj.)) | Qoil estimated | Qsys. | ED | Cf | Awet |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 62.5 | 6655.3 | 688.2 | 2768.7 | 1320.9 | 410.70 | 1098.88 | 0.83 | 0.17 | 222.01 | 1320.887 | 0.20 | 2.5E-06 | 0.18 |
| 81.25 | 8651.8 | 894.6 | 3529.4 | 1852.1 | 664.47 | 1559.10 | 0.84 | 0.16 | 293.02 | 1852.121 | 0.21 | 2.5E-06 | 0.18 |
| 90.625 | 9650.1 | 997.9 | 3863.6 | 2206.9 | 828.16 | 1826.01 | 0.83 | 0.17 | 380.89 | 2206.899 | 0.23 | 2.5E-06 | 0.18 |
| 95.3125 | 10149.3 | 1049.5 | 4017.2 | 2410.3 | 921.42 | 1970.89 | 0.82 | 0.18 | 439.38 | 2410.273 | 0.24 | 2.5E-06 | 0.18 |
| 97.65625 | 10398.9 | 1075.3 | 4031.9 | 2631.8 | 1014.68 | 2089.96 | 0.79 | 0.21 | 541.81 | 2631.763 | 0.25 | 2.5E-06 | 0.18 |
| 98.828125 | 10523.6 | 1088.2 | 4053.6 | 2714.9 | 1050.99 | 2139.17 | 0.79 | 0.21 | 575.70 | 2714.87 | 0.26 | 2.5E-06 | 0.18 |
| 99.4140625 | 10586.0 | 1094.6 | 4024.0 | 2834.3 | 1099.42 | 2194.05 | 0.77 | 0.23 | 640.26 | 2834.311 | 0.27 | 2.5E-06 | 0.18 |
| 99.70703125 | 10617.2 | 1097.9 | 3998.2 | 2915.4 | 1131.98 | 2229.84 | 0.76 | 0.24 | 685.54 | 2915.378 | 0.27 | 2.5E-06 | 0.18 |
| 99.96337891 | 10644.5 | 1100.7 | 3981.4 | 2975.1 | 1156.16 | 2256.84 | 0.76 | 0.24 | 718.26 | 2975.099 | 0.28 | 2.5E-06 | 0.18 |
| 99.99542236 | 10647.9 | 1101.0 | 3944.9 | 3049.0 | 1185.00 | 2286.03 | 0.75 | 0.25 | 762.95 | 3048.977 | 0.29 | 2.5E-06 | 0.18 |
| 99.9994278 | 10648.4 | 1101.1 | 3918.1 | 3101.2 | 1205.33 | 2306.40 | 0.74 | 0.26 | 794.83 | 3101.236 | 0.29 | 2.5E-06 | 0.18 |
| 99.99992847 | 10648.4 | 1101.1 | 3885.6 | 3163.9 | 1229.70 | 2330.78 | 0.74 | 0.26 | 833.16 | 3163.944 | 0.30 | 2.5E-06 | 0.18 |
| 99.99999553 | 10648.4 | 1101.1 | 3885.4 | 3164.4 | 1229.87 | 2330.95 | 0.74 | 0.26 | 833.42 | 3164.373 | 0.30 | 2.5E-06 | 0.18 |
| 99.99999972 | 10648.4 | 1101.1 | 3869.0 | 3195.9 | 1242.13 | 2343.21 | 0.73 | 0.27 | 852.72 | 3195.932 | 0.30 | 2.5E-06 | 0.18 |
| 99.99999993 | 10648.4 | 1101.1 | 3852.7 | 3227.4 | 1254.36 | 2355.44 | 0.73 | 0.27 | 871.95 | 3227.385 | 0.30 | 2.5E-06 | 0.18 |
| 99.99999997 | 10648.4 | 1101.1 | 3831.0 | 3269.3 | 1270.64 | 2371.72 | 0.73 | 0.27 | 897.56 | 3269.287 | 0.31 | 2.5E-06 | 0.18 |
| 100 | 10648.4 | 1101.1 | 3830.8 | 3269.7 | 1270.81 | 2371.89 | 0.73 | 0.27 | 897.82 | 3269.714 | 0.31 | 2.5E-06 | 0.18 |

It can see from the Table 6.9, Table 6.10 above and Table 6.11 below, that the contact angles continue to decrease when the temperature raised to 100 C$^{\circ}$ to the value of 57$^{\circ}$which means the core has switched to water wet in addition to the decreasing of interfacial tension to the value of 22.7 dyne/cm. The success results indicate that the general formula is still valid to exam- ine the wettability alteration of chalk.

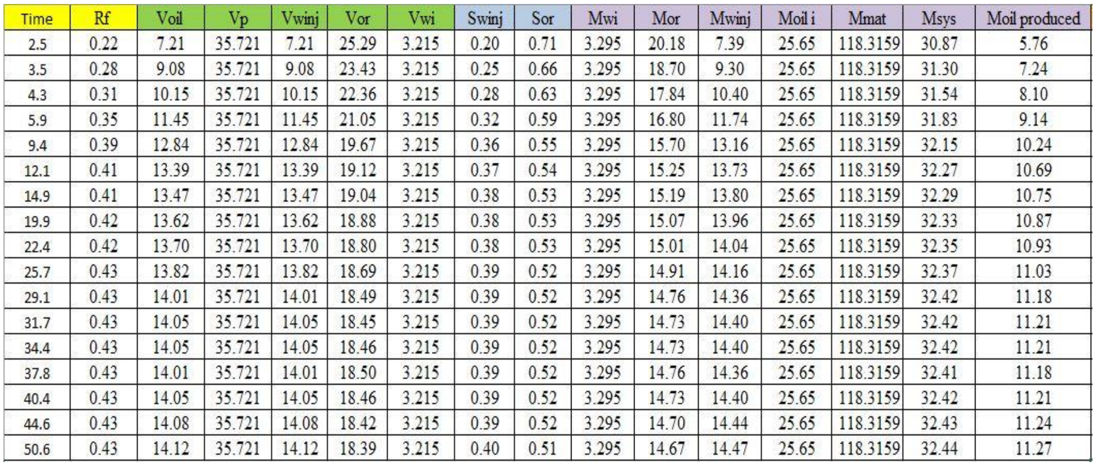
Table 6.11. Part 3 calculations of Oil A, AN=2, T=100 C°



| Aoil wet | H | ρbrine | µbrine | µOil | X | (µbrine/µOil) | LogX | Log(µbrine/µOil) | Y | 10^-Y(Dratio) | θow100 | Cosθ | Interfacial tension Ϭow | Rf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.82 | 616615233.7 | 0.98 | 0.49 | 3.18 | 4 | 0.1554 | 0.602 | -0.81 | -0.206 | 0.6217 | 85.45 | 0.079 | 153.85 | 0.20 |
| 0.82 | 664677238.4 | 0.97 | 0.39 | 2.50 | 1.6 | 0.1544 | 0.204 | -0.81 | -0.607 | 0.2470 | 74.77 | 0.263 | 46.43 | 0.21 |
| 0.82 | 709635565.2 | 0.96 | 0.34 | 2.22 | 1.23076923 | 0.1538 | 0.090 | -0.81 | -0.723 | 0.1892 | 67.33 | 0.385 | 31.66 | 0.23 |
| 0.82 | 736467091.6 | 0.96 | 0.32 | 2.09 | 1.10344828 | 0.1533 | 0.043 | -0.81 | -0.772 | 0.1692 | 62.91 | 0.455 | 26.79 | 0.24 |
| 0.82 | 784367289.8 | 0.96 | 0.31 | 2.03 | 1.04918033 | 0.1531 | 0.021 | -0.82 | -0.794 | 0.1606 | 60.47 | 0.493 | 24.75 | 0.25 |
| 0.82 | 799055527.6 | 0.96 | 0.31 | 2.00 | 1.024 | 0.1529 | 0.010 | -0.82 | -0.805 | 0.1566 | 59.18 | 0.512 | 23.81 | 0.26 |
| 0.82 | 828788547.5 | 0.96 | 0.30 | 1.98 | 1.01185771 | 0.1528 | 0.005 | -0.82 | -0.811 | 0.1546 | 58.51 | 0.522 | 23.35 | 0.27 |
| 0.82 | 849470892.8 | 0.96 | 0.30 | 1.98 | 1.00589391 | 0.1528 | 0.003 | -0.82 | -0.813 | 0.1537 | 58.15 | 0.528 | 23.12 | 0.27 |
| 0.82 | 864121833.9 | 0.96 | 0.30 | 1.97 | 1.00514202 | 0.1528 | 0.002 | -0.82 | -0.814 | 0.1535 | 58.00 | 0.530 | 23.02 | 0.28 |
| 0.82 | 884756184.8 | 0.96 | 0.30 | 1.97 | 1.0006411 | 0.1528 | 0.000 | -0.82 | -0.816 | 0.1529 | 57.80 | 0.533 | 22.89 | 0.29 |
| 0.82 | 899335538.4 | 0.96 | 0.30 | 1.97 | 1.00008011 | 0.1528 | 3.4791E-05 | -0.82 | -0.816 | 0.1528 | 57.76 | 0.534 | 22.87 | 0.29 |
| 0.82 | 916955520.1 | 0.96 | 0.30 | 1.97 | 1.00001001 | 0.1528 | 4.34877E-06 | -0.82 | -0.816 | 0.1528 | 57.73 | 0.534 | 22.85 | 0.30 |
| 0.82 | 916518763.6 | 0.96 | 0.30 | 1.97 | 1.00000134 | 0.1528 | 5.82476E-07 | -0.82 | -0.816 | 0.1528 | 57.71 | 0.534 | 22.84 | 0.30 |
| 0.82 | 925093610.2 | 0.96 | 0.30 | 1.97 | 1.00000008 | 0.1528 | 3.63939E-08 | -0.82 | -0.816 | 0.1528 | 57.69 | 0.535 | 22.82 | 0.30 |
| 0.82 | 933626436.3 | 0.96 | 0.30 | 1.97 | 1 | 0.1528 | 1.82404E-09 | -0.82 | -0.816 | 0.1528 | 57.66 | 0.535 | 22.81 | 0.30 |
| 0.82 | 945168915.1 | 0.96 | 0.30 | 1.97 | 1 | 0.1528 | 3.47436E-10 | -0.82 | -0.816 | 0.1528 | 57.64 | 0.535 | 22.80 | 0.31 |
| 0.82 | 944713202.5 | 0.96 | 0.30 | 1.97 | 1 | 0.1528 | 2.60577E-10 | -0.82 | -0.816 | 0.1528 | 57.62 | 0.536 | 22.78 | 0.31 |

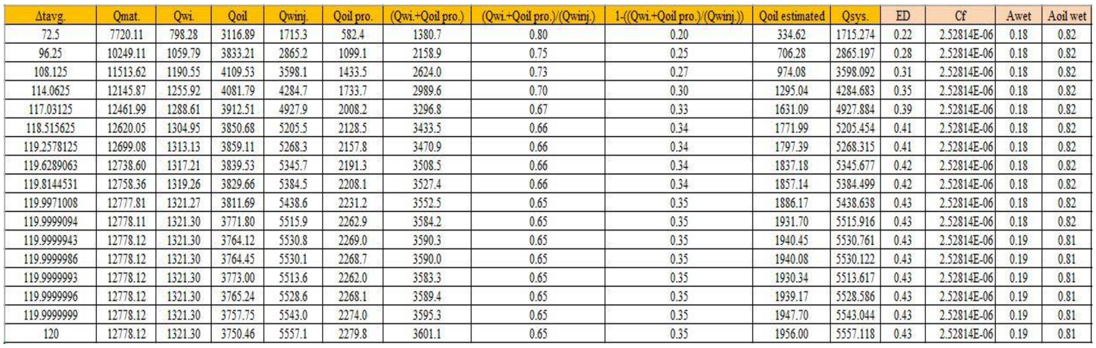
Table 6.12, Table 6.13, and Table 6.14 below summarize the overall calculations that have done of oil A, AN=2, T=120 C°:

