A COMPARISON OF WETTABILITY AND SPONTANEOUS IMBIBITION EXPERIMENTS OF SURFACTANT SOLUTION IN SANDSTONE AND CARBONATE ROCKS

David José Nunes Rebelo

Thesis to obtain The Master of Science Degree in

Petroleum Engineering

Supervisor: Profª Maria João Correia Colunas Pereira

Examination Committee

Chairperson: Prof. Amilcar de Oliveira Soares
Supervisor: Profª Maria João Correia Colunas Pereira
Members of the Committee: Profª Maria Amélia Alves Rangel Dionísio

October 2016
Acknowledgments

Firstly, I would like to thank the Instituto Superior Técnico and Clausthal University of Technology for this agreement, principally to Prof. Amilcar Soares and Prof. Leonhard Ganzer, for giving this opportunity to study this interesting topic, their support and work in a different culture.

I would like to thank Profª Maria João Pereira and Dr. Leonardo Azevedo for guidance and support in my thesis in Instituto Superior Tecnico.

I would like to thank MSc. Hendrik Foedish, MSc. Rafael Hincapie and Dr. Jonas Wegner for their guidance, support and supervision in EOR laboratory of Clausthal University of Technology.

Finally, I would like to thank my friends and family mainly to my sister and my mother for support me in this journey.
Abstract

The main objective of the oil and gas industries in terms of production is to recover more oil from the reservoirs. The use of Enhance Oil Recovery methods is the key to increase this recovery. The spontaneous imbibition of aqueous phase is the main mechanism to recover oil in fractured and low permeability reservoirs. The objective of this thesis is to demonstrate the increase of the oil recovery using surfactants by lowering the interfacial tension or altering the wettability. For this purpose brines with different salinities were used and rocks wettability was measured.

One non-ionic surfactant (calamide C®) with a solvent (isopropanol) was tested in different concentrations, together with brines ranging from high salinity (95 000 ppm) to low salinity (3 4000 ppm). The surfactant with different concentration 1 wt%, 2wt% or 4wt% of calamide C®, 1wt% of isopropanol and with a varying wt% of brine to complete the solution was spontaneous imbibed. The spontaneous imbibition was measure in a sandstone, a Bentheimer form the North of Germany and a Carbonate from France with non-determined origin.

The Wettability of the rocks was measured using the Two-Phase Separation Method and the Spontaneous imbibition of water by Amott-Harvey Test. All the cores were water-wet, because in the Two-Phase Separation, where it was analysed the preference of the rock grains by oil and brine, the rock grains prefer brine. The cores by the Amott-Harvey Test imbibe brine between 15-30 % of the original oil in place (OOIP).

In sandstone, the spontaneous with brine imbibition recovered more oil at high salinity than at low salinity. In carbonates, more oil was recovered at low salinity than in sandstones. This might be explained by the salt composition or due to the pH of the brine. The pH decrease of the brine allowed to recover more oil in sandstone, while in carbonate was the opposite.

The oil recovery by spontaneous imbibition using surfactant allowed to determine that the surfactant had a good performance at low and high salinity. In high salinity, the surfactant did not form microemulsion, so it was difficult to determine the mechanism in this environment. However, at low salinity the surfactant formed microemulsion achieving the Windsor type III, with three different phases. It was a good indicator of the decrease of interfacial tension between oil-water phases and of the capillary pressure.

Keywords: Conventional Reservoirs, Non-ionic Surfactant, Spontaneous Imbibition and Wettability, Interfacial Tension, Amott Harvey Test, Two-Phase Separation Method
Resumo

Recuperar mais petróleo dos reservatórios é o principal objetivo em termos de produção da indústria petrolífera. O uso de métodos de Recuperação Avançada de Petróleo é a chave para aumentar a recuperação de petróleo. A imbibição espontânea da fase aquosa é o principal mecanismo para recuperar petróleo pela diminuição da tensão interfacial injetando substâncias tensioactivas. Para tal foram utilizadas salmouras de diferentes salinidades e foi determinada a molhabilidade das rochas.

Neste estudo foi testado um tensioativo não-iônico (calamide c®) com solvente (isopropanol) e salmoura de alta e baixa salinidade, respetivamente de 95 000 ppm3 400 ppm de concentração salina. O tensioativo foi embebidio espontaneamente com diferentes concentrações de 1w%, 2wt% and 4wt% of calamide c®, 1wt% de isopropanol e wt% variável de salmoura para completar a solução. As amostras de rochas usadas foi o arenito de Bentheimer do Norte da Alemanha e um carbonato de França de origem não identificada.

Para medir a molhabilidade das rochas foi usado o método de Two-Phase Separation e o teste Amott-Harvey de imbibição espontânea. Todas as amostras foram molháveis por água, porque os resultados do método Two-Phase Separation onde foi analisada a preferência dos grãos da rocha por salmoura e petróleo, revelaram que os grãos da rocha preferiam neste caso a salmoura. As amostras pelo teste Amott-Harvey embeberam salmoura entre 15 – 30 % do óleo inicial no reservatório.

A recuperação de petróleo pela imbibição espontânea através do teste Amott Harvey, revelou que a salmoura de alta salinidade recuperou mais petróleo que a salmoura em baixa salinidade em arenitos. No entanto em carbonatos foi recuperado mais petróleo que nos arenitos. Esta diferença poderá ser explicada pela composição do sal ou devido ao pH da salmoura. A descida do pH da salmoura permitiu recuperar mais petróleo nos arenitos, enquanto nos carbonatos aconteceu o contrário.

A recuperação de petróleo por imbibição espontânea usando tensioativo permitiu determinar que o tensioativo teve um bom desempenho em alta e baixa salinidade. Em alta salinidade, o tensioativo não formou microemulsão, pelo que foi difícil de determinar o mecanismo atuante. No entanto, em baixa salinidade o tensioativo formou microemulsão atingindo o terceiro estado de Windsor, com três fases. Trata-se de um bom indicador da diminuição da tensão interfacial entre a fase água e óleo e a pressão capilar.

Palavras-Chave: Reservatórios Convencionais Tensioativo Não-Iônico, Imbibição Espontânea e Molhabilidade, Tensão Interfacial, Teste de Amott Harvey, Método Two-Phase Separation
List of Contents
Acknowledgments ........................................................................................................ iii
Abstract ....................................................................................................................... v
Resumo ......................................................................................................................... vii
List of Contents .......................................................................................................... ix
List of Figures .............................................................................................................. xiii
List of Tables ................................................................................................................ xv
Nomenclature ............................................................................................................... xvii
1. Introduction ............................................................................................................. 1
  1.1. Motivation .......................................................................................................... 1
  1.2. Objectives ......................................................................................................... 2
2. Literature Review .................................................................................................... 3
  2.1. Petrophysical Characteristics ........................................................................... 3
      2.1.1. Porosity ...................................................................................................... 3
      2.1.2. Saturation .................................................................................................. 4
      2.1.3. Permeability ............................................................................................. 4
      2.1.4. Capillary Pressure .................................................................................... 6
      2.1.5. Interfacial Tension .................................................................................... 7
      2.1.6. Adhesion Tension ..................................................................................... 7
      2.1.7. Contact Angle ......................................................................................... 8
  2.2. Reservoir Wettability and Imbibition ................................................................. 9
      2.2.1. Types of Wettability: ............................................................................... 10
      2.2.2. Mechanism of Wettability Alteration by Crude Oil ................................ 11
      2.2.3. Surface Chemical Properties of Carbonate and Sandstones .................. 12
      2.2.4. Influence of Wettability in Water Flooding ............................................. 14
      2.2.5. Influence of Capillary Pressure in Imbibition ......................................... 16
      2.2.6. Analysis of Relative Permeability Curves .............................................. 17
      2.2.7. Upscaling the Imbibition ........................................................................ 17
  2.3. Surfactants ......................................................................................................... 19
      2.3.1. Types of Surfactants ............................................................................... 19
      2.3.2. Factors that influence the surfactants performance ................................ 20
      2.3.3. Surfactants Mechanisms on Wettability Alteration ............................... 21
      2.3.4. Microemulsion ....................................................................................... 22
      2.3.5. Micelles ..................................................................................................... 24
      2.3.6. Model of Wettability Alteration .............................................................. 25
      2.3.7. Adsorption .............................................................................................. 25
2.4. Measure the Wettability and Imbibition ................................................................. 27
  2.4.1. Amott Harvey Test ......................................................................................... 27
  2.4.2. USBM method ............................................................................................... 28
  2.4.3. Combined USBM method and Amott test ...................................................... 29
  2.4.4. Imaging Method ............................................................................................ 30
  2.4.5. Centrifuge Method ....................................................................................... 31
  2.4.6. Capillary Rise Method .................................................................................. 32
3. Materials ..................................................................................................................... 33
  3.1. Synthetic Brines ................................................................................................... 33
  3.2. Synthetic Oil ....................................................................................................... 34
  3.3. Surfactant ........................................................................................................... 34
  3.4. Cores .................................................................................................................. 35
4. Methodology ................................................................................................................ 37
  4.1. Amott-Harvey test ............................................................................................. 38
    4.1.1. Measure the Pore Volume .......................................................................... 39
    4.1.2. Saturating a sample with brine .................................................................. 39
    4.1.3. Saturating a sample with oil ...................................................................... 39
    4.1.4. Amott Harvey test measurement ............................................................... 39
  4.2. Two-Phase Separation Method .......................................................................... 40
    4.2.1. Crushing the rock into powder .................................................................... 41
    4.2.2. Washing with a solvent ............................................................................. 41
    4.2.3. Drying a sample in an oven ...................................................................... 41
    4.2.4. Imbibide the sample with synthetic oil ....................................................... 41
    4.2.5. Two Phase Saturation analyse ................................................................... 41
5. Results and Discussions .............................................................................................. 43
  5.1. Wettability Measurement .................................................................................... 43
  5.2. Spontaneous Imbibition ...................................................................................... 43
    5.2.1. Comparison of the oil recovery by surfactant and brine at high salinity in sandstone 44
    5.2.2. Comparison of the oil recovery by surfactant and brine at low salinity in sandstone 46
    5.2.3. Comparison of the oil recovery by surfactant and brine at low salinity in carbonate 48
    5.2.4. Comparison of the oil recovery by different surfactants at low salinity in sandstone 50
    5.2.5. Comparison of the performance of different surfactants with viscosity and their concentrations 52
    5.2.6. Comparison of the performance of different surfactants on sandstone and carbonate 53
    5.2.7. Comparison of the performance of different brines on sandstone and carbonate 54
6. Conclusions .................................................................................................................. 55
7. Future Work .................................................................................................................. 57
8. References.................................................................................................................... 59
9. Appendix....................................................................................................................... 63