Table 6.12. Part 1 calculations of Oil A, AN=2, T=120 C°



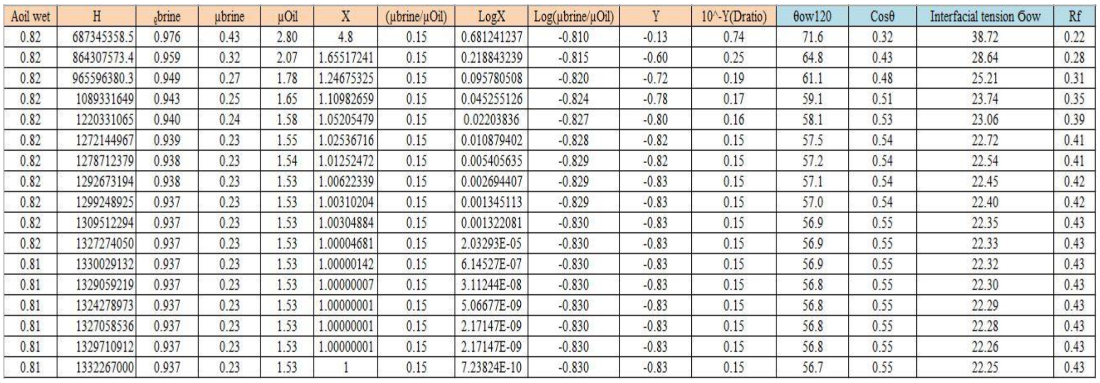
| Time | Rf | Voil | Vp | Vwinj | Vor | Vwi | Swinj | Sor | Mwi | Mor | Mwinj | Moil i | Mmat | Msys | Moil produced |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.5 | 0.22 | 7.21 | 35.721 | 7.21 | 25.29 | 3.215 | 0.20 | 0.71 | 3.295 | 20.18 | 7.39 | 25.65 | 118.3159 | 30.87 | 5.76 |
| 3.5 | 0.28 | 9.08 | 35.721 | 9.08 | 23.43 | 3.215 | 0.25 | 0.66 | 3.295 | 18.70 | 9.30 | 25.65 | 118.3159 | 31.30 | 7.24 |
| 4.3 | 0.31 | 10.15 | 35.721 | 10.15 | 22.36 | 3.215 | 0.28 | 0.63 | 3.295 | 17.84 | 10.40 | 25.65 | 118.3159 | 31.54 | 8.10 |
| 5.9 | 0.35 | 11.45 | 35.721 | 11.45 | 21.05 | 3.215 | 0.32 | 0.59 | 3.295 | 16.80 | 11.74 | 25.65 | 118.3159 | 31.83 | 9.14 |
| 9.4 | 0.39 | 12.84 | 35.721 | 12.84 | 19.67 | 3.215 | 0.36 | 0.55 | 3.295 | 15.70 | 13.16 | 25.65 | 118.3159 | 32.15 | 10.24 |
| 12.1 | 0.41 | 13.39 | 35.721 | 13.39 | 19.12 | 3.215 | 0.37 | 0.54 | 3.295 | 15.25 | 13.73 | 25.65 | 118.3159 | 32.27 | 10.69 |
| 14.9 | 0.41 | 13.47 | 35.721 | 13.47 | 19.04 | 3.215 | 0.38 | 0.53 | 3.295 | 15.19 | 13.80 | 25.65 | 118.3159 | 32.29 | 10.75 |
| 19.9 | 0.42 | 13.62 | 35.721 | 13.62 | 18.88 | 3.215 | 0.38 | 0.53 | 3.295 | 15.07 | 13.96 | 25.65 | 118.3159 | 32.33 | 10.87 |
| 22.4 | 0.42 | 13.70 | 35.721 | 13.70 | 18.80 | 3.215 | 0.38 | 0.53 | 3.295 | 15.01 | 14.04 | 25.65 | 118.3159 | 32.35 | 10.93 |
| 25.7 | 0.43 | 13.82 | 35.721 | 13.82 | 18.69 | 3.215 | 0.39 | 0.52 | 3.295 | 14.91 | 14.16 | 25.65 | 118.3159 | 32.37 | 11.03 |
| 29.1 | 0.43 | 14.01 | 35.721 | 14.01 | 18.49 | 3.215 | 0.39 | 0.52 | 3.295 | 14.76 | 14.36 | 25.65 | 118.3159 | 32.42 | 11.18 |
| 31.7 | 0.43 | 14.05 | 35.721 | 14.05 | 18.45 | 3.215 | 0.39 | 0.52 | 3.295 | 14.73 | 14.40 | 25.65 | 118.3159 | 32.42 | 11.21 |
| 34.4 | 0.43 | 14.05 | 35.721 | 14.05 | 18.46 | 3.215 | 0.39 | 0.52 | 3.295 | 14.73 | 14.40 | 25.65 | 118.3159 | 32.42 | 11.21 |
| 37.8 | 0.43 | 14.01 | 35.721 | 14.01 | 18.50 | 3.215 | 0.39 | 0.52 | 3.295 | 14.76 | 14.36 | 25.65 | 118.3159 | 32.41 | 11.18 |
| 40.4 | 0.43 | 14.05 | 35.721 | 14.05 | 18.46 | 3.215 | 0.39 | 0.52 | 3.295 | 14.73 | 14.40 | 25.65 | 118.3159 | 32.42 | 11.21 |
| 44.6 | 0.43 | 14.08 | 35.721 | 14.08 | 18.42 | 3.215 | 0.39 | 0.52 | 3.295 | 14.70 | 14.44 | 25.65 | 118.3159 | 32.43 | 11.24 |
| 50.6 | 0.43 | 14.12 | 35.721 | 14.12 | 18.39 | 3.215 | 0.40 | 0.51 | 3.295 | 14.67 | 14.47 | 25.65 | 118.3159 | 32.44 | 11.27 |

Table 6.13. Part 2 calculations of Oil A, AN=2, T=120 C°



| Δtavg. | Qmat. | Qwi. | Qoil | Qwinj. | Qoil pro. | (Qwi.+Qoil pro.) | (Qwi.+Qoil pro.)/(Qwinj.) | 1-((Qwi.+Qoil pro.)/(Qwinj.)) | Qoil estimated | Qsys. | ED | Cf | Awet | Aoil wet |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 72.5 | 7720.11 | 798.28 | 3116.89 | 1715.3 | 582.4 | 1380.7 | 0.80 | 0.20 | 334.62 | 1715.274 | 0.22 | 2.52814E-06 | 0.18 | 0.82 |
| 96.25 | 10249.11 | 1059.79 | 3833.21 | 2865.2 | 1099.1 | 2158.9 | 0.75 | 0.25 | 706.28 | 2865.197 | 0.28 | 2.52814E-06 | 0.18 | 0.82 |
| 108.125 | 11513.62 | 1190.55 | 4109.53 | 3598.1 | 1433.5 | 2624.0 | 0.73 | 0.27 | 974.08 | 3598.092 | 0.31 | 2.52814E-06 | 0.18 | 0.82 |
| 114.0625 | 12145.87 | 1255.92 | 4081.79 | 4284.7 | 1733.7 | 2989.6 | 0.70 | 0.30 | 1295.04 | 4284.683 | 0.35 | 2.52814E-06 | 0.18 | 0.82 |
| 117.03125 | 12461.99 | 1288.61 | 3912.51 | 4927.9 | 2008.2 | 3296.8 | 0.67 | 0.33 | 1631.09 | 4927.884 | 0.39 | 2.52814E-06 | 0.18 | 0.82 |
| 118.515625 | 12620.05 | 1304.95 | 3850.68 | 5205.5 | 2128.5 | 3433.5 | 0.66 | 0.34 | 1771.99 | 5205.454 | 0.41 | 2.52814E-06 | 0.18 | 0.82 |
| 119.2578125 | 12699.08 | 1313.13 | 3859.11 | 5268.3 | 2157.8 | 3470.9 | 0.66 | 0.34 | 1797.39 | 5268.315 | 0.41 | 2.52814E-06 | 0.18 | 0.82 |
| 119.6289063 | 12738.60 | 1317.21 | 3839.53 | 5345.7 | 2191.3 | 3508.5 | 0.66 | 0.34 | 1837.18 | 5345.677 | 0.42 | 2.52814E-06 | 0.18 | 0.82 |
| 119.8144531 | 12758.36 | 1319.26 | 3829.66 | 5384.5 | 2208.1 | 3527.4 | 0.66 | 0.34 | 1857.14 | 5384.499 | 0.42 | 2.52814E-06 | 0.18 | 0.82 |
| 119.9971008 | 12777.81 | 1321.27 | 3811.69 | 5438.6 | 2231.2 | 3552.5 | 0.65 | 0.35 | 1886.17 | 5438.638 | 0.43 | 2.52814E-06 | 0.18 | 0.82 |
| 119.9999094 | 12778.11 | 1321.30 | 3771.80 | 5515.9 | 2262.9 | 3584.2 | 0.65 | 0.35 | 1931.70 | 5515.916 | 0.43 | 2.52814E-06 | 0.18 | 0.82 |
| 119.9999943 | 12778.12 | 1321.30 | 3764.12 | 5530.8 | 2269.0 | 3590.3 | 0.65 | 0.35 | 1940.45 | 5530.761 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |
| 119.9999986 | 12778.12 | 1321.30 | 3764.45 | 5530.1 | 2268.7 | 3590.0 | 0.65 | 0.35 | 1940.08 | 5530.122 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |
| 119.9999993 | 12778.12 | 1321.30 | 3773.00 | 5513.6 | 2262.0 | 3583.3 | 0.65 | 0.35 | 1930.34 | 5513.617 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |
| 119.9999996 | 12778.12 | 1321.30 | 3765.24 | 5528.6 | 2268.1 | 3589.4 | 0.65 | 0.35 | 1939.17 | 5528.586 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |
| 119.9999999 | 12778.12 | 1321.30 | 3757.75 | 5543.0 | 2274.0 | 3595.3 | 0.65 | 0.35 | 1947.70 | 5543.044 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |
| 120 | 12778.12 | 1321.30 | 3750.46 | 5557.1 | 2279.8 | 3601.1 | 0.65 | 0.35 | 1956.00 | 5557.118 | 0.43 | 2.52814E-06 | 0.19 | 0.81 |

Table 6.14. Part 3 calculations of Oil A, AN=2, T=120 C°



| Aoil wet | H | ρbrine | μbrine | μOil | X | (μbrine/μOil) | LogX | Log(μbrine/μOil) | Y | 10^-Y(Dratio) | θow120 | Cosθ | Interfacial tension Ϭow | Rf |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.82 | 687345358.5 | 0.976 | 0.43 | 2.80 | 4.8 | 0.15 | 0.681241237 | -0.810 | -0.13 | 0.74 | 71.6 | 0.32 | 38.72 | 0.22 |
| 0.82 | 864307573.4 | 0.959 | 0.32 | 2.07 | 1.65517241 | 0.15 | 0.218843239 | -0.815 | -0.60 | 0.25 | 64.8 | 0.43 | 28.64 | 0.28 |
| 0.82 | 965596380.3 | 0.949 | 0.27 | 1.78 | 1.24675325 | 0.15 | 0.095780508 | -0.820 | -0.72 | 0.19 | 61.1 | 0.48 | 25.21 | 0.31 |
| 0.82 | 1089331649 | 0.943 | 0.25 | 1.65 | 1.10982659 | 0.15 | 0.045255126 | -0.824 | -0.78 | 0.17 | 59.1 | 0.51 | 23.74 | 0.35 |
| 0.82 | 1220331065 | 0.940 | 0.24 | 1.58 | 1.05205479 | 0.15 | 0.02203836 | -0.827 | -0.80 | 0.16 | 58.1 | 0.53 | 23.06 | 0.39 |
| 0.82 | 1272144967 | 0.939 | 0.23 | 1.55 | 1.02536716 | 0.15 | 0.010879402 | -0.828 | -0.82 | 0.15 | 57.5 | 0.54 | 22.72 | 0.41 |
| 0.82 | 1278712379 | 0.938 | 0.23 | 1.54 | 1.01252472 | 0.15 | 0.005405635 | -0.829 | -0.82 | 0.15 | 57.2 | 0.54 | 22.54 | 0.41 |
| 0.82 | 1292673194 | 0.938 | 0.23 | 1.53 | 1.00622339 | 0.15 | 0.002694407 | -0.829 | -0.83 | 0.15 | 57.1 | 0.54 | 22.45 | 0.42 |
| 0.82 | 1299248925 | 0.937 | 0.23 | 1.53 | 1.00310204 | 0.15 | 0.001345113 | -0.829 | -0.83 | 0.15 | 57.0 | 0.54 | 22.40 | 0.42 |
| 0.82 | 1309512294 | 0.937 | 0.23 | 1.53 | 1.00304884 | 0.15 | 0.001322081 | -0.830 | -0.83 | 0.15 | 56.9 | 0.55 | 22.35 | 0.43 |
| 0.82 | 1327274050 | 0.937 | 0.23 | 1.53 | 1.00004681 | 0.15 | 2.03293E-05 | -0.830 | -0.83 | 0.15 | 56.9 | 0.55 | 22.33 | 0.43 |
| 0.81 | 1330029132 | 0.937 | 0.23 | 1.53 | 1.00000142 | 0.15 | 6.14527E-07 | -0.830 | -0.83 | 0.15 | 56.9 | 0.55 | 22.32 | 0.43 |
| 0.81 | 1329059219 | 0.937 | 0.23 | 1.53 | 1.00000007 | 0.15 | 3.11244E-08 | -0.830 | -0.83 | 0.15 | 56.8 | 0.55 | 22.30 | 0.43 |
| 0.81 | 1324278973 | 0.937 | 0.23 | 1.53 | 1.00000001 | 0.15 | 5.06677E-09 | -0.830 | -0.83 | 0.15 | 56.8 | 0.55 | 22.29 | 0.43 |
| 0.81 | 1327058536 | 0.937 | 0.23 | 1.53 | 1.00000001 | 0.15 | 2.17147E-09 | -0.830 | -0.83 | 0.15 | 56.8 | 0.55 | 22.28 | 0.43 |
| 0.81 | 1329710912 | 0.937 | 0.23 | 1.53 | 1.00000001 | 0.15 | 2.17147E-09 | -0.830 | -0.83 | 0.15 | 56.8 | 0.55 | 22.26 | 0.43 |
| 0.81 | 1332267000 | 0.937 | 0.23 | 1.53 | 1 | 0.15 | 7.23824E-10 | -0.830 | -0.83 | 0.15 | 56.7 | 0.55 | 22.25 | 0.43 |

Finally, the contact angles still decreasing to a value of 56° of Oil A-chalk system when the temperature still increasing. In addition to the contact angles decreasing, the interfacial tensions decrease to a value of 22.2 dyne/cm as well. In conclusion, the general formula has successfully matched the experimental results of getting water-wet condition using smart brine-chalk system in a way close to idealism.

# 7.THE CONCLUSION AND RECOMMENDATIONS

By using the general formula, the aim of this work has precisely matched the experimental measurements in regarding of getting a water-wet condition on water flooding test of chalk. The integration of the physical and the chemical concepts with the thermal comprehension of the gradual changes in the entered/departed quantities within the control volume have given the motivation to complete this work to understand the interacting relationships between the candidate parameters logically through finding an approach that is possible to contain a conceptual convergence point. The following figures have drawn using Excel to show the responses of the major results of wettability alteration on chalk using the proposed general formula mentioned formerly:

From Figure 7.1, it can easily observe that when the average temperature increased gradually as in (Table 6.4 pg 56) inside the system, the contact angles continue to decrease. At the final proposed temperature of the test which is 70 C°, the system reached to its magnitude of the conservative heat energy, and the contact angle stabilized at a value of 58°.

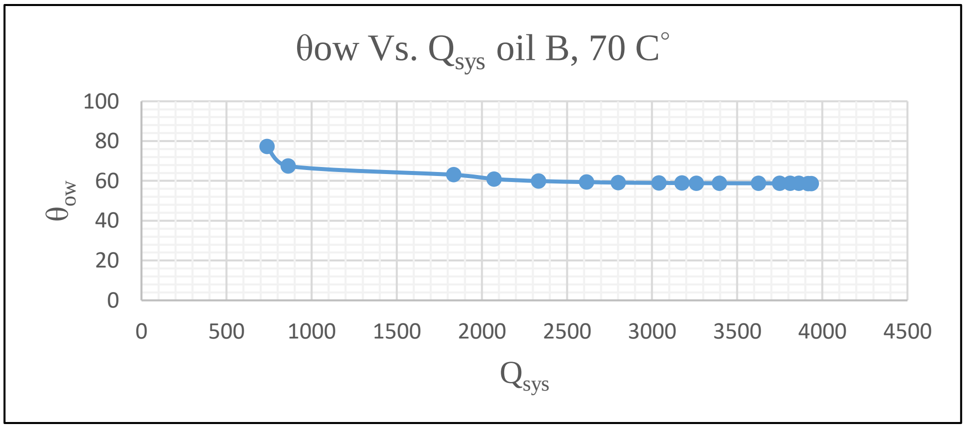


Figure 7.1. Contact Angle vs. System heat energy, Oil B, 70 C°

From Figure 7.2 below, the increase of displacement sweep efficiency due to the reduction of remaining oil saturation during the imbibition time of the test leads to decrease the contact angle. When the system reached to its highest oil recovery in which the remaining oil saturation will be at the lowerest value, the contact angle reached to the combined value of 58°at the end of the imbibition time regardless the rate of oil produced.

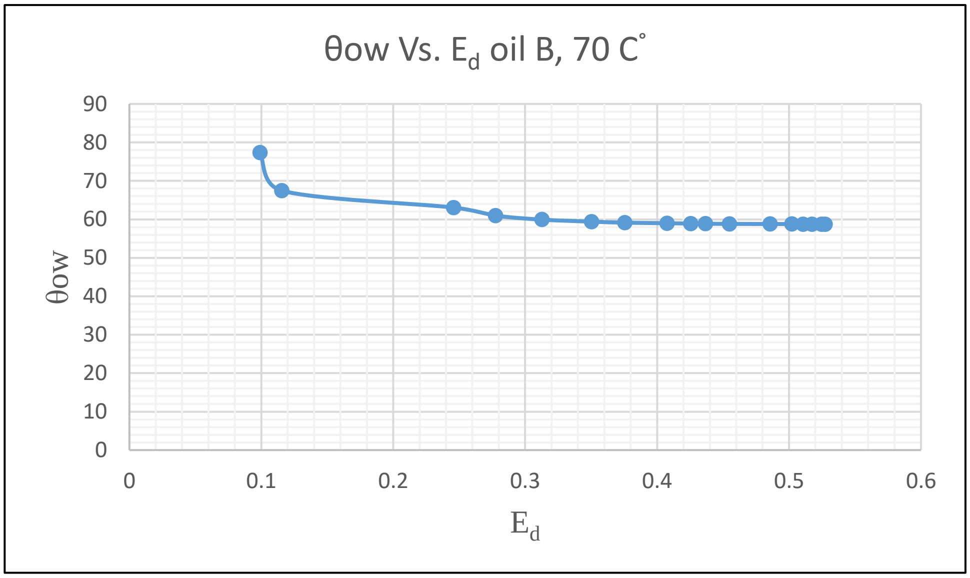


Figure 7.2. Contact Angle vs. $E_d$

Both Figures 7.1 and 7.2 show the same response which means the continuous heat flow of energy is in the same path of the decreasing of the oil remaining saturation or in another word; it is on the same route with macroscopic displacement tendency.

The diffusivity ratio $D_{ratio}$ refers to the diffusion of oil to the diffusion of brine. In Figure 7.3 below, when the diffusion ratio decreases the contact angle decrease as well. The fact behind that behavior is when the diffusivity ratio reduction means the dissemination of oil onto the rock surface is less than the diffusion of brine. In another word, the higher the diffusion of brine compared to the oil diffusion the larger reduction of contact angle and then the bigger chance to get water wet faster. With temperature increasing of the system, the oil and brine viscosities will decrease gradually but, the rate of reduction of oil viscosity is higher than the rate of reduction of brine viscosity. (Table 6.5 Pg. 56), shows the brine viscosity to oil viscosity ratio. This ratio will continue to increase as the temperature will increase which means that the denominator (oil viscosity) will reduce faster the numerator (brine viscosity).

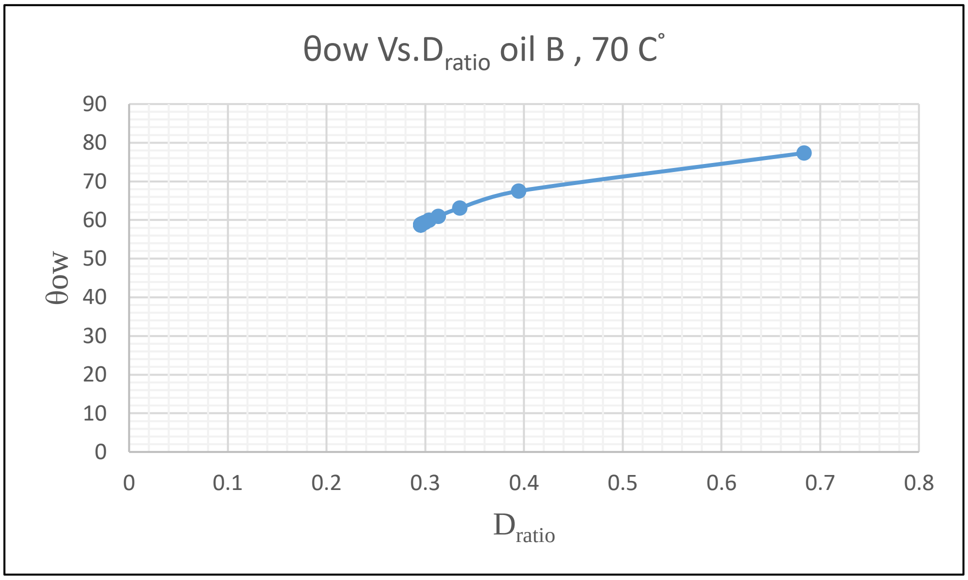


Figure 7.3. θow vs. $D_{ratio}$ oil B, 70 C°

Figure 7.4, shows the increase of viscosity ratio will lead to minimizing the possibility of the affinity of the diffused fluids towards the rock surface. Increasing viscosity ratio will result in lower the D ratio which means will lower the diffusion of oil compared to the diffusion of brine. The presence of low viscosity oil and low diffusion ratio of oil will enhance the sweep efficiency of brine to displace more oil and to increase the water wet area sites on the chalk surface chemically.

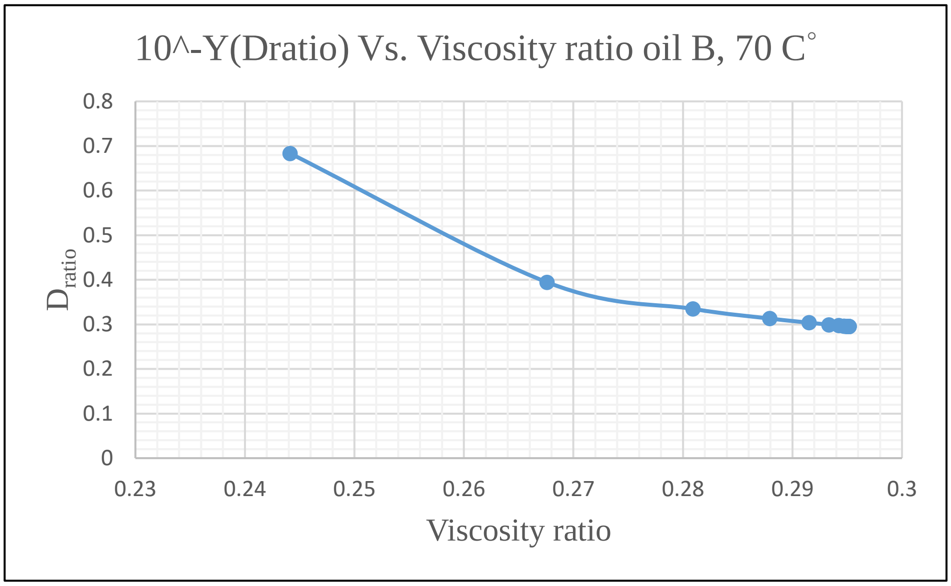


Figure 7.4. $D_{ratio}$ vs. $\mu_{ratio}$, oil B, 70 C$^{\circ}$

Figure 7.5 below, shows the precise behavior of brine density reduction with increasing the average system temperature. The brine density will be constant at the equilibrium temperature 70 C$^{\circ}$.