9.1. Spontaneous imbibition in Bentheimer at high salinity using surfactant ............... 63
9.2. Spontaneous imbibition in Bentheimer at high salinity using brine ..................... 64
9.3. Spontaneous imbibition in Bentheimer at low salinity using Surfactant ............... 66
9.4. Spontaneous imbibition in Bentheimer at low salinity using Brine ...................... 67
9.5. Spontaneous imbibition in Carbonate at low salinity using Surfactant ............... 68
9.6. Spontaneous imbibition in Carbonate at low salinity using Brine ....................... 70
9.7. Spontaneous imbibition in Bentheimer at low salinity with 4% Calamide in Surfactant...... 71
9.8. Spontaneous imbibition in Bentheimer at low salinity with 1% Calamide in Surfactant...... 72
9.9. Tables of the results from spontaneous imbibition realized in this study at EOR laboratory. 73
List of Figures

Figure 1 Different types of porosity are dependent of the sediments disposition (adapted from Torsaeter and Abtahi, 2003) ...................................................................................................................... 3
Figure 2 (a) interaction between molecules in the fluid; b) and at the surfaces or interface (Donaldson and Alam, 2008) ....................................................................................................................... 7
Figure 3 Contact Angle (Torsaeter e Abtahi, 2003) ................................................................................................. 8
Figure 4 Different Types of Wettability (Abdallah et al., 2007) ................................................................................. 10
Figure 5 Polar interaction (left) and Surface Precipitation (Right) (Yefei, 2011) ......................................................... 11
Figure 6 Acid/Base interaction (left) and Ion-binding (right) (Yefei, 2011) ................................................................. 11
Figure 7 Mechanism Carbonate Surface - Crude Oil (Olsen, 2007) ............................................................................ 13
Figure 8 Plot of Water injected versus Recovery Efficiency for different wettability (Donaldson and Alam, 2008) ........................................................................................................................................... 15
Figure 9 Comparison of the water saturation versus capillary pressure and relative permeability (Abdallah et al., 2007) .......................................................................................................................... 16
Figure 10 Different type of Surfactants, 1) Non-anionic, 2) Anionic, 3) Cationic, 4) Amphoteric (NPTEL, 2016) .................................................................................................................................................. 20
Figure 11 Mechanisms in Wettability alteration by Surfactant; forming a monolayer by anionic surfactants (left image) and ion-par mechanism formed by cationic surfactant (right image) (Sheng, 2013) ........................................................................................................................................ 21
Figure 12 Different phase by surfactant application (Mehta and Kaur, 2011) ................................................................. 22
Figure 13 Plot of the Optimal Salinity (Najafabadi, 2009) ............................................................................................ 23
Figure 14 Comparison between the Surfactant and Micelles with the Interfacial Tension (Behrens, 2013) .................................................................................................................................................... 24
Figure 15 Distance from the surface versus concentration of surfactants (Salehi, 2009) .............................................. 26
Figure 16 USBM plot after the method to measure the USBM index (Pabón et al., 2014) ............................................... 29
Figure 17 Plot Combine Amott and USBM method (Engler, 2010) ................................................................................ 29
Figure 18 Different contact angles of the wetting fluid (Engler, 2010) ......................................................................... 30
Figure 19 Capillary Rise Method (Glover, 2000) ........................................................................................................ 32
Figure 20 Cocamide DEA Molecule (Monographs, 2016) ............................................................................................ 34
Figure 21 Experimental Design ...................................................................................................................................... 37
Figure 22 Amott Harvey Preparation Steps ................................................................................................................ 38
Figure 23 Amott Harvey Test Calculations of Oil and Water Saturation ........................................................................ 40
Figure 24 Two-Phase Separation Method Steps ........................................................................................................ 40
Figure 25 Two Phase Separation Method Apparatus (Salehi, 2009) .......................................................................... 41
Figure 26 Oil Recovery with brine and surfactant at High Salinity in Sandstone ........................................................... 44
Figure 27 Comparasion of the volume of oil and microemulsion recovery in Core N1 ............................................. 45
Figure 28 Oil Recovery with brine and surfactant at Low Salinity in Sandstone ........................................................... 46
Figure 29 Comparison of the volume of oil and microemulsion recovery in Core N6 ............................................... 47
Figure 30 Oil Recovery with brine and surfactant at Low Salinity in Carbonates ......................................................... 48
Figure 31 Comparison of the volume of oil and microemulsion recovery in Core FR8 ............................................. 49
Figure 32 Oil Recovery at Low Salinity in Sandstones with different concentration of surfactants ........................ 50
Figure 33 Comparison of the volume of oil and microemulsion recovery in Core N4 ............................................... 51
Figure 34 Comparison of the volume of oil and microemulsion recovery in Core U1 ............................................. 51
Figure 35 Comparasion of the viscosity of the different concentration of surfactant .................................... 52
Figure 36 Comparison of the Oil Recovery by Surfactants ........................................................................................ 53
Figure 37 Comparison of the Oil Recovery by Brine .................................................................................................. 54
List of Tables

Table 1 Relation between wettability and contact angle (Zolotukhin and Ursin, 2000) ...................... 9
Table 2 Amott Index and their Wettability ......................................................................................... 28
Table 3 Composition of High Salinity Brine ..................................................................................... 33
Table 4 Composition of Low Salinity Brine ....................................................................................... 33
Table 5 Decane Characteristics ......................................................................................................... 34
Table 6 Characteristics of Cocamide DEA ....................................................................................... 34
Table 7 Characteristics of Bentheimer Cores .................................................................................... 35
Table 8 Characteristics of Carbonate Cores ...................................................................................... 35
Table 9 Results of Oil Recovery by spontaneous imbibition in Sandstones at high salinity .......... 73
Table 10 Results of Oil Recovery by spontaneous imbibition in Sandstones at low salinity .......... 73
Table 11 Results of Oil Recovery by spontaneous imbibition in Carbonates at low salinity ........ 74
Table 12 Results of Oil Recovery by spontaneous imbibition in Sandstones at low salinity with surfactantes with different wt% of calamide ................................................................. 74
Nomenclature

$\varphi$, or $\phi$ Absolute porosity

$V_p$ Total pore volume

$V_b$ Bulk volume of the rock.

$\varphi_{ef}$ Effective porosity

$S_n$ Saturation of a specific fluid

$V_n$ Volume of the specific fluid

$S_{wi}$ Irreducible water saturation

$S_{or}$ Residual Oil Saturation

$q$ Flow rate

$k$ Permeability

$\Delta P$ Differential pressure

$A$ Cross-section area of fluid flow

$L$ Length of the sample

$\mu$ Fluid viscosity

$k_{ei}$ Effective permeability

$K_{ri}$ Relative permeability

$S_w$ Water Saturation

$C_p$ Capillary pressure

$r_c$ Capillary radius

$\theta$ Contact angle

$\sigma$ Interfacial tension

$T_a$ Adhesion Tension

$\sigma_{os}$ oil-solid interfacial tension

$\sigma_{ws}$ water-solid Interfacial tension

$\sigma_{ow}$ oil-water Interfacial tension

$L_c$ Characteristic length

$t_g$ Gravity reference time

$\Delta p$ Difference of density between water-oil

$\mu_o$ Viscosity of the oil

$t_o$ Dimensionless time for oil recovery.

$S_wf$ Water saturation at water front

$p_c*$ Capillary pressure at water front

$M_e*$ Effective mobility at water displacement front

$c$ Ratio of gravity force

$I$ Amott-Harvey Index

$I_w$ Water index

$I_o$ Oil index

$V_{asp}$ Volume of oil recovery by spontaneous imbibition of water

$V_{tot}$ Volume of total oil recovery

$V_{asp}$ Volume of water recovery by spontaneous imbibition of oil

$V_{tot}$ Volume of total water recovery

$W$ USBM Index

$A_1$ Work required to displace the water

$A_2$ Work required to displace the oil.

$\rho_1$ and $\rho_2$ Densities of the phases

$r_b$ and $r_t$ Radii of bottom and top to

$R$ Rotation

$g$ Gravitation acceleration

$h$ Height the fluid rise or lower

$P_v$ Pore Volume
1. Introduction

1.1. Motivation

The World oil demand continues to increase due to the growing global population, but the oil trapped in the conventional reservoir is high and a simultaneously shrinking of crude oil reserves. The carbonates reservoirs are approximately 50% of the more reservoir in the world. The carbonates have a complex structure and heterogeneity that are not fully understood. Analysing the wettability of the reservoir that is the preference of the rock adsorb one fluid in present of other fluid, indicates that most of carbonates are oil to intermediate wet. (ElMofty, 2012)

The oil-wet reservoir does not imbibe water spontaneously because the rock has high molecular interaction with oil. So, increase the oil recovery by injecting a huge amount of water with pressure higher than the capillary pressure is the solution. The capillary pressure is the pressure that depends of the interfacial tension of the fluid with the rock, if the rock has higher interaction with the fluid, it will form a higher pressure that is difficult to eliminate.

On the other hand, the sandstones have a more homogeneous property and their wettablity is intermediate to water-wet. This reservoir is easier to study the petrophysical properties due to their homogeneities proprieties and elaborate the best method to recovery oil compared with the carbonates. If the sandstones were water-wet, they could imbibe water spontaneously without any external forces only by capillary forces. (Tiab and Donaldson, 2004)

Recovery oil from a reservoir depend on different recoveries. The primary recovery results from the mechanisms of the reservoir allow a recovery of 5-30% of Oil initial in Place (OOIP). The secondary recovery is applied by the injection of a fluid to sustain the pressure in the reservoir allows a recovery of 30-40% of the OOIP. The tertiary recovery, known as Enhanced Oil Recovery (EOR), allows a recovery between 40% and 60% or more of the OOIP. (ElMofty, 2012)

The process of EOR can be divided into chemical, thermal and miscible. The chemical process analyse in this study is the Surfactants. Surfactants react with the oil phase to low the interfacial tension or with the carbonate and sandstone surface to alter the wettablity toward more water-wet. Altering the wettablity allows the increasing of the spontaneous imbibition of water because the rock will prefer adsorb water. The surfactants, due to their chemical properties allow decrease the interfacial tension between oil and water phase and the capillary pressure. It is easier to water flow through the pores filled with oil and displace the oil due to the low tension within the phases. The surfactants can be divided into anionic, non-ionic, cationic and amphoteric.
In this study, a non-ionic surfactant will be used. This surfactant should have different mechanisms that allow recovery more oil in the conventional reservoirs with difficult characteristics. Normally the non-ionic surfactant is used with a co-solvent or co-surfactant to decrease the interfacial tension to ultra-low values. The interfacial tension of the surfactant used in this study can reach until 0.003 mN/m. (Iglauer et al., 2014)

The analyse of the spontaneous imbibitions using this surfactant are the first did until know. The mixture of calamide c® with isopropanol show that they have a good performance either in high and low salinity. This surfactant form a microemulsion at low salinity that proves the interfacial tension achieved in the study of Iglauer.

1.2. Objectives

The objective of this work is to study the effect different environments in oil recovery by spontaneous imbibition. The environments studied are in high and low salinity (brine with 95 000 and 3 4000 ppm), different surfactant concentration and in two different rocks, sandstone and carbonate. This recovery is the main mechanism in low permeability and fractured reservoirs, mostly in carbonates. In this cases, the wettability of the reservoirs is one of the main factors that influence the spontaneous imbibition mechanism. Thus, to study wettability of the rocks is crucial to understand spontaneous imbibition.

Understand the mechanism behind the spontaneous imbibition of brine and surfactant is other of the main objectives of this study to allow increase the oil recovery. Study the mechanism is important to apply this mechanism to the industry and understand the physical and chemical phenomenon behind this recovery type of recovery.
2. Literature Review

2.1. Petrophysic Characteristics

2.1.1. Porosity

Porosity is one of the main petrophysic parameters to analyse a petroleum reservoir. The porosity measures the capacity of storage of a reservoir (Torsaeter and Abtahi, 2003). The pore volume is the total volume of pores present in the rock and can be determined through the porosity.

The porosity can be split into primary and secondary. During the deposition of the sediment the primary porosity is formed like in figure 1, while the second porosity is formed after the deposition, caused by certain geological phenomena. The porosity is influenced by several factors like degree of cementation, compaction after and before deposition, regularity of grain size. (Tiab and Donaldson, 2004)

![Figure 1 Different types of porosity are dependent of the sediments disposition (adapted from Torsaeter and Abtahi, 2003)](image)

The porosity is divided into absolute porosity and effective porosity. All the pores in the rock characterize the absolute porosity. The caternary pores are interconnect to other pores by more than 2 pore throats, while the cul-de-sac are interconnected by only one pore. The closed pores aren’t interconnected with other pores (Tipura, 2008). The absolute porosity ($\phi_a$) [equation 1.1] is all the pore space within the rock, it is determined by the ratio of pore space within the rock in volume ($V_{pa}$) to volume of rock bulk ($V_b$).

$$\phi_a = \frac{V_{pa}}{V_b} \quad [1.1]$$

To categorise a reservoir, the effective porosity [equation 1.2] is the most important factor. It is the space of the rock that can be occupied by fluids, because it is characterized by the interconnected pores (caternary pores and cul-de-sac). Effective porosity ($\phi_{ef}$) is the ratio of interconnected pores within the rock ($V_p$) to volume of rock bulk.

$$\phi_{ef} = \frac{V_p}{V_b} \quad [1.2]$$

Sandstones have an effective porosity closer to the absolute porosity compared with a carbonate or cement rocks due to the geometry of the carbonates and cement rocks. (Tiab and Donaldson, 2004)
2.1.2. Saturation

The pores space within the reservoir can be saturated with oil, gas and water. The pore volume is the sum of all the fluids present in the pore space. The $V_p$ is the volume of pores [equation 1.3], $V_w$ is the volume of water, $V_o$ is the oil volume and $V_g$ is the gas volume in the pores space. The equation is expressed as: (Tipura, 2008)

$$V_p = V_w + V_o + V_g$$ \[1.3\]

Saturation [equation 1.4] is a fraction of pore space occupied by a specific fluid. The $S_n$ is the saturation of a specific fluid, $V_n$ is the volume of the specific fluid and $V_p$ is the pore volume.

$$S_n = \frac{V_n}{V_p}, \quad n = 1, \ldots, m$$ \[1.4\]

The equilibrium of the saturation system is expressed by the next equation [equation 1.5], where the sum of saturation of all fluids present in the porous medium is equal to one.

$$\sum_{n=1}^{m} S_n = 1$$ \[1.5\]

Saturation is a factor that influences the wettability of the reservoir and the oil recovery. Endpoint saturation gives an indication of the performance of the reservoir due to the imbibition and drainage process. During the oil migration into the reservoir the water is displaced until the $S_{wi}$, irreducible water saturation is achieved. During the waterflood into the reservoir there occurs an increase of saturation of water that displaces oil until the residual oil saturation, $S_{or}$. Therefore, between $S_{wi}$ and $S_{or}$ the fluids can be mobilized in the reservoir. (Tangen, 2012)

2.1.3. Permeability

The permeability is the capability of a fluid to flow through interconnected pores in the rock at a response to a fluid pressure gradient. The permeability is affected by such as cementation degree and consolidation, distribution of the grain size, shape of the grain and grain size.
The permeability during the formation of the rock is split into primary and secondary. The primary permeability is known as the matrix permeability and is formed over time by the deposition and lithification of the sediments. The secondary permeability forms after the formation of the rock by the alteration of the rock matrix. The causes of the formation of the secondary permeability come from fracturing, cementation, compaction and solution. The fluid flow of some reservoirs like carbonates are influenced by secondary permeability. While the sandstones are influenced by the primary formation. (Tiab and Donaldson, 2004)

The permeability is divided into absolute permeability or permeability, relative permeability and effective permeability. Absolute permeability [equation 1.6] is the capability of one fluid flowing through a pore space. The permeability is determined by Darcy’s law (1856) Darcy performed an experiment about the flow of water through sands. Darcy’s law is applied to incompressible fluid, horizontal flow and linear. (Torsaeter and Abtahi, 2003)

\[
\frac{q}{A} = v = \frac{k \Delta P}{\mu L} \rightarrow k = \frac{q \mu L}{A \Delta P}
\]  

[1.6]

The flow rate is represented by \(q\) [cm\(^3\)/s], permeability is \(k\) [D], differential pressure is \(\Delta P\) [atm], \(A\) is the area of cross-section where fluid flows [cm\(^2\)], the length of the sample is represented as \(L\) [cm], \(\mu\) is the fluid viscosity [cP].

**Effective permeability** [equation 1.7] is the ability to preferentially transmit a fluid in the presence of other immiscible fluids in the reservoir. It can be expressed as a modification in the Darcy’s laws equation:

\[
k_{ei} = \frac{q_i \mu_i L}{A \Delta p}
\]

[1.7]

The \(i\) is specific phase, \(k_{ei}\) is the permeability of the specific phase, \(\mu_i\) is the specific phase viscosity, \(q_i\) is the flow rate of the specific phase.

**Relative permeability** of a specific fluid [equation 1.8] is determined as the ratio of the effective permeability of a specific fluid to the absolute permeability of the rock.

\[
k_{ri} = \frac{k_{ei}}{K}
\]

[1.8]

Where the relative permeability of a specific fluid is \(K_{ri}\), the absolute permeability is \(K\) and the effective permeability of a fluid is \(K_{ei}\).

Relative permeability of fluids is influenced by pore geometry, saturation history, fluid saturation, wettability and interfacial tension. It is a multi-phase flow parameter that should be measured accurately because it predicts both the reservoir performance predictions and the flow rate calculation. The sandstones have a high permeability compared with carbonates. Thus, it is possible to understand the difference in oil recovery between a carbonate and sandstone. The permeability influences the capillary pressure and interfacial tension, so both will influence the flow behaviour of the fluids and the oil recovery.
2.1.4. Capillary Pressure

The capillary pressure occurs in a pore medium in the presence of two immiscible fluids. The molecules within the fluids have electrostatic forces to stay together, cohesion. However, when two fluids do not have strong electrostatic forces they can mix forming together a single fluid, it is called miscible fluids. While immiscible fluids have the highest electrostatic forces between molecules within the fluids that don’t mix with others fluids. When a fluid is attracted to the rock surface by electrostatic forces called adhesion. (Zolotukin and Ursin, 2000)

Capillary pressure is generated by the interface of two immiscible fluids in a capillary tube, where the wetting fluid due to the stronger adhesive forces build a curved interface with another fluid. The curvature is axisymmetric meniscus, convex toward to the wetting fluid and the contact angle is measured between the wall and the aqueous phase. The two different radii can characterize the interface. This parameter is one of the main factors that influences the fluid distribution. The molecular difference between the non-wetting fluid and the wetting fluid represents the capillary pressure [equation 1.9]. (Tipura, 2008)

\[ P_c = P_{nw} - P_w \]  \[\text{[1.9]}\]

The capillary pressure is \( P_c \), the pressure of the wetting fluid is \( P_w \) and the pressure of the non-wetting fluid is \( P_{nw} \).