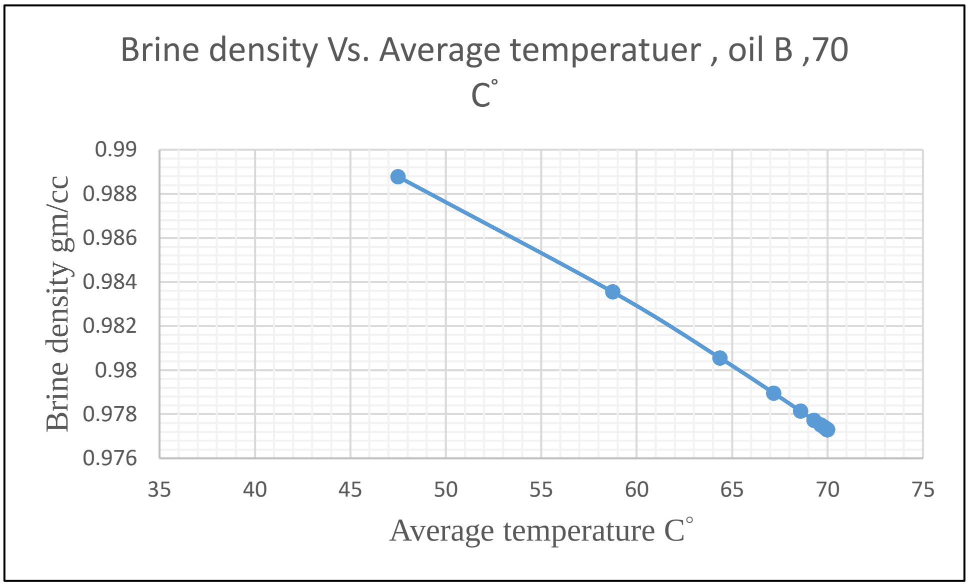


Figure 7.5. Brine density vs. Avg. Temperature oil B, 70 C°

In Figure 7.6 below, the increase in temperature will lead to reducing the brine density and then enhance the displacement efficiency. The best improve of displacement efficiency happens at the equilibrium temperature of the system specifically at $E_d$ from 0.3 up to 0.5 at which the brine reached to its lower value of 0.977 gm/cc.

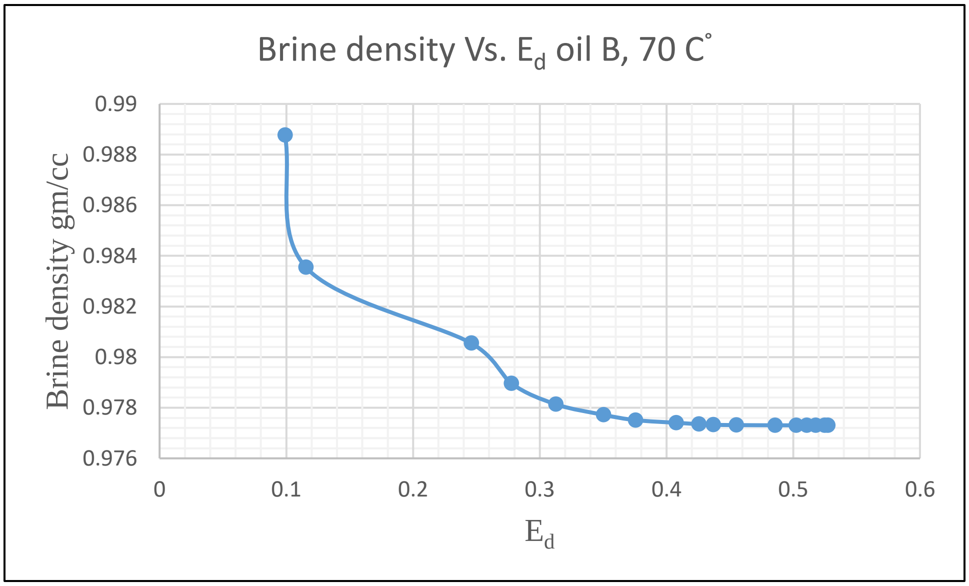


Figure 7.6. Brine density vs. $E_d$, oil B, 70 C°

From Figure 7.7 below, the best displacement efficiency happens from the range 0.3 up to 0.5 when the oil viscosity has reduced from 2.5 cp to its applicable lowerest value of 1.5cp.

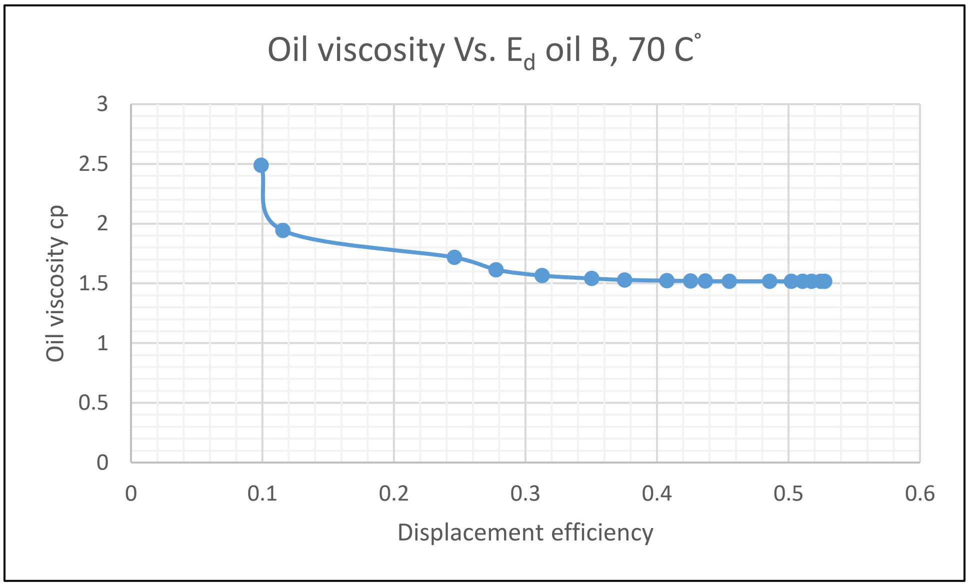


Figure 7.7. Oil viscosity vs. $E_d$, oil B, 70 C°

From the Figure 7.8 below, it is easy to know that when the temperature will increase the viscosity ratio will increase as well; the physical meaning of this behavior that the decreasing rate in oil viscosity is faster the declining rate of brine viscosity at the same ambient temperature because of the differences between the brine consistency properties and that one of oil.

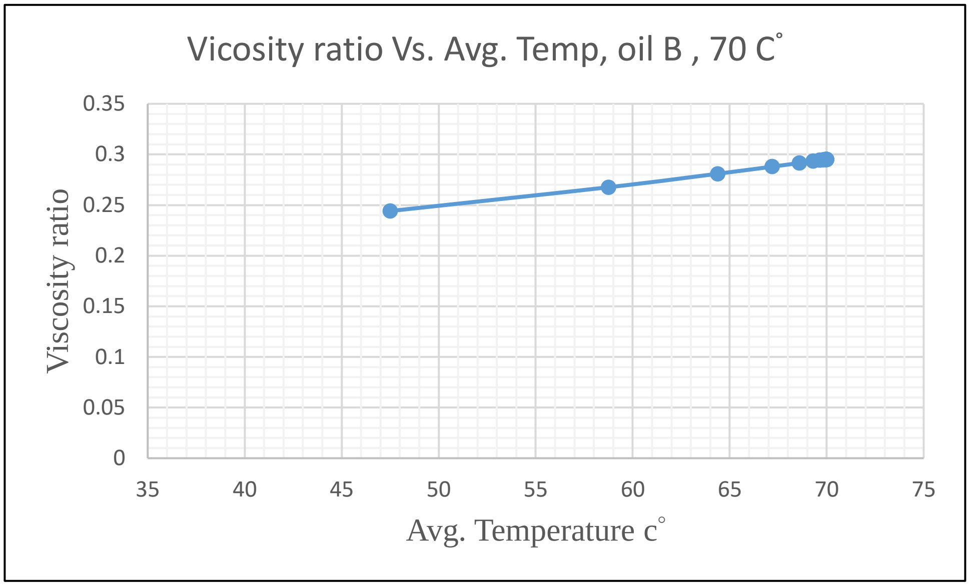


Figure 7.8. Viscosity ratio vs. Avg. Temperature, oil B, 70 C°

In Figure 7.9 below, the system has reached its peak oil recovery at the final ambient temperature and regardless the increasing of oil rate, the interfacial tension of the system still at fixed value of 23 dyne/cm and doesn't improve since it is a function of the temperature which has reached to its final value of 70 C°.

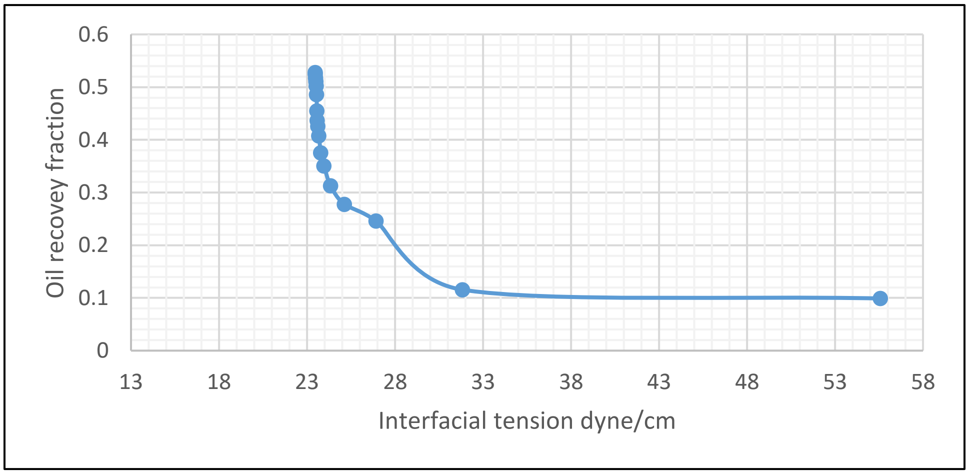


Figure 7.9. Interfacial tension vs. Oil recovery oil B, 70 C°

Oil B at 90 C°, oil A at 100 C°and 120 C° show the same behavior as in oil B,70 C°as in the following figures:

From Figure 7.10 below, it can easily observe that when the average temperature increased gradually as in (Table 6.7 pg 57) inside the system, the contact angles continue to decrease. At the final proposed temperature of the test which is 90 C°, the system reached to its magnitude of the conservative heat energy, and the contact angle stabilized at a value of 55°.