The capillary pressure increases during the drainage process, while decreasing during the imbibition process. Because during the drainage process the non-wetting fluid displaces the wetting fluid that has a high adhesion with the rock, so it has a high tension. While in the imbibition process, the capillary pressure is a driven mechanism that displaces the non-wetting fluid (Tangen, 2001). Capillary pressure allows determining of the reservoir’s initial saturation, the pressure supported by the cap rock, and the relative permeability. (Glover, 2000)

According to the Laplace equation, the capillary pressure results from the curvature of the fluid interfaces given by two different radius and the tension in the interface [equation 1.10]. Simplifying the equation by using the equal radius is shown in the next equation:

\[ P_c = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = \frac{2\sigma}{r} \]  \[\text{[1.10]}\]

It is possible to analyse in a capillary tube with two immiscible fluid the capillary pressure, given the radius of the throat pores. Shift this radius in the equation, the expression is:

\[ r = \frac{r_c}{\cos \theta_c} \rightarrow P_c = \frac{2\sigma_{ow} \cos \theta_c}{r_c} \times A \]  \[\text{[1.11]}\]

In [equation 1.11], \( C_p \) is the capillary pressure [psi], \( r_c \) is the capillary radius [cm], the contact angle is \( \theta \) [degrees], the interfacial tension is \( \sigma \) [dynes/cm] and \( A \) is to convert to psi \( (145 \times 10^{-3}) \). Capillary pressure is inversely proportional to pores radius but it is directly proportional to interfacial tension.
2.1.5. Interfacial Tension

The interfacial tension occurs in the interface of two immiscible liquids by a finite thickness where the properties change. It is a small interface created by the reaction forces of two liquids. Interfacial tension is the difference of molecular interactions between two immiscible liquids. Normally the molecules tend to attract each other in all directions by electrostatic forces within the liquid like in figure 2 (a), but in the interface between two liquids, the molecules of one liquid tend to attract only in its own direction, reducing the liquid surface like figure 2 (b).

The tension or energy required to minimize the surface and attraction of the fluids is called interfacial tension. The molecular activity creates a membrane where the molecules are in tension. This tension is the free energy in the surface of the interface of two different liquids.

![Figure 2 (a) interaction between molecules in the fluid; b) and at the surfaces or interface (Donaldson and Alam, 2008)](image)

2.1.6. Adhesion Tension

The adhesion tension [equation 1.12] is the tension in the interface between the solid and the fluid. It is the water-solid and oil-solid interfacial tension and is measured by an adhesion Tension (Tₐ), such as:

\[ Tₐ = \sigma_{os} - \sigma_{ws} = \sigma_{wo} \cos \theta_{ow} \]  \[1.12\]

The Tₐ is the adhesion tension, the oil-solid interfacial tension is represented as \( \sigma_{os} \) [dyne/cm], the water-solid interfacial tension is \( \sigma_{ws} \) [dyne/cm], the oil-water interfacial tension is \( \sigma_{ow} \) [dyne/cm] and the contact angle measured in the water phase is expressed as \( \theta \) [degrees].

When the interfacial tension is equal to 0 and the contact angle is 0, the interfacial tension in oil and water is equal to the adhesion tension. (Donaldson and Alam, 2008)

The wetting fluid has a higher interaction between fluid molecules and rock molecules than mutual attraction of the molecules within the fluid. The non-wetting fluid has low molecular interactions with the rock because the attraction of the molecules within the fluid is greater than the fluid and rock interactions. So, this phenomenon allows the fluid to spread through the rock surface lowering the interfacial tension and the capillary pressure, and increasing the water spontaneous imbibition process in water-wet rock or the oil spontaneous imbibition process in oil-wet rock.
2.1.7. Contact Angle

The qualitative measurement that measures the rock wettability is by the contact angle. It is the angle of the aqueous phase in the reservoir pore space in the presence of another immiscible fluid. It is associated with the interfacial forces between different phases in the rock/oil/water system. (Anderson b, 1986)

The contact angle depends on the composition of crude oil, surface electric properties, pressure, temperature, rock surface roughness, heterogeneity of rock and dynamic forces. While the wetting fluid advances, it is possible to measure the advancing contact angle. The advancing angle is significantly larger than the receding contact angle due to surface roughness (Valvatne and Blunt, 2004).

The equation [equation 1.13] that measures the contact angle is known as Young’s equation (1805). It is based on the equilibrium of the oil-brine-rock system, based on interfacial tension.

\[ \sigma_{os} - \sigma_{ws} = \sigma_{ow} \times \cos \theta \]  \hspace{1cm} [1.13]

The \( \sigma_{os} \) is the interfacial tension oil-solid [dyne/cm], \( \sigma_{ws} \) is the interfacial tension water-solid [dyne/cm], \( \sigma_{ow} \) is interfacial tension of the oil-water [dyne/cm] and \( \theta \) is the contact angle of the aqueous phase [degrees].

In figure 3, it is observe that the rock-oil interfacial tension is the opposite of the interfacial tension of water-rock interface. The tension of water-oil is tangential at drop surface and it is the tension that equilibrates the system and defines the wettability of the rock.

It is possible to correlate the contact angle of the water phase with the interfacial tension [equation 1.14].

If \( \sigma_{os} > \sigma_{ws} \), then \( \cos \theta > 0 \), and \( \theta < 90^\circ \)

If \( \sigma_{os} < \sigma_{ws} \), then \( \cos \theta < 0 \), and \( \theta > 90^\circ \)  \hspace{1cm} [1.14]

The relation between wettability and contact angle can be quantified as strongly water-wet, preferential water-wet, intermediate wet, preferential oil-wet and strongly oil-wet, (table 1). When the water phase spreads completely through a rock surface, the rock is strongly water-wet given a contact angle of 0°. While when the rock is strongly oil-wet, a water drop is formed without interacting with the rock surface given a 180° angle. When the rock is intermediate wet, the rock does not have any preference neither water or oil and the angle is 90°.
2.2. Reservoir Wettability and Imbibition

Wettability is defined as the preference of the rock to adsorb a fluid in the presence of another fluid in the pore space of a reservoir. The rock creates a better attraction with a fluid that wets the rock than the other fluid. The fluid that wets the rock is called wetting fluid, while the fluid that doesn’t wet the rock is called non-wetting fluid. (Abdallah et al., 2007)

The wettability is a very important parameter in the characterization of a reservoir due to its direct relationship with the oil recovery. Wettability affects the capillary pressure, fluid flow behaviour, electric properties and relative permeability. Thus, reservoir wettability affects directly the recovery of oil by spontaneous imbibition, which is the main factor that increases the oil recovery in a reservoir with low permeability and fractured.

Wettability depends on numerous factors such as composition of the oil, brine composition (i.e. salinity, pH, multivalent cations) and film thickness, saturation history of the reservoir, mineral composition of the rock and their chemical properties, temperature and pressure. Altering the wettability of the rock to water-wet is the main factor that allows recovery of more oil by spontaneous imbibition. Normally the sandstones are water to intermediate wet, while the carbonates are oil to intermediate wet. Below is an explanation of the different types of wettability. (Anderson a, 1986)

### Table 1 Relation between wettability and contact angle (Zolotukhin and Ursin, 2000)

<table>
<thead>
<tr>
<th>Wettability</th>
<th>Contact Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly water-wet</td>
<td>0-30</td>
</tr>
<tr>
<td>Preferential water-wet</td>
<td>30-90</td>
</tr>
<tr>
<td>Intermediate wet</td>
<td>90</td>
</tr>
<tr>
<td>Preferential oil-wet</td>
<td>90-150</td>
</tr>
<tr>
<td>Strongly oil-wet</td>
<td>150-180</td>
</tr>
</tbody>
</table>
2.2.1. Types of Wettability:

There are three main types of wettability on rock-oil-brine system. The water-wet is the preference of the rock by water, oil-wet preference of the rock by oil and intermediate characterize that the rock do not have preference by any fluid. In figure

Water-Wet:
The rock is water-wet, when the rock preferential adsorbs water in the presence of another fluid. The rock-water interface has a high molecular interaction. Initially in the formation of the rocks by burial depth, the rocks during their formation have water in pores space. The interaction of the rock surface with brine creates an acidic system, which attracts the basic compounds of crude oil. (Engler, 2010)

Oil-Wet:
The rock is oil-wet when preferential adsorbs oil in the presence of another fluid. The wettability of the rock changes from water to oil-wet by the process that will be explained below. This normally occurs due to oil migration into the reservoir through attraction of the oil with the rock surface in the reservoir environment, depending on the different type of rocks.

Intermediate-Wet:
In intermediate wet, the rock does not have any preference for water or oil. It is divided into:

Fractional-wet: is present in rocks that in some parts are preferential water-wet, whereas in other parts it is preferential oil-wet. This occurs due to the different mineral composition of the rock surface with different chemical properties. (Engler, 2010)

Mixed-Wet: Salathiel in 1973 defined mixed wettability of special fractional wettability. This type of rock is water-wet in small pores and oil-wet in large pores. This phenomenon occurs due to oil migration into the reservoir rock. Initially the reservoirs are water-wet, the oil migrates into the center of large pores due to the low capillary pressure compared to small pores. Over time and due to the increase of oil saturation, the oil will destroy the electrostatic forces and the film of water connate to the rock surface. Thus, the wettability of the rock changes to oil-wet in large pores because the polar active compounds present in the oil will react directly with the rock surface. (Tiab and Donalson, 2004)

Figure 4 Different Types of Wettability (Abdallah et al., 2007)
2.2.2. Mechanism of Wettability Alteration by Crude Oil

The crude oil interacts with the rock surface by different mechanisms. These mechanisms alter the reservoir wettability toward more oil-wet depending on the composition of the phases of the system, the chemical and physical phenomenon. The mechanisms that change the wettability of the rock in the crude oil-rock-water system are:

Polar interactions: in figure 5 (left) is represented this mechanism, it is predominant when there is no film of water between oil and rock. The interaction is stronger between polar molecules with atoms such as Nitrogen, Sulphur and Oxygen and polar rock surface sites. The aqueous phase can have a stronger interaction than the polar interactions. (Morrow, 1986)

Surface Precipitation: in figure 5 (right) is represented this mechanism, it depends mainly on the asphaltenes in the crude oil. Oil composition, temperature and pressure change the properties of solvents like asphaltenes. The precipitation of asphaltenes occurs due to chemical reaction by altering the equilibrium state of the system. The most common causes are the decreasing pressure and injection of a solvent. (Petrowiki, 2007)

Acid/Base: in figure 6 (left) is represented this mechanism, it is based on the Coulombic interactions between acid and basic compounds. It usually occurs in the presence of water in the system. When the surface is negative, it attracts with positive charges (basic), while if the surface is positive it attracts with negative charges (acid). If a monovalent salt solution is present at low concentration, the pH of the water controls the oil-rock interaction. (Buckley, 1996)

Ion Binding interactions: in figure 6 (right) is represented this mechanism, it is based on specific interactions between charge compounds and high valence ions in the crude oil. The crude oil has divalent or multivalent ions that can create a bond between oil-rock or water. Mineral surface and water are important in acid-basic and ion binding mechanism. (Buckley, 1996)
2.2.3. Surface Chemical Properties of Carbonate and Sandstones

The surface energy between the contact of fluid-fluid or solid-fluid depends on the chemical composition of the compounds. The surface properties of the different types of rock such as shale, sandstones and carbonates affect the wettability. It can be explained by analysing the chemical structure of the rock. Thus, the surface interaction and preference for a fluid is influenced by the mineral composition of the rock surface.

Carbonates:

The carbonate minerals most abundant are the calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). Other minerals that normally compose carbonates such as anhydrite, chert and quartz. The main carbonate rocks are limestone and dolomite. In limestones, more than 50% is composed of carbonates, more than half is calcite. The dolomites are composed of more than 50% carbonates. Normally the dolomites form good reservoir properties, by precipitation from a solution containing Mg, Ca and carbonate ions. (Schon, 2015)

It is important to understand the chemical and mineral composition of the carbonate, because the carbonate adsorbs different fluids depending on the wettability. Most of the reservoirs are water-wet before the oil migration from the source rock into the reservoir rock. Clean Carbonates are water-wet. (Olsen, 2007) Sharma determined that the carbonate rock is oil to intermediate wet due to the rock having a positive zeta potential. (ElMofty, 2012) The surface of carbonate is basic and attached to acid compound of the crude oil, determined Lowe in his study. McCffery and Mungan determined in their study that the calcite is strongly attached to stearic acid. (Tiab and Donaldson, 2004)

The acid compound of the crude oil such as phenolic compounds, carboxylic acids and ring structures containing sulphur and oxygen that affect the carbonate surfaces. These compounds of crude oil have a strong reaction with the carbonate surface due to the carbonate having a positive charge and behaves like weak bases, figure 7. Therefore, due to these interactions the carbonates are intermediate to oil wet.

The pH of the Brine due to acid-base interactions of the rock and oil can alter the wettability, as it is mentioned before. If the pH of the brine is less than 7-8, the carbonate is positively charged and adsorbs negatively charged organic compounds (acid). However, when the brine has a pH higher than 8, the carbonate becomes negatively charged and adsorbs positively charged organic compounds (basic). (Tiab and Donaldson, 2004)

In 2006 Tweheyo studied the effect of SO₄²⁻, Ca²⁺ and Mg²⁺ (divalente ions) on changing the wettability in carbonates at 100°C and more, without utilizing surfactants. Gupta and Mohanty determined in 2010 that in temperatures above 90°C the magnesium alone doesn’t change the wettability, while calcium alone does alter the wettability. (Gupta and Mohanty, 2010).
Sandstones:

The sandstones are composed of sand grains (SiO$_2$), this molecule can react with salt water forming silanol group. The sandstones are normally constituted of silica, clay and sand and they are intermediate to water wet because of their acidic surface due to the presence of brine with a pH of less than 7. The sandstones adsorb basic compounds of crude oil, but normally crude oil is composed of weak acids that are repelled from the surface. This is shown by Block and Simms, who determined that stearic acid is hardly adsorbed while an octa-decynamine is strongly adsorbed in a glass. The basic compounds of the crude oil like esters have a high attraction to an acid rock surface, such as sandstones. (Tiab and Donaldson, 2004).

The pH of the brine has a great importance on the sandstone adsorption. When brine has a pH higher than 7, the rock surface attacks to acid organic compounds of crude oil due to the dissociation of hydrogen not occurring. The next metals, Al$^{+++}$, Fe$^{+++}$, Cu$, Ba^{+}$ and Ca$^{++}$ in brine are adsorbed by the rock surface and allows adsorption of the acid compounds of the crude oil in silica.

The crude oil due to the surface active compounds alter the wettability of the reservoir. These compounds can change the chemicals of the fluid and rock surface by depending on the type of the surface active compounds, salinity and pH.
2.2.4. Influence of Wettability in Water Flooding

Wettability influences the flow behaviour of different liquids in a reservoir. In a reservoir can occur an imbibition and drainage process. The drainage is the process of non-wetting fluid displacing the wetting fluid, while the imbibition is when the wetting fluid displaces the non-wetting fluid in a porous medium. The imbibition or drainage can occur by forced or spontaneous imbibition. The spontaneous imbibition occurs due to the driven capillary pressure, while on the other hand, the forced imbibition is due to applying external force. The drainage only occurs due to the external force, because the fluid does not have a high interaction with the rock to flow through the porous medium without any force. (Anderson b, 1986)

- During the water flooding in a water-wet rock saturated with oil and water in their pores space, the water firstly flows by the small pores and connected to the rock surface in the large pores. This happens due to the high electrostatic forces between the water and the rock. With the increase of water saturation, the oil is displaced by water in the center of the large pores. When the pores have a high water saturation, some oil stays trapped in the center of the large pores by snap-off. It occurs because small pore throat/pore body ratio for the big oil globules that stay in the center of the pores and because the water that disconnect path to producing well. (Tiab and Donaldson, 2004)

- In an intermediate wet rock, during the water flooding, the water flows readily by the small pores and to the center of the large pores. The water flows through the center of the large pores, because the pores are oil-wet so have a high molecular interaction between oil and rock surface. As residual oil saturation decreases due to the increase of the water saturation, some oil remains in the pores. However, the oil flows by a continuous path to the production well by connection to the rock surface due to the large pores being oil-wet. This is the main reason that intermediate wet has the lowest residual oil in the ultimate recovery.

- In the presence of an oil-wet rock, during the water flooding the oil occupies either the large or small pores. Initially the water flows by the center of the large pores due to the oil having a high interaction molecular with the rock that remains connate to the rock surface in the large pores. The oil remains in the small pores due to the geometry of the pores and interactions of the oil-rock surface that create a high capillary pressure making it difficult for the water to penetrate. With the increasing of water saturation, the oil that remained connate to the rock surface in large pores and in the small pores start displacing due to the imbalance of the oil film. Some oil remains trapped and is bypassed in the small pores, because of the high capillary entry pressure of the water. One of the solution uses surfactants to reduce the interfacial tension and the capillary pressure will decrease.
Analysing the figure 8, a strongly water-wet formation during the water flooding, the oil recovery is greater before breakthrough, on the other hand after the breakthrough is very low. Thus, the water/oil ratio rises a lot after the breakthrough. It occurs due to high molecular interaction with the water and the rock that displaces the oil on one front without it being necessary to inject large volumes of water.

While in a strongly oil-wet formation, the recovery of oil is continuous before and after the breakthrough. Thus, after the breakthrough the water/oil ratio increases slowly. It occurs due to the necessary injection of water to displace the oil, because the oil has a high molecular interaction with the rock. (Anderson f, 1986)

![Figure 8 Plot of Water injected versus Recovery Efficiency for different wettability (Donaldson and Alam, 2008)](image)
2.2.5. Influence of Capillary Pressure in Imbibition

During the spontaneous imbibition, the capillary pressure goes down to zero due to the increase in saturation of the wetting fluid in the rock. The imbibition rate is influenced by different factors like the porosity, fluid viscosity, permeability, rock boundary, grain shape and interfacial tension.

In a strongly water wet formation, the core imbibes water until $S_{wos}$, so the work to displace the oil is near to zero because of the attraction forces. Therefore, when the system becomes less water wet, it is necessary to do more work to displace oil, so the amount and rate of spontaneous imbibition decreases. In an intermediate wet rock, the oil doesn’t imbibe when the saturation of water is $S_{or}$, and the water doesn’t imbibe when the saturation of oil is $S_{oi}$. When a sample only imbibes a small amount of water at $S_{w0}$, the formation is mixed or fractional wet.

In the figure 9 it is possible to analyse capillary pressure depending on water saturation for different types of wettability. The different processes represent the drainage and imbibition process in a rock. If the rock is water-wet like sandstones, the work needed to displace the water is greater than the work needed to displace the oil, which is almost spontaneous. While if the rock is oil-wet like carbonates the work needed to displace water is almost zero and the work to displace the oil is high.

The entry pressure is important because it is the pressure needed to enter the first drop of oil into the rock, when the rock is completely saturated with water. This represents the migration of oil into the reservoir when the rock is water-wet like most of the sandstones, on the other hand in an oil-wet rock like most of the carbonates, it is the pressure needed to enter the first drop of water during the water flooding. (Anderson d, 1986)

![Figure 9 Comparison of the water saturation versus capillary pressure and relative permeability](Abdallah et al., 2007)
When the capillary pressure of water and oil is equal to zero, it is called free water level (FWL), and there do not exist any forces to displace the fluids spontaneously. When the entry pressure is equal to the capillary pressure, there occurs the water-oil contact. During oil migration, the pressure must be equal or higher than the entry pressure and is a function of the diameter of pore throat for the oil to displace the water (Donaldson and Alam, 2008). The transition zone is the mobile zone for oil and water in the reservoir. It ranges from the irreducible water saturation to free water level. (Jackson et al., 2005).

2.2.6. Analysis of Relative Permeability Curves

The relative permeability as a function of the water saturation, as in figure 9, determines the wettability of the rock by analysing the performance of the rock in the transition zone. The disadvantage of this method is that it is not possible to analyse small changes in wettability, but it is an accurate method to differentiate the strongly oil-wet and strongly water-wet. Craig suggested same rules to analyse the relative permeability versus saturation: (Craig, 1971)(Anderson e, 1986)

- In water-wet rock, the initial water saturation is greater than 20 to 25% of Pore volume, while in oil-wet it is less than 10% Pore volume;
- In a water-wet the intersection of the water and oil relative permeabilities occurs in water saturation higher than 50%, when the system is oil-wet it occurs less than 50% of water saturation;
- When the system is water-wet the total water relative permeability is at maximum 30%, while if the total water relative permeability is greater than 50%, the system is oil-wet.