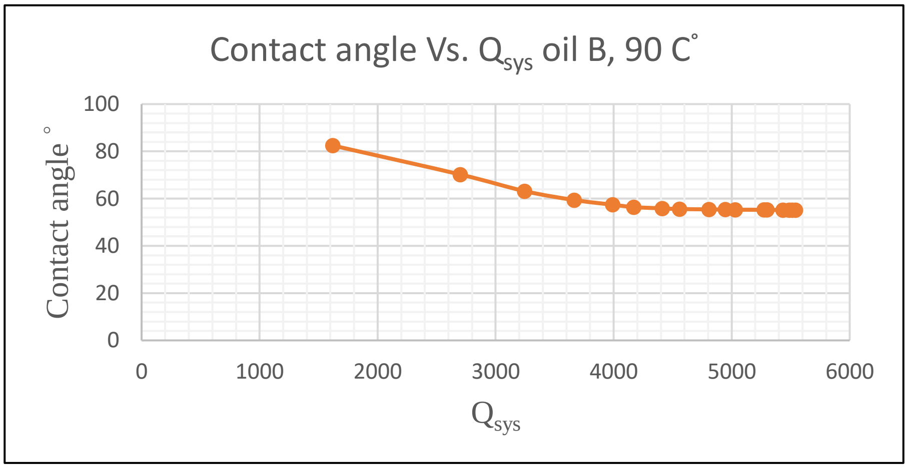


Figure 7.10. Contact Angle vs. The system heat, oil B, 90 C°

From Figure 7.11 below, the increase of displacement sweep efficiency due to the reduction of remaining oil saturation during the imbibition time of the test leads to decrease the contact angle. When the system reached to its highest oil recovery in which the remaining oil saturation will be at the lowerest value, the contact angle reached to the combined value of 55°at the end of the imbibition time regardless the rate of oil produced.

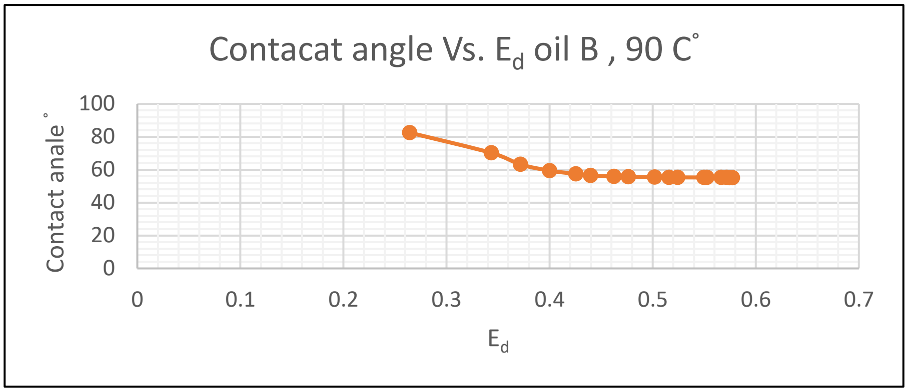


Figure 7.11. Contact Angle vs. $E_d$, oil B, 90 C$^{\circ}$.

Figure 7.12 below, shows the precise behavior of brine density reduction with increasing the average system temperature. The brine density will be constant at the equilibrium temperature 90 C$^{\circ}$.

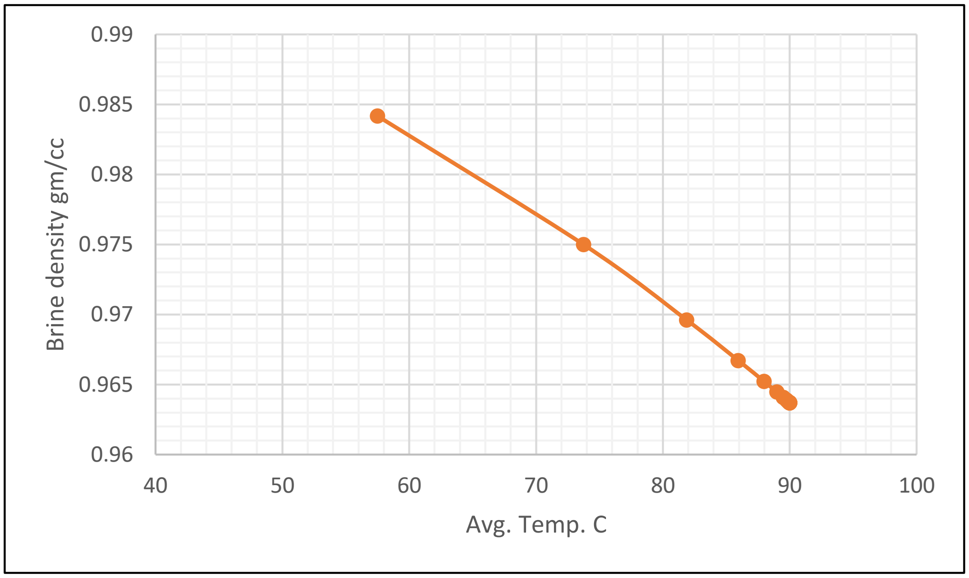


Figure 7.12. Brine density vs. Avg. Temp. , oil B, 90 C$^{\circ}$

In Figure 7.13 below, the increase in temperature will lead to reducing the brine density and then enhance the displacement efficiency. The best improve of displacement efficiency happens at the equilibrium temperature of the system specifically at $E_d$ from 0.49 up to 0.55 at which the brine reached to its lower value of 0.964 gm/cc

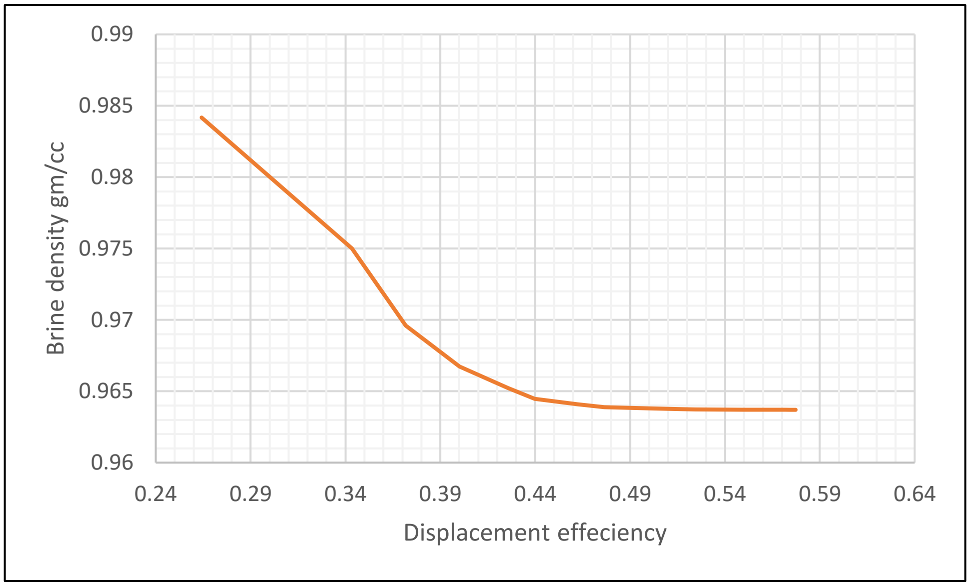


Figure 7.13. Brine density vs. Disp. Eff. , oil B, 90 C°.

Figure 7.14, shows the increase of viscosity ratio will lead to minimizing the possibility of the affinity of the diffused fluids towards the rock surface. Increasing viscosity ratio will result in lower the D ratio which means will lower the diffusion of oil compared to the diffusion of brine. The presence of low viscosity oil and low diffusion ratio of oil will enhance the sweep efficiency of brine to displace more oil and to increase the water wet area sites on the chalk surface chemically.

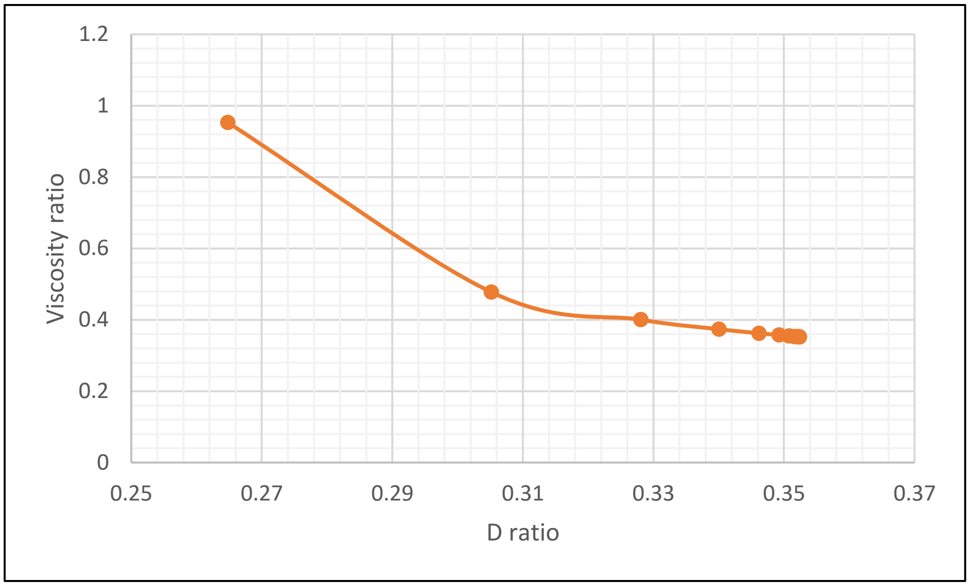


Figure 7.14. Viscosity ratio vs. D ratio. Oil B, 90 C°

Figure 7.15 below, when the diffusion ratio decreases the contact angle decrease as well. The fact behind that behavior is when the diffusivity ratio reduction means the dissemination of oil onto the rock surface is less than the diffusion of brine. In another word, the higher the diffusion of brine compared to the oil diffusion the larger reduction of contact angle and then the bigger chance to get water wet faster. With temperature increasing of the system, the oil and brine viscosities will decrease gradually but, the rate of reduction of oil viscosity is higher than the rate of reduction of brine viscosity. (Table 6.8 Pg. 58), shows the brine viscosity to oil viscosity ratio. This ratio will continue to increase as the temperature will increase which means that the denominator (oil viscosity) will reduce faster the numerator (brine viscosity).

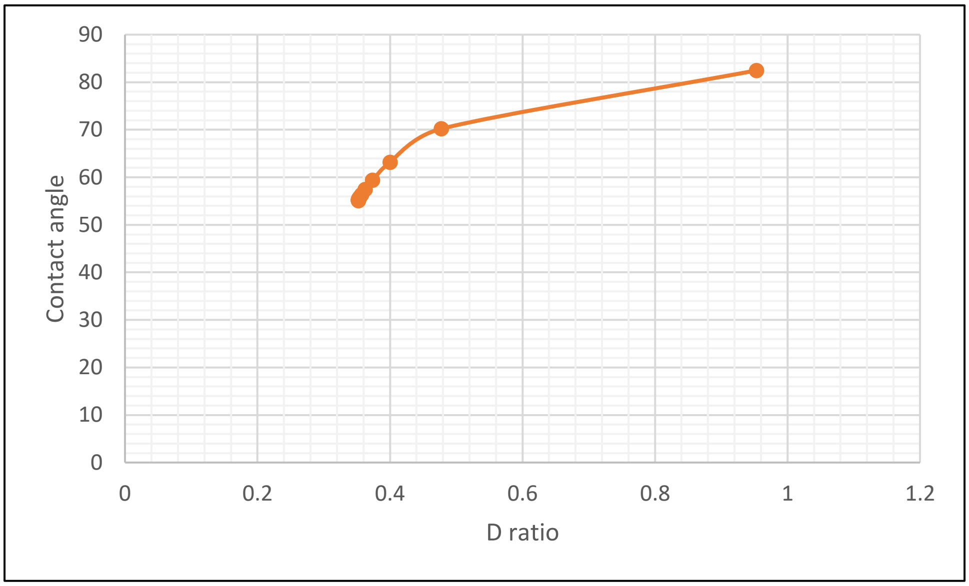


Figure 7.15. Contact Angle vs. D ratio, oil B, 90 C°

From Figure 7.16 below, it can see easily that when the average temperature sill increasing the $D_{ratio}$ decrease which means the diffusion of oil less than the diffusion of brine for this reason piston like displacement for oil by brine lead to enhanced the oil recovery at 90 C°.