Some non-wetting fluid remains trapped in the pores space, and the capillary pressure is affected by that. Therefore, it is the reason to plot the hysteresis in the relative permeability for the non-wetting phase. (Geffren, 1951)

2.2.7. Upscaling the Imbibition

The imbibition is influenced by some factors such as the fluid viscosity, shape and boundary condition, porosity, permeability and interfacial tension. The process of changing the wettability is slow, so it is essential upscale the laboratory scale to field scale. (Mattax et a., 1962) They determined one expression for upscaling the capillary imbibition, [equation 1.15]. The expression is defined in dimensionless time as:
The porosity is $\phi$, $\mu$ is the viscosity, $t$ is the actual time, non-wetting fluid and wetting fluid interfacial tension is represented by $\sigma$, $k$ is the rock permeability, characteristic length is $L_c$. The square characteristic length is inversely proportional to the imbibition rate.

Ma, Zhang and Morrow executed a test to study the influence of oil/brine viscosity ratio. They determined that a geometric mean of water and oil ratio is inversely proportional to the oil recovery rate, [equation 1.16]. (Morrow and Mason, 2001)

$$t_D = t \frac{\sigma \sqrt{k/\phi}}{\mu \mu^2 L_c^2}$$

The $u_o$ is the oil viscosity, the $u_w$ is the water viscosity. The other parameters are similar to the equation 1.15.

The next upscaling [equation 1.17] is based on gravity force as a function of the ratio of viscosity to gravity forces determined by (Cuiec et al., 1994):

$$t_g = \frac{L_c \mu_o}{k \Delta \rho g} \rightarrow t_D = \frac{k \Delta \rho g}{L_c \mu_o} t$$

The $t_g$ is the gravity reference time, $\Delta \rho$ is the oil-water density difference, $\mu_o$ is the oil viscosity, actual time is expressed as $t$, $g$ is the gravitational force, the permeability is $k$ and the characteristic length is $L_c$. The expression gives oil recovery dimensionless time by $t_D$.

Another upscaling expression [equation 1.18] measures the dimensionless time that derives from capillary pressure and mobility defined by Li and Horne: (Li and Horne, 2006)

$$t_D = c^2 \left( \frac{M_e^* p_c (S_{wf} - S_{wi})}{\phi L_c^2} \right) t$$

The initial water saturation is $S_{wi}$, the saturation of water at water front is $S_{wf}$, capillary pressure at water front is $p_c^*$, $M_e^*$ is the effective mobility at water displacement front, the porosity is $\phi$, $c$ is ratio of gravity force and the characteristic length is $L_c$. The ratio of gravity force is given by [equation 1.19].

$$c = \frac{\Delta \rho g L_c}{p_c^* (S_{wf} - S_{wi})}$$
2.3. Surfactants

**Surfactants**, known as Surfactants, are amphiphilic. An amphiphilic is an organic compound with two different molecular compounds in its structure, the hydrophobic and hydrophilic group. The hydrophobic group is the part of the molecule that is water-insoluble while the hydrophilic group is water-soluble.

This two compounds have a specific terminology, the tail is the hydrophobic group while the head is the hydrophilic group. The surfactants are attracted to the interface between two fluids decreasing the interfacial tension and reacting with some compounds in the rock surface that alter the rock wettability allowing imbibed water spontaneously. The surfactant can be divided as anionic, cationic, non-ionic and amphoteric. (ElMofty, 2012)

2.3.1. Types of Surfactants

**Anionic Surfactants:**

The anionic surfactants represented in figure 10 (1) have negative charge and they are the most used type of surfactant in the world. They are electrically neutralized with an organic metal cation. They can be found as soaps, sulphates, phosphates and sulfosuccinates. When dissolved in water, the molecules ionize into a cation and anionic monomer. The cations in general are quaternary ammonium or alkaline metal (Na+, K+). This surfactant changes the wettability and lowers the interfacial tension (Njafabadi, 2009).

**Non-ionic Surfactants:**

The non-ionic surfactants represented in figure 10 (2) do not have charge in their head and they are the second most used type of surfactant. This type of surfactants does not ionize in aqueous solution due to the electronegativity contrasts between their constituents. They interact due to the polarity of the molecule. These surfactants are poor compared to anionic surfactant, but work much better in high salinity. This type of surfactant is fatty acids (i.e.: ethoxylated alcohol, ethoxylated Sorbian fatty ester, sulfoxides). While, the lipophilic group is alkyl or alkyl-benzene. Normally this type of surfactant is used with a co-surfactant in a specially designed concentration to lower the IFT to ultralow values. (Mosayed and Abedini, 2012)

**Cationic Surfactants:**

These surfactants represented in figure 10 (3) have positive charge and they are the surfactants that due to their synthesis are the most expensive. This surfactant is electrically neutralized with an inorganic anion. The cationic surfactants can be such as amine oxides, amine salts, quaternary ammonium. This type of surfactants can be easily attracted by a negatively charged surface of clays. This type of surfactants don’t lower the IFT to ultralow values but change the wettability of the rock.
Amphoteric or Zwitterionic Surfactant:
The amphoteric surfactants represented in figure 10 (4) have positive and negative charge in their head. They are divided into anionic and cationic, such as betaines and sulfobetaines. This type of surfactant can be imidazole, betaines, sulfobetains, amino acids, lecithins.

![Figure 10 Different type of Surfactants, 1) Non-anionic, 2) Anionic, 3) Cationic, 4) Amphoteric (NPTEL, 2016)](image)

2.3.2. Factors that influence the surfactants performance

Surfactants are influenced by pH, salt, the class of surfactants, the purity of surfactants and the temperature.

- The surface tension and interfacial tension can be different if there is present a small amount of impurity of surfactant.
- The classes of surfactant are influential. To lower interfacial tension the better surfactants are the non-ionic and anionic. While the cationic surfactants have more effect on changing the wettability.
- The interfacial rheology properties are affected by the temperature. By increasing the temperature, the velocity of absorption and diffusion of the surfactants increases at the interface. The temperature increases the solubility of solvents and reduces of the critical micelle concentration.
- The salinity influences the surfactant-oil/water solubility. At low salinity, the surfactant is soluble in water while it is soluble in oil at high salinity.

Using a co-surfactant allows the reduction of the interfacial tension to low values. The critical micelle concentration increases when two surfactant are mixed. (Mosayed and Abedini, 2012)
2.3.3. Surfactants Mechanisms on Wettability Alteration

Injecting water with dissolved surfactant improves the oil recovery by changing the reservoir wettability to more water-wet and decreases the oil-water interfacial tension to lower the capillary pressure. This alteration accelerates the spontaneous imbibition in the reservoir that is the main mechanism to recover the oil at low permeability and fracturated reservoirs.

Gogarty in 1969, the study of surfactants is directly related to the injection of microemulsion to the reservoir with a high concentration of surfactant, co-solvent and oil. At the time due to the low oil price and chemical costs, this was not economically practical, but it achieved good results. (Austad et al., 1998) studied 2000 cases of surfactant flooding based on the reduction of the concentration of surfactant and added the polymers to maintain the mobility.

The study developed by Salehi, Johnson and Liang determined the main mechanisms that alter the wettability by using surfactants are the ion-pair formation and form a layer with surfactant molecules by interaction with the crude oil in the rock. It is possible observe in figure 11 both mechanisms.

Austad (Austad et al., 1998) studying the oil-wet chalk cores, determined that for changing the wettability toward more water-wet, the better surfactant is the cationic surfactants. He proposed that the mechanism based on interaction between the head of acid compound in the rock and the head of surfactant alter the wettability, given the name of ion-par. The original water-wet carbonate rock is exposed because the surfactant is attracted to crude oil and strips that from the rock surface.

However, the anionic surfactant interacts by its tail that is the hydrophobic part with crude oil on rock, creating a monolayer of surfactants on the surface of the carbonate. Therefore, the hydrophilic head groups alter the rock wettability toward more water-wet because it is water-soluble. The hydrophobic interaction is less strong than ion-par.

Salehi, Johnson and Liang determine that the surfactant with more charge in the head group is more efficient to change the wettability to more water-wet, because the main mechanism is the ion-pair formation. (Salehi et al., 2008)

![Figure 11 Mechanisms in Wettability alteration by Surfactant; forming a monolayer by anionic surfactants (left image) and ion-par mechanism formed by cationic surfactant (right image) (Sheng, 2013)]
2.3.4. Microemulsion

Another mechanism created by the surfactants is the emulsions or microemulsion. The difference between them is the size of the molecules and it is possible to analyse that if the emulsion is transparent then it is a microemulsion. The salinity of brine and temperature of co-solvent concentration are the main factors that control the phase behaviour of the oil-brine-surfactant system. Winsor classified phase behaviour of the system in four types, show in figure 12.

![Figure 12 Different phase by surfactant application (Mehta and Kaur, 2011)](image)

The Winsor type I system is classified when exist a pure oil and a microemulsion phase. The microemulsion is constituted by surfactant, brine and some oil in the center of the micelles. This phenomenon occurs at low brine salinity, because same surfactants exhibit poor oil-phase solubility and good aqueous-phase solubility.

The Winsor type II occurs at high brine salinity, when the surfactant solubility is very low in an aqueous phase due to the electrostatic forces. The two phases are the pure brine without surfactant and a microemulsion composed of surfactant, oil and some brine in the center of the micelles.

In the Winsor type III three phases coexist, this occurs when the brine salinity is intermediate to Winsor type I and II. The third phase behaviour is constituted by oil phase, brine phase and microemulsion phase. The microemulsion phase can be compounded by oil or water depending on the composition and salinity. This phase is the best compared with the Winsor type I and type II because it decreases the interfacial tension between the brine-oil interface by forming a new density phase.

The last type of system, the type IV is only composed by a microemulsion, which is composed by surfactant, oil and brine.

The interfacial tension between the phases in the Winsor type I decreases as brine salinity increases, while the interfacial tension between the phases in the Winsor II increases as brine salinity increases.
Figure 13 correlates the interfacial tension with the phase behaviour system developed by Reed and Healy in 1974. As can be seen, low interfacial tension is obtained in the Winsor type III where oil, water and microemulsion coexist. The interfacial tension $\sigma_{32}$ is between microemulsion-oil and $\sigma_{31}$ is between microemulsion-water. It is observed that water-microemulsion interfacial tension increases with the salinity increase, while oil-microemulsion interfacial tension decreases.