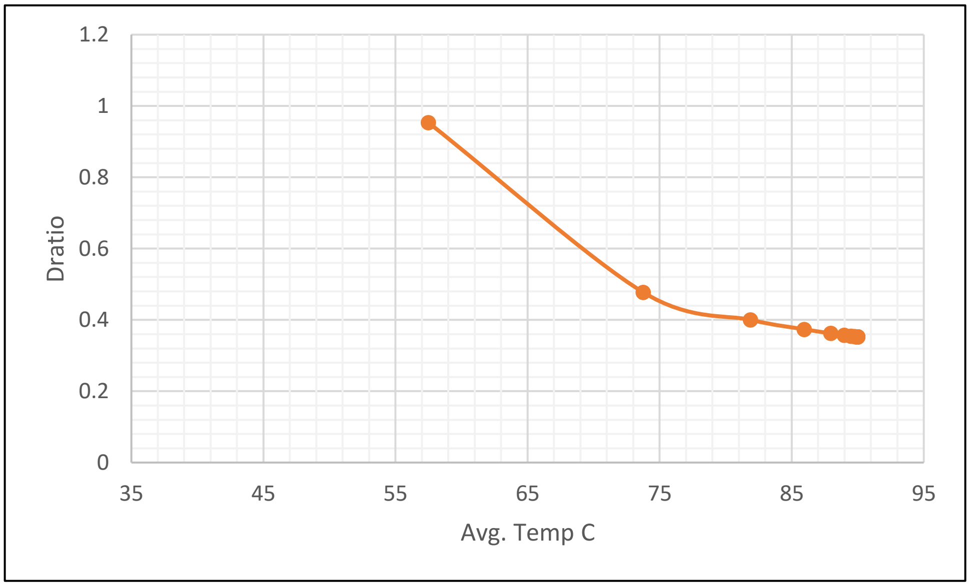


Figure 7.16. Dratio vs. Avg. Temp. Oil B, 90 C°

In Figure 7.17 below, the system has reached its peak oil recovery at the final ambient temperature and regardless the increasing of oil rate, the interfacial tension of the system still at fixed value of 21 dyne/cm and doesn’t improve since it is a function of the temperature which has reached to its final value of 90 C°.

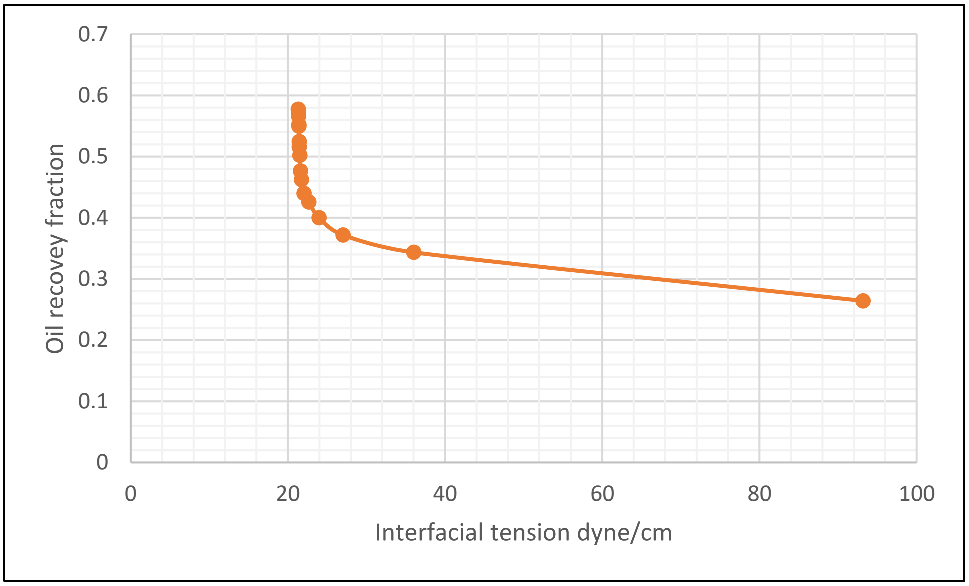


Figure 7.17. Oil Recovery vs. Interfacial tension dyne/cm at 90 C°

From Figure 7.18 below, it can easily observe that when the average temperature increased gradually as in (Table 6.10 pg 59) inside the system, the contact angles continue to decrease. At the final proposed temperature of the test which is 100 C°, the system reached to its magnitude of the conservative heat energy, and the contact angle stabilized at a value of 57°.

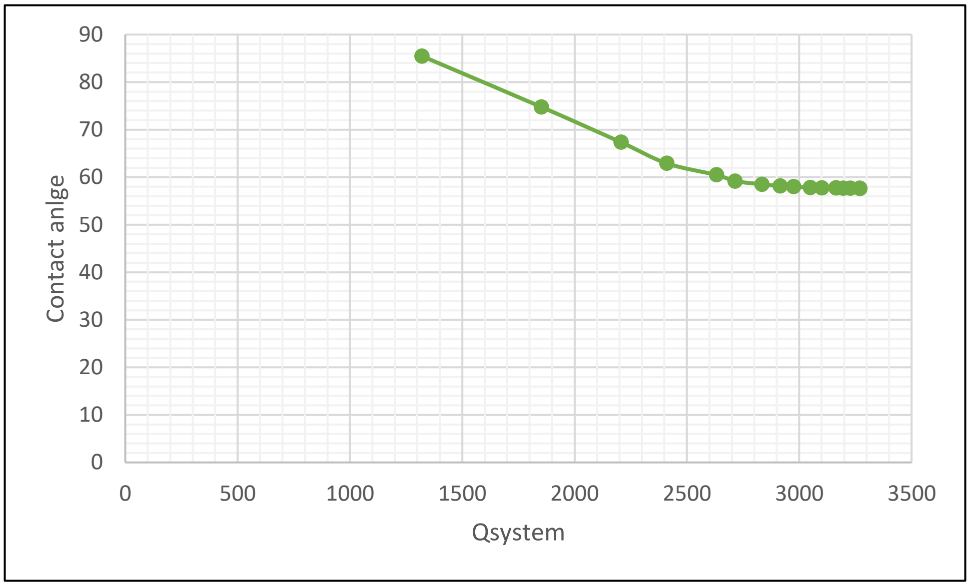


Figure 7.18. Contact Angle vs. Q system, oil A, 100 C°

From Figure 7.19 below, the increase of displacement sweep efficiency due to the reduction of remaining oil saturation during the imbibition time of the test leads to decrease the contact angle. When the system reached to its highest oil recovery in which the remaining oil saturation will be at the lowerest value, the contact angle reached to the combined value of 57°at the end of the imbibition time regardless the rate of oil produced.

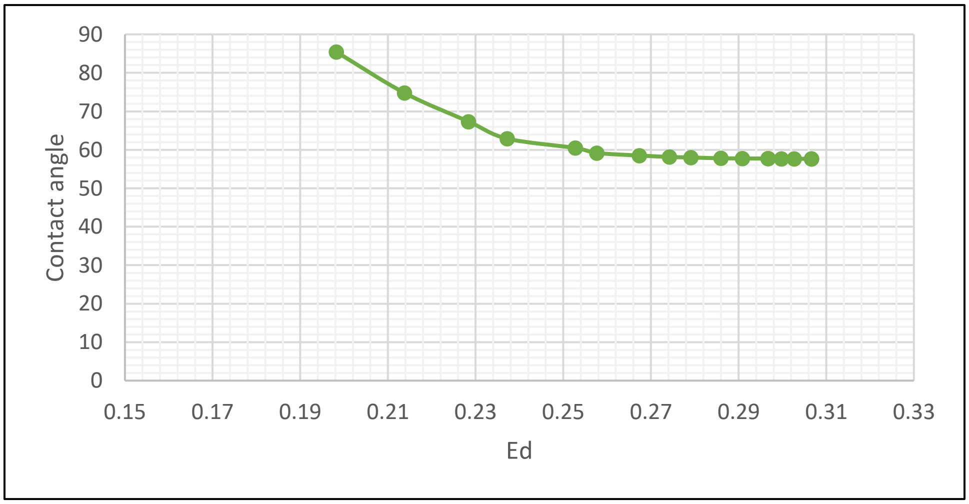


Figure 7.19. Contact Angle vs. Ed, oil A, 100 C°

Figure 7.20 below, shows the precise behavior of brine density reduction with increasing the average system temperature. The brine density will be constant at the equilibrium temperature 100 C°.

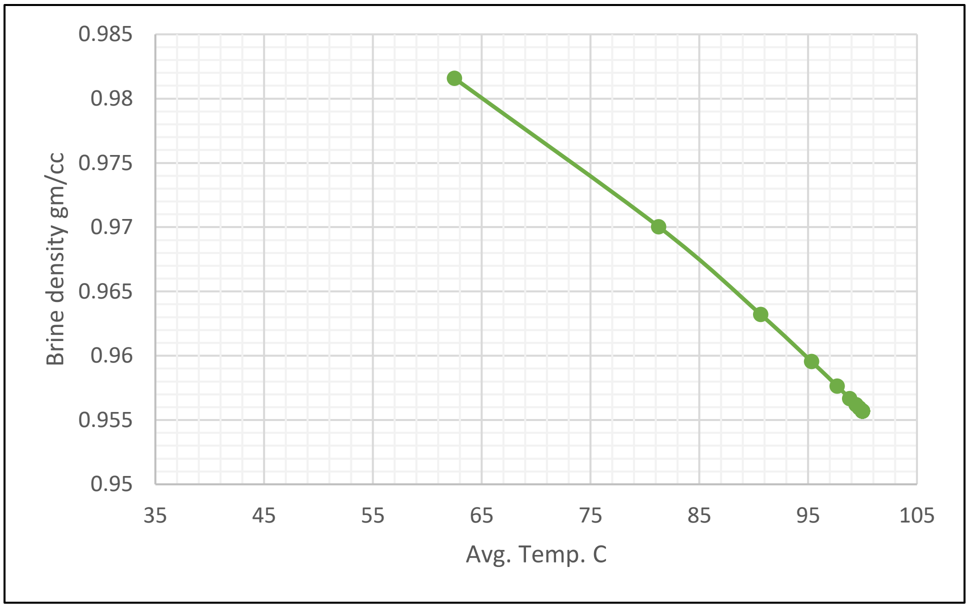


Figure 7.20. Brine density vs. Avg. Temp. , Oil A, 100 C°

In Figure 7.21 below, when the average temperature exceeds 90 C°, the viscosity ratio has decreased, and the reason is that beyond 90 C° the $Ca^{+2}$ affinity will increase compared to the affinity of sulfate and the recovery still improved but in less degree compared to Oil B at 70 C° and 90 C°.

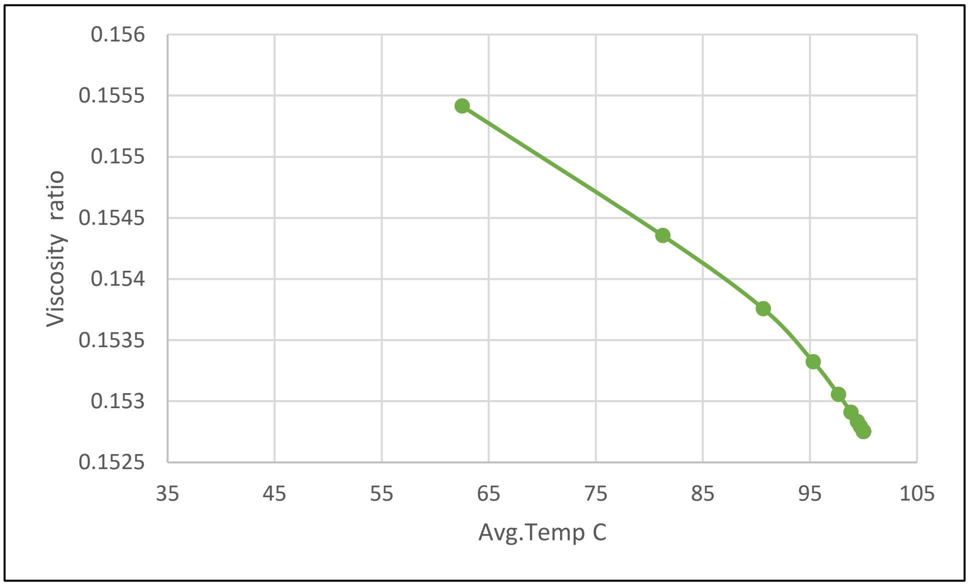


Figure 7.21. Viscosity ratio vs. Avg. Temp. , oil A, 100 C°

In Figure 7.22 below, the diffusivity ratio will be affected by the new active $Ca^{+2}$ affinity onto the chalk surface. The presence of $Ca^{+2}$ besides sulfate will obstacle the sulfate effectiveness to be the preferable solute of wetting.