Salinity on the cross point of the two interfacial tension is called optimum salinity, and where the interfacial tension is minimized. Normally at this salinity the interfacial tension is to 1 $\mu$N/m that is a good interfacial tension to recover the oil. (Najafabadi, 2009).

Figure 13 Plot of the Optimal Salinity (Najafabadi, 2009)

In the contact of oil-water phase the surface activity degree, molecular structure and the coefficient of water/oil partition determines if the microemulsion is water-in-oil (w/o), is oil-in-water (o/w) or the formation of a liquid crystalline.

Using non-ionic surfactants there can occur a phenomenon that is phase-inversion temperature (PIT). When the temperature does the inversion between the phases within the emulsion. For example, when an o/w microemulsion changes to w/o emulsion or the opposite. The phase-inversion temperature occurs when a temperature rises, and the water-non-ionic interaction decreases. (Kanicky et al., 2001)
2.3.5. Micelles

The concentration of the surfactant is an essential factor in oil recovery. Some types of surfactants like an anionic surfactant dissolved in aqueous phase develop a cation an anionic monomer. The micelles depend on the structure of surfactant molecules, temperature, pH and ionic composition.

In a porous medium the surfactant dissolved in water, the free energy of the system increases and the entropy decreases due to the tail of the surfactant. Thus, all the surfactants accumulate in the interfaces of brine-rock surface and oil-brine to lower the surface energy of the system and lower the work needed to increase the interfacial area. When the interface is full with monomers of surfactants, the surfactants start to aggregate in liquid bulk to continue to lower the free energy of the system and form micelles in the solution to reduce the exposure of the tail to the aqueous solution. The concentration of surfactants to start forming micelles is called Critical Micelle Concentration. The micelles are thermodynamically stable with different properties from monomers.

The Critical Micelle Concentration (CMC) can be explained as it is the maximum solubility of a monomer in a solvent (Akstinat, 1981). After the Critical Micelle Concentration, the only result obtained is the formation of micelles because the concentration is spread over all the interfaces and the mechanism of changing the wettability and lowering the interfacial tension is the same of the critical micelle concentration. It is possible to analyse it by observing figure 14.

![Figure 14 Comparison between the Surfactant and Micelles with the Interfacial Tension (Behrens, 2013)](image)

*Figure 14 Comparison between the Surfactant and Micelles with the Interfacial Tension (Behrens, 2013)*
2.3.6. Model of Wettability Alteration

Some studies realized before by wettability alteration allow some researchers to model that alteration. Delshad (Delshad et al., 2009) determined the modelling that defines the relative permeability curves [equation 1.20] and capillary curves [equation 1.21] by using surfactants. (Sheng, 2013)

\[
k_r = \omega k_r^{ww} + (1 - \omega)k_r^{ow} \quad [1.20]
\]

\[
P_c = \omega P_c^{ww} + (1 - \omega)P_c^{ow} \quad [1.21]
\]

\[
\omega = \frac{C_{surf}}{C_{surf}^{*}} \quad [1.22]
\]

The relative permeability is \( k_r \), the capillary pressure is the \( P_c \), the subscript \( ow \) is oil-wet and \( ww \) is water-wet. The [equation 1.22] interpolation scaling factor is \( w \), \( C_{surf}^{*} \) is the adsorbed surfactant and \( C_{surf} \) is the equilibrium concentration of surfactant.

2.3.7. Adsorption

Adsorption is when a component of a system prefers to accumulate in an interface. Adsorbate is the name given when the component is in the adsorbed state. The material to be adsorbed in the interface is Adsorpt and Adsorbent is the place where the adsorption occurs.

The surfactant retention is caused by some mechanisms such as surfactant loss by adsorption, precipitation by divalent ions and entrapment in residual oil phase. In an interface, the higher concentration of solute indicates a positive adsorption of solute molecules.

Some parameters are important factors to understand the adsorbed mechanism, such as:

- Material adsorbed in an area;
- At which concentration of the solute the saturation occurs;
- Molecules orientation with regard to solution and surface;
- Influence on solid properties by the effect of adsorption.
Figure 15 gives the relation between concentration and distance from interface of the fluid molecules. It is possible to understand in the interfacial region, the adsorption of the surfactants depending on the concentration.

![Figure 15 Distance from the surface versus concentration of surfactants (Salehi, 2009)](image)

The simple type of absorption can be described as the [equation 1.23].

\[ r = k_H C \]  \[1.23\]

The \( r \) is the amount adsorbed, \( k_H \) is a constant in units of \( \text{L/m}^2 \) and \( C \) is the concentration.

The adsorption of the surfactant in the rock surfaces depends on the nature of the rock surfaces. The main natures of the adsorbent are such:

- Hydrophobic surfaces or nonpolar;
- Polar surfaces without significant charges;
- Strongly charged surfaces.
2.4. Measure the Wettability and Imbibition

The methods integrated in this topic are part of Special Core Analyse. It is possible to analyse a reservoir in a laboratory with sand-packs, cores or micromodels. In this topic, the analysis is made by cores and it is evaluated by different methods that can determine different parameters to guide a full evaluation of that type of rock.

The parameters are essential to analyse the wettability of the rock by quantitative methods such as the contact angle and the imbibition methods of Amott and USBM method. To study the spontaneous imbibition, it is important to determine the wettability and determine some important parameters to understand the performance of the rock to imbibition. Other methods are chosen for a complete analysis such as capillary pressure and interfacial tension. If the core samples are not clean and the porosity and permeability are not measured, it is essential to measure the porosity and permeability and clean the core. The experiments to study the wettability and spontaneous imbibition are described at next: (Anderson b, 1986)

- Imbibition process (Amott Harvey Test / USBM method and Combination);
- Contact angle (Imaging Method);
- Capillary Pressure (Centrifuge Method);
- Interfacial Tension (Capillary Rise Method);

2.4.1. Amott Harvey Test

The Amott Harvey Test was suggested by Amott (Amott, 1959) and it is the most used test to measure the wettability by quantitative measurement. This method is based on force and spontaneous imbibition of water and oil. The spontaneous imbibition of oil or water depends on the rock wettability and executed by placing a core filled with oil/brine into a flask filled with brine or surfactant/oil, and observing the recovery of the fluid. The forced imbibition/drainage of water or oil can be made by a centrifugal mechanism or by high flow pressure displacing a fluid by another fluid with constant pressure until the equilibrium. The Amott Harvey test measures the wettability by the Amott Index and the oil recovery over time by spontaneous imbibition.

The Index is the ratio of water index less the ratio of oil index:

\[ I = I_w - I_o = \frac{V_{osp}}{V_{ot}} - \frac{V_{wsp}}{V_{wt}} \]  

[1.24]

The Amott-Harvey Index [equation 1.24] is expressed by I, the water index is \( I_w \), oil index is \( I_o \) \( V_{ot} \) is the total volume of oil produced (forced and imbibition) and \( V_{osp} \) is the oil volume produced by spontaneous imbibition of water. The \( V_{wt} \) is the total volume of water produced (forced and imbibition) and \( V_{wsp} \) is the volume of water produced by spontaneous imbibition of oil.
The index values are based on the ratio of the volume of the fluid displaced by the imbibition process. If the ratio is near to 1, the volume of that fluid wets the rock. When the Amott Index is positive the rock is water-wet, inversely, if the Amott Index is negative then the rock is oil-wet. The Amott Index is near to 0 when the rock doesn’t have any preference for any fluid, (table 2).

A negative point of the Amott method is when the angle is between 60° to 120°, then the wetting fluid is not spontaneously imbibed. (Lejla, 2008)

<table>
<thead>
<tr>
<th>Wettability</th>
<th>Amott Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Wet</td>
<td>0.3 - 1</td>
</tr>
<tr>
<td>Weakly Water Wet</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>Intermediate Wet</td>
<td>-0.1 - 0.1</td>
</tr>
<tr>
<td>Weakly Oil Wet</td>
<td>-0.3 - 0.1</td>
</tr>
<tr>
<td>Oil Water</td>
<td>-1 - 0.3</td>
</tr>
</tbody>
</table>

2.4.2. USBM method

This method named United States Bureau of Mines (USBM) quantifies the wettability by USBM index, presented by Donaldson in 1969. The USBM index is determined by capillary pressure curves that areas obtained by force imbibition or drainage using a centrifugal device or linear pressure device, to displace a fluid by another fluid. (Anderson b, 1986)

Before measuring the index, it is important to know the difference between $S_w$ and $S_o$, the areas under the capillary pressure. These areas represent the work needed to displace a fluid present in the core. The displacement of wetting fluid by non-wetting fluid requires more energy that the displacement of the non-wet fluid by wetting fluid because of the spontaneous imbibition that uses the capillary pressure as a driven force.

The USBM index [equation 1.25] is based on a logarithm of the ratio between the area for displacement of the water to the area for displacement of the oil, possible analyse in figure 16. If the Index is positive, it indicates that the formation is water wet, in contrast, if the index is negative, the formation is oil wet. The Index equal to 1 indicates Strongly Water Wet, the Index equal to -1 indicates Strongly Oil Wet and the Index near to 0 indicates intermediate wet.

\[ W = \log \left( \frac{A_1}{A_2} \right) \]

The $W$ is the USBM Index, $A_1$ is the work required to displace the water and $A_2$ is the work required to displace the oil.
2.4.3. Combined USBM method and Amott test

Integration of the USBM method and the Amott test allows an analysis of the wettability by spontaneous imbibition and forced imbibition. The method starts with a core saturated with water (1) and the first process is the displacement of water by oil (2), representing the oil migration in the reservoir.

Then the sample is spontaneous imbibition by water (3), and then the displacement of oil by water until the $S_{or}$ (4). This preview process represents the water flooding into the reservoir. In order to complete the process, the sample is firstly spontaneously imbibed by oil (5) and then to finalize displacement of water by oil (6). The steps mention before are possible to observe in figure 17.

A disadvantage of the USBM method is that it is unable to recognize strongly water wet and strongly oil wet.
2.4.4. Imaging Method

The Imaging Method is another method that quantifies the wettability by the observation of the contact angle of the wetting fluid. This method allows us to determine the preference of the rock to adsorb one of the two fluids present in the system.