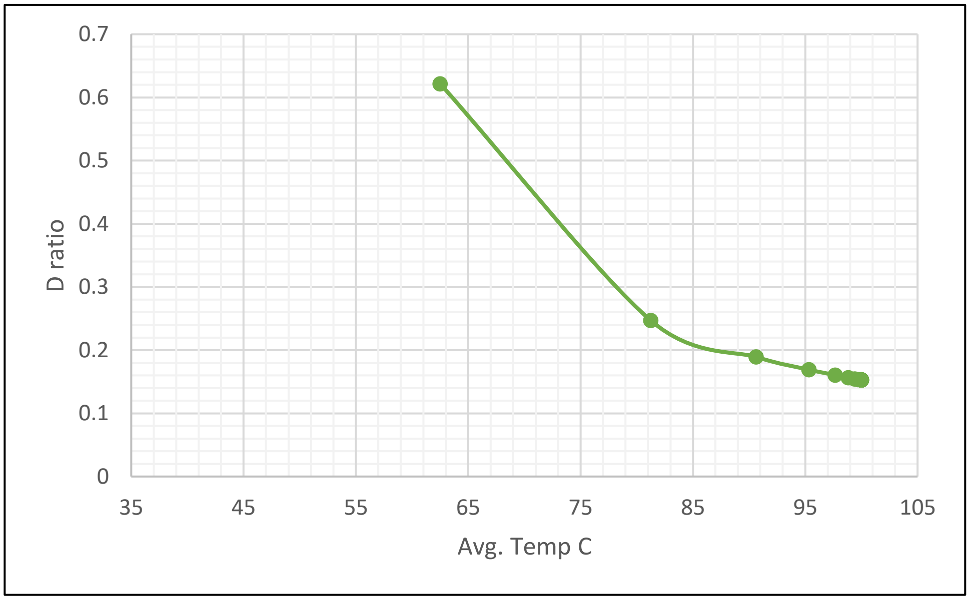


Figure 7.22. D ratio vs. Avg. Temp. , Oil A, 100 C°

Figure 7.23 below, when the diffusion ratio decreases the contact angle decrease as well. The fact behind that behavior is when the diffusivity ratio reduction means the dissemination of oil onto the rock surface is less than the diffusion of brine. In another word, the higher the diffusion of brine compared to the oil diffusion the larger reduction of contact angle and then the bigger chance to get water wet faster. With temperature increasing of the system, the oil and brine viscosities will decrease gradually but, the rate of reduction of oil viscosity is higher than the rate of reduction of brine viscosity. (Table 6.11 Pg. 60), shows the brine viscosity to oil viscosity ratio. This ratio will continue to increase as the temperature will increase which means that the denominator (oil viscosity) will reduce faster the numerator (brine viscosity).

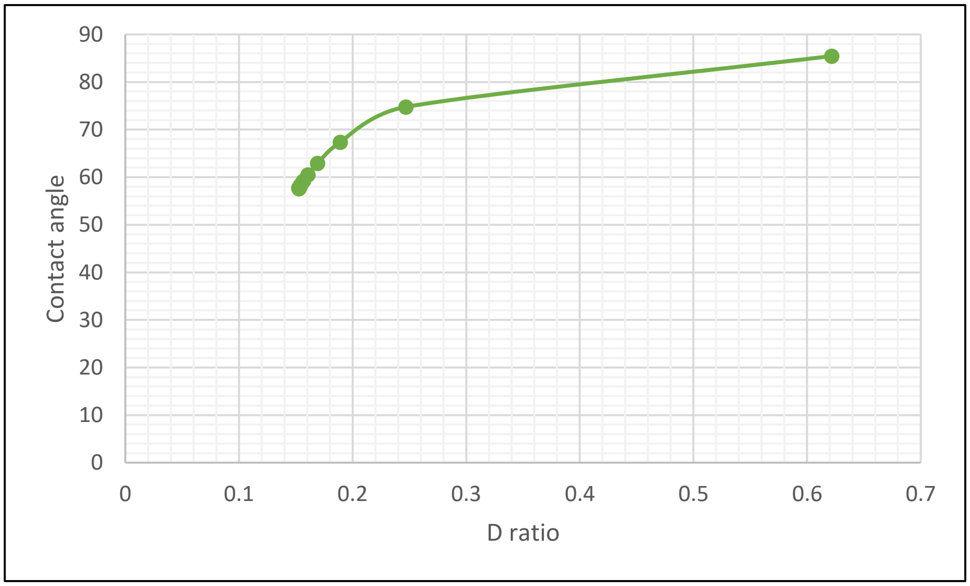


Figure 7.23. Contact Angle vs. D ratio, oil A, 100 C°

Figure 7.24 below, shows that the possibility of oil fingering is great since the oil A has a viscosity (3.38 cp) higher than in oil B (2.6 cp) in addition to the high temperature above 90 C° will encourage $Ca^{+2}$ to diffuse more and obstacle the sulfate diffusion for this reason oil will diffuse more onto the rock surface and will lead to increase the D ratio. The another reason is the possibility of Anhydrite mineral deposition which is as mentioned before an exothermic reaction. The increasing of temperature will reverse the Anhydrite reaction to endothermic which means less aqueous sulfate inside the porous medium in addition to the affinity of $Ca^{+2}$ that has improved after raising the core temperature above 90 C°.

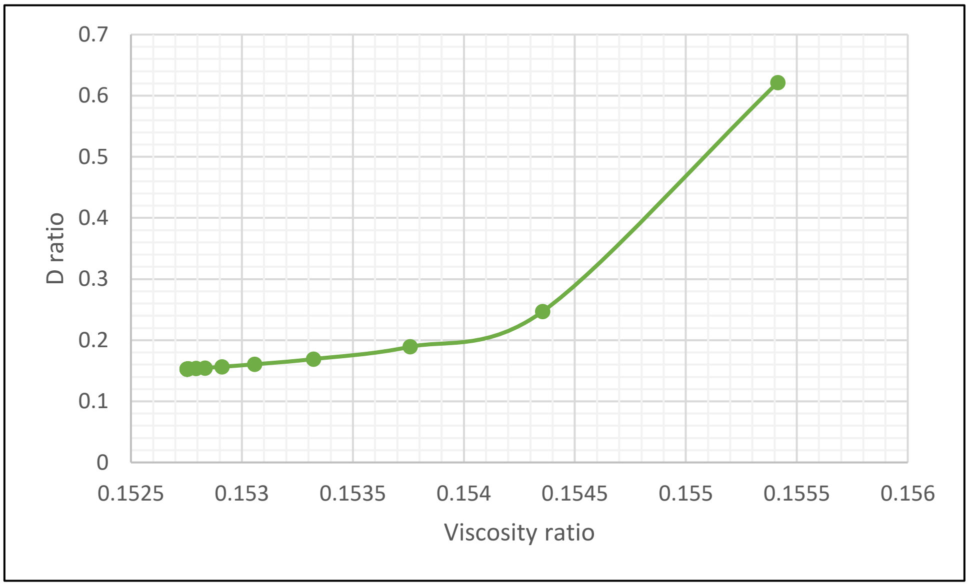


Figure 7.24. D ratio vs. Viscosity ratio, oil A, 100 C°

In Figure 7.25 below, the system has reached its peak oil recovery at the final ambient temperature and regardless the increasing of oil rate, the interfacial tension of the system still at fixed value of 22 dyne/cm and doesn’t improve since it is a function of the temperature which has reached to its final value of 100 C°.

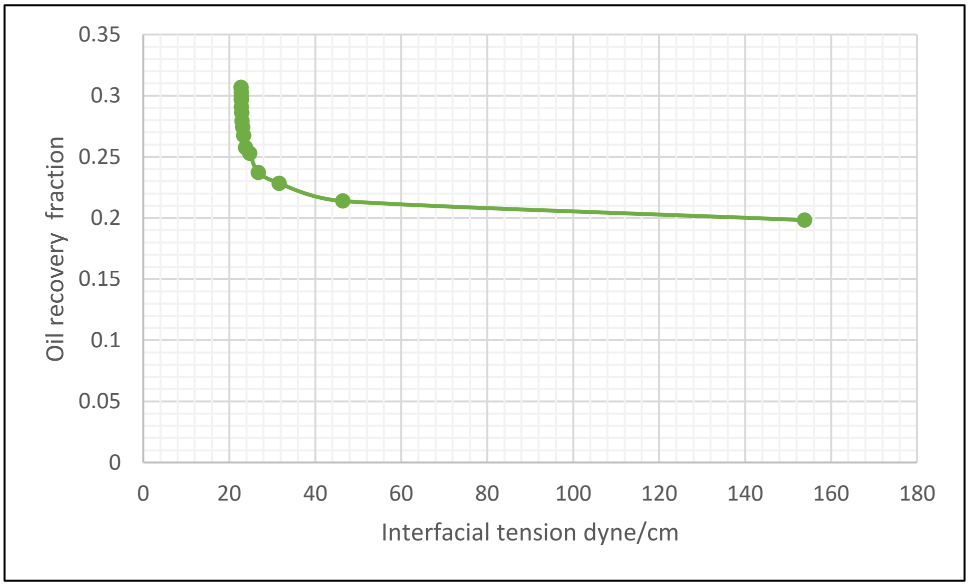


Figure 7.25. Oil recovery vs. Interfacial tension oil A, 100 C°

From Figure 7.26 below, it can easily observe that when the average temperature increased gradually as in (Table 6.13 pg 60) inside the system, the contact angles continue to decrease. At the final proposed temperature of the test which is 120 C°, the system reached to its magnitude of the conservative heat energy, and the contact angle stabilized at a value of 56°.

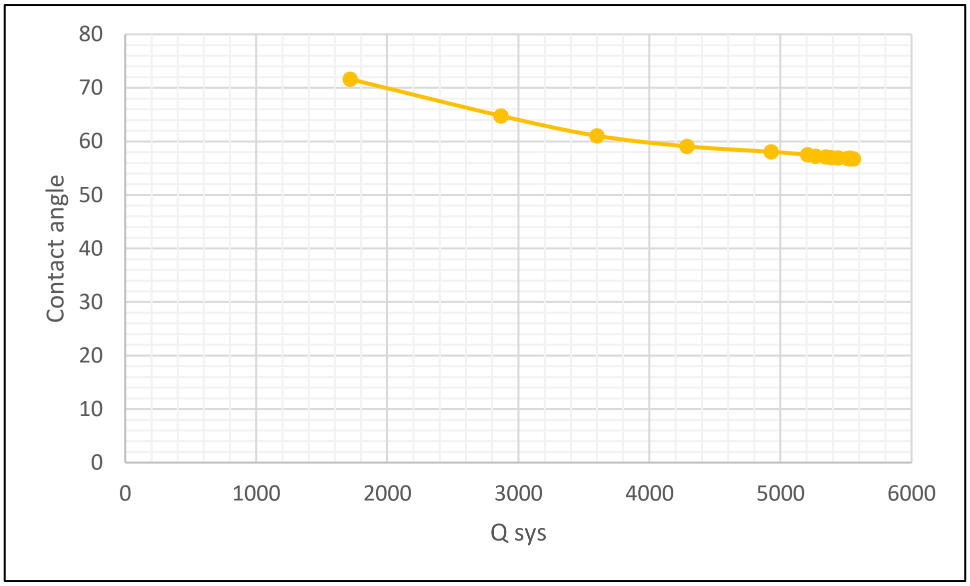


Figure 7.26. Contact Angle vs. Qsys, oil A, 120 C°

From Figure 7.27 below, the increase of displacement sweep efficiency due to the reduction of remaining oil saturation during the imbibition time of the test leads to decrease the contact angle. When the system reached to its highest oil recovery in which the remaining oil saturation will be at the lowerest value, the contact angle reached to the combined value of 56°at the end of the imbibition time regardless the rate of oil produced.

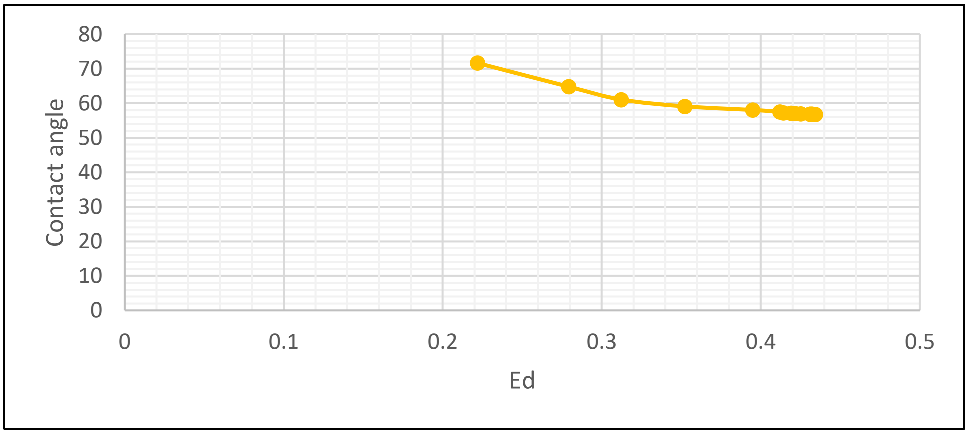


Figure 7.27. Contact Angle vs. Ed oil A, 120 C°

In Figure 7.28 below, the increase in temperature will lead to reducing the brine density and then enhance the displacement efficiency. The best improve of displacement efficiency happens at the equilibrium temperature of the system specifically at $E_d$ from 0.41 up to 0.45 at which the brine reached to its lower value of 0.937 gm/cc

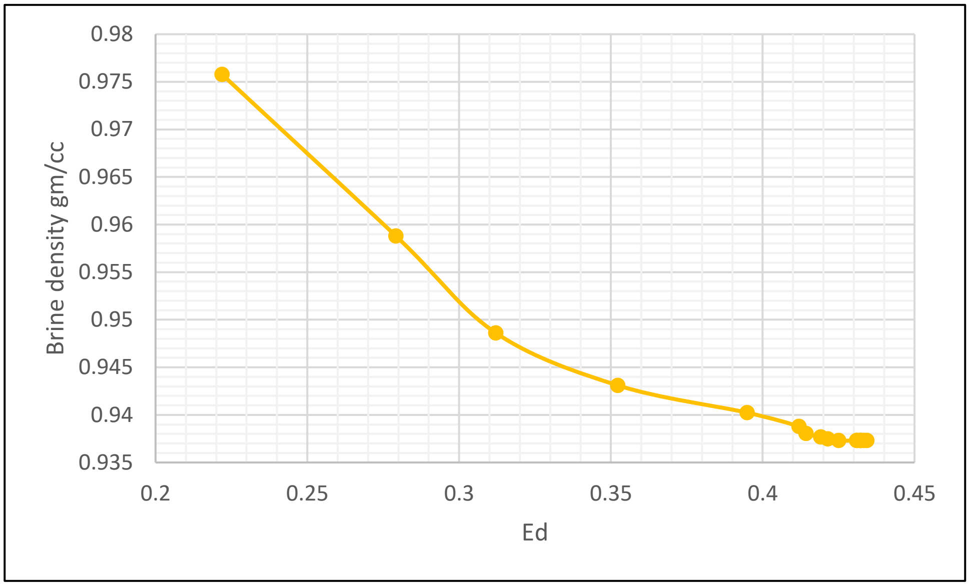


Figure 7.28. Brine density vs. Ed oil A, 120 C°

Figure 7.29 below, shows that the possibility of oil fingering is great since the oil A has a viscosity (3.38 cp) higher than in oil B (2.6 cp) in addition to the high temperature above 90 C° will encourage $Ca^{+2}$ to diffuse more and obstacle the sulfate diffusion for this reason oil will diffuse more onto the rock surface and will lead to increase the D ratio. The another reason is the possibility of Anhydrite mineral deposition which is as mentioned before an exothermic reaction. The increasing of temperature will reverse the Anhydrite reaction to endothermic which means less aqueous sulfate inside the porous medium in addition to the affinity of $Ca^{+2}$ that has improved after raising the core temperature above 90 C°.

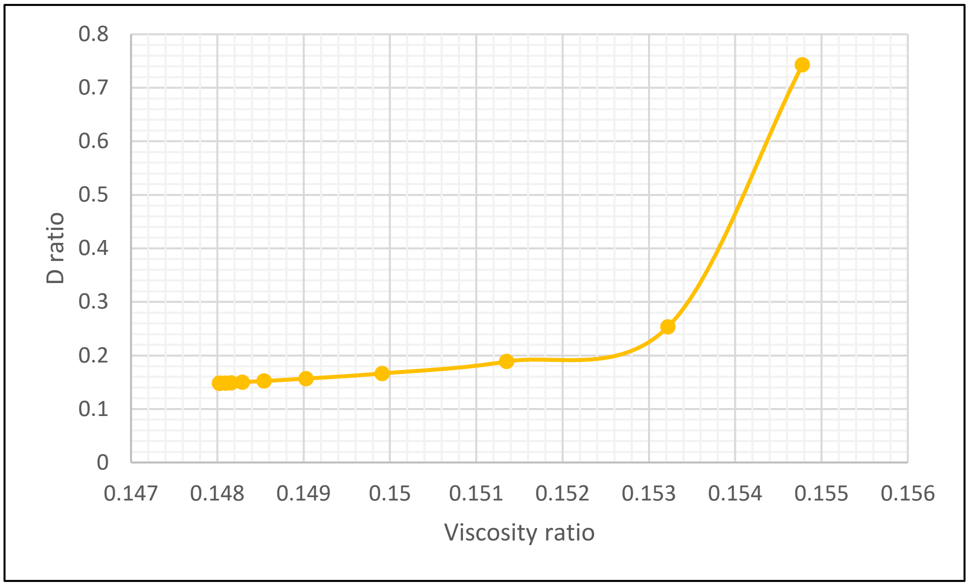


Figure 7.29. Dratio vs. Viscosity ratio, oil A, 120 C°

Figure 7.30 below, shows the clear behavior of crude oil A. As the temperature still rising the viscosity ratio will decrease but since above 90 C° the affinity of sulfate will be lower due to the fact of existing new determining ion will be activated. Based on Le Chatelier principle in reversal reactions the increasing of average temperature gradually inside the porous medium will reinforce the chalk thermal cracking reaction mention below to stay in an Endothermic forward reaction which means more $Ca^{+2}$ will present in the solution. On the other hand, the existing of Anhydrite as undesirable mineral which is Exothermic reaction will lead to reduce the amount of aqueous sulfate in the solution which means the reaction will be reversed to backward direction when the temperature still increasing in a way that lead to deposit Anhydrite in front of the path of flow. The existing of deposition means lowering the possibility of sulfate to diffuse and enhance the oil recovery.

$\mathrm{CaCo_3} \leftrightarrow \mathrm{Ca^{+2}} + \mathrm{Co_3}^{-2}$ is Endothermic reaction

$\mathrm{CaSo_4} \leftrightarrow \mathrm{Ca^{+2}} + \mathrm{So_4}^{-2}$ is Exothermic reaction

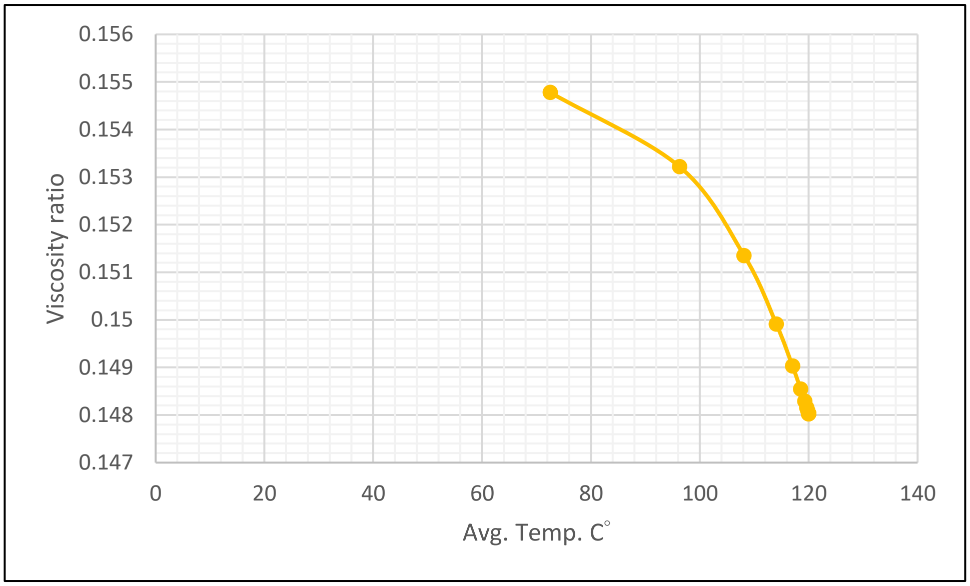


Figure 7.30. Viscosity ratio vs. Avg. Temp. , oil A, 120 C°

In conclusion, the general formula proposed has calculated the contact angles from neutral wet to water wet in the presence of sulfate with two types of crude oil, oil A, and B and has concluded that:

1. There is a chemical, and physical connection of the candidate relationships used with the stability of the reactions – thermal conditions happening inside the porous medium.
2. The general formula created by Buckingham pi theorem and by trial and error attempts to control the handle of dominant conceptual parameters has succeeded to give an idea about the way of wettability alteration mechanism going on.

3. Sulfate is the best determining ion in the ranges of 70 C°, 90 C°due to the smooth interpretations obtained from figures to describe the wettability alteration by using the general formula.
4. The general formula is valid for ranges 100 C°and 120 C°and has successfully diagnosed the offset in sulfate affinity behavior and shows the affinity of $Ca^{+2}$ when the temperature exceeds 90 C°.
5. The proposed concepts such as the D ratio and Viscosity ratio are another diagnosing tool about the reverse attitude of the wetting and non-wetting regarding diffusivity differences.
6. The figures obtained using the general formula can easily use to detect the presence of fingering especially in oil type A.
7. The general formula approved the reality of the importance of temperature as the main crucial factor of wettability alteration mechanism in carbonate.
8. The general formula has introduced the physical properties and the thermal reactions of the exposed surfaces of the porous medium to the wetting phase used in an easy and logical way starting with a macroscopic understanding of the quantities that accompany with the gradual growth of the flow and heat distributions.
9. This work has given a different explanation to the mineral deposition probability through the figures created by the general formula.

The recommendations after this work are:

1. Start to examine the general formula validity to the other determining ions such as $Ca^{+2}$, $Mg^{+2}$.
2. Imply the economic factor in the case of using this formula practically.
3. Examine the results of the general formula with a different range of temperatures.
4. Using the general formula with different carbonate rocks such as limestone and dolomite.
5. Modify the general formula by adding another factor that will not contradict with Darcy assumptions in flow through the porous medium and the salinity ranges of carbonates.

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# VITA

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