Measuring the wettability in a carbonate formation, a carbonate block is used, while for measuring the wettability in sandstone formation, a polished quartz is used. (Torsaeter and Abtahi, 2003) This method starts by placing a piece of rock into a cell filled with oil. Then with a syringe dropping a water droplet onto the rock surface, and analysing the angle over time by taking photos with a high-resolution camera.

This technique measures the contact angle of the wetting fluid from 0 to 180 degrees, observed in figure 18. In 0 degrees, the rock is strongly water wet, in 90 degrees the rock doesn’t have any preference for any fluid, it is intermediate or neutral, and when it has 180 degrees the rock is strongly oil wet.

![Figure 18 Different contact angles of the wetting fluid (Engler, 2010)](image-url)
2.4.5. Centrifuge Method

The Centrifuge method is used to measure the capillary pressure in a drainage and imbibition process by force. It is one of the methods more widely used in the USA oil and gas industry due to being a rapid method. The advantage of this process is that it can operate at high temperatures and it is rapid, while the disadvantage is that the capillary pressure gradient gives a saturation gradient (Glover, 2000).

The centrifuge method process starts by placing a core saturated with a fluid, brine or oil, into a core holder filled with oil or brine in a centrifugal device. Define a rotation speed to measure the volume of fluid recovery until the equilibrium of the system. After that, the rotation speed must be increased and the process repeated. The process is finished when all the volume of fluid is displaced. (Torsaeter and Abatahi, 2003).

The expression that gives a Capillary pressure by spinning the core is given as (Glover, 2000):

\[ C_p = 7.9 \times 10^{-8} (p_1 - p_2)R^2 (r_b^2 - r_t^2) \]  \[1.26\]

The expression \[1.26\], \( C_p \) is the capillary pressure [psi], \( r_b \) and \( r_t \) are the radii of the center of the apparatus to the bottom and top of the core, \( R \) is the rotation [rpm] and the phases densities are expressed by \( p_1 \) and \( p_2 \).
2.4.6. Capillary Rise Method

The interfacial tension can be measured in a laboratory by using different methods. One of the most used methods is the Capillary Rise method, observed in figure 19. This method depends on the electrostatic forces of the fluid molecules and capillary tube wall.

This method uses different liquids to measure the water and oil interfacial tension. For measuring the water interfacial tension water is used, while to measure oil interfacial tension mercury is used. This method is based on the height that the liquid rises to or lowers from the free liquid level. In the system the gravity force is opposed by the capillary suction. (Torsaeter and Abtahi, 2003).

![Figure 19 Capillary Rise Method (Glover, 2000)]

The [equation 1.27] that determines the interfacial tension in this method is given as:

\[
\sigma = \frac{gphr}{2 \cos \theta} = \frac{r\Delta p}{2 \cos \theta}
\]  

[1.27]

The \(\sigma\) is the interfacial tension, \(g\) is the gravitation acceleration, \(p\) is the fluid density, the height the fluid rises or falls to compare with the free level is expressed by \(h\), \(\theta\) is the contact angle of the wetting phase, capillary tube radius is \(r\) and \(\Delta p\) is hydrostatic pressure.
3. Materials

The materials used in this study are the synthetic brine, surfactant, synthetic oil and core samples. All the materials are prepared in the laboratory of Surfactants in Enhanced Oil Recovery Laboratory within the Ite at the Institute of Technological University of Clausthal.

3.1. Synthetic Brines

The synthetic brines used are composed of a mixture of different salts and de-ionized water. The concentration of the salts in de-ionized water depends on the experiment required for the study.

The main concentration of salt used in this study is 95 000 and 3 400 ppm. The Brine High Salinity (95 000 ppm) is considered brine (table 3), while Brine at Low Salinity (3 400 ppm) is considered Highly Brackish water (table 4).

<table>
<thead>
<tr>
<th>Table 3 Composition of High Salinity Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Salinity Brine</strong></td>
</tr>
<tr>
<td>pH=7</td>
</tr>
<tr>
<td>95000 ppm</td>
</tr>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>MgCl2x6H2O</td>
</tr>
</tbody>
</table>

| pH=7                                      |
| (95g/L)                                   |
| (g/L)                                     |
| 75,82                                     |
| 40,95                                     |

<table>
<thead>
<tr>
<th>Table 4 Composition of Low Salinity Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Salinity Brine</strong></td>
</tr>
<tr>
<td>pH= 8,5</td>
</tr>
<tr>
<td>3 400 ppm</td>
</tr>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Sr</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>SO4</td>
</tr>
<tr>
<td>HCO3</td>
</tr>
<tr>
<td>Acetate</td>
</tr>
</tbody>
</table>

| pH= 8,5                                   |
| (3,4 g/L)                                 |
| (g/L)                                     |
| 0,68                                      |
| 0,6                                       |
| 0,071                                     |
| 0,003                                     |
| 0,01                                      |
| 0,0016                                    |
| 0,0019                                    |
| 0,292                                     |
| 0                                         |
| 0,0045                                    |
| 1,818                                     |
| 0                                         |
3.2. Synthetic Oil

The synthetic oil is composed of a mixture of Decane (C\textsubscript{10}H\textsubscript{22}) and Tracer (C\textsubscript{30}H\textsubscript{18}) with 500 ppm. Then it is mixed for 1 hour. The tracer is used in small amounts on the decane, it increases an insignificant decane density, so the decane characteristics are used, (table 5).

<table>
<thead>
<tr>
<th>Table 5 Decane Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Decane</strong></td>
</tr>
<tr>
<td>Chemical formula</td>
</tr>
<tr>
<td>Molar mass</td>
</tr>
<tr>
<td>Appearance</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Boiling point</td>
</tr>
</tbody>
</table>

3.3. Surfactant

The surfactant used is Calamide C® a Non-ionic Surfactant, (table 6). The Calamide C® is known as Coacamide DEA, the molecule is observed in figure 20, and it is a coconut fatty acid amide of diethanolamine. The hydrophilic group is a polymerized alkene oxide. It is a mixture of Calamide C®, isopropanol and brine. The non-ionic surfactant is used with a solvent like isopropanol to improve the performance.

The surfactant used was mixed before the experiments during one hour with different weight percent of different compounds depending on the experiment. It is used 1 wt%, 2wt% and 4 wt% of calamide. In all the experiments are used 1 wt% of isopropanol. The other wt% is constitute by brine with the salinity pretend for the experiment.

![](Figure_20_Coacamide_DEA_Molecule_Monographs_2016.png)

<table>
<thead>
<tr>
<th>Table 6 Characteristics of Cocamide DEA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cocamide DEA</strong></td>
</tr>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>Mol. Wt</td>
</tr>
<tr>
<td>Melting Point</td>
</tr>
<tr>
<td>Boiling Point</td>
</tr>
<tr>
<td>Specific Gravity</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Solubility in Water</td>
</tr>
</tbody>
</table>
3.4. Cores

The core samples used in this study are cylindrical samples of Bentheimer (table 7), a sandstone from Nordhorn in Germany and a Carbonate (table 8) from France, taken from outcrops. The characteristics of the different cores used in this study are presented next. The parameters of volume and saturation of water and oil are used to analyse the spontaneous imbibition of each core in different environments. The carbonates are heterogeneity rock so it is difficult to know the mineral composition of the carbonate rock in this study.

The Bentheimer is sandstone very studied in geothermal engineering, wellbore drilling and petroleum recovery. (Al-Yaseri et al., 2015) The mineral composition of Bentheimer was determined by X-ray Fluorescence and X-ray Diffraction. Mineral: Quartz 91.7 wt%, Kaolinite 2.5 wt%, Montmorillonite 0.18 wt%, Orthoclase 4.86 wt%, Dolomite 0.26 wt%, Calcite 0.15 wt%, Hematite 0.16 wt%, Rutile 0.03 wt%, Pyrite 0.01 wt%, Ca-phosphate 0.07 wt%, Halite 0.03. (Hemert et al., 2013)

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Core N1</th>
<th>Core N2</th>
<th>Core N4</th>
<th>Core N5</th>
<th>Core N6</th>
<th>Core U1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenght [mm]</td>
<td>59,94</td>
<td>60,09</td>
<td>60,13</td>
<td>60,09</td>
<td>60,11</td>
<td>60,16</td>
</tr>
<tr>
<td>Diameter [mm]</td>
<td>29,10</td>
<td>28,87</td>
<td>29,61</td>
<td>29,44</td>
<td>29,55</td>
<td>29,11</td>
</tr>
<tr>
<td>Area [mm²]</td>
<td>664,75</td>
<td>654,28</td>
<td>688,25</td>
<td>680,37</td>
<td>685,46</td>
<td>665,20</td>
</tr>
<tr>
<td>Volume [mm³]</td>
<td>39 844,87</td>
<td>39 315,65</td>
<td>41384,5</td>
<td>40 883,44</td>
<td>41 203,24</td>
<td>40 018,60</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>23,10</td>
<td>24,50</td>
<td>23,22</td>
<td>23,56</td>
<td>24,00</td>
<td></td>
</tr>
<tr>
<td>Permeability [D]</td>
<td></td>
<td></td>
<td>1,64</td>
<td>1,85</td>
<td>2,3</td>
<td>2,57</td>
</tr>
<tr>
<td>Pore Volume [mm³]</td>
<td>9 204,16</td>
<td>9 632,33</td>
<td>9613,62</td>
<td>9 493,14</td>
<td>9 707,48</td>
<td>9756,53</td>
</tr>
<tr>
<td>Volume of Oil [mm³]</td>
<td>7 000,00</td>
<td>8 000,00</td>
<td>6 500,00</td>
<td>7 500,00</td>
<td>8 300,00</td>
<td>7000,00</td>
</tr>
<tr>
<td>Volume of Water [mm³]</td>
<td>2 204,16</td>
<td>1 632,33</td>
<td>3 113,62</td>
<td>1 993,14</td>
<td>1 407,48</td>
<td>2 756,53</td>
</tr>
<tr>
<td>Oil Saturation (%)</td>
<td>76,05</td>
<td>83,05</td>
<td>67,61</td>
<td>79,00</td>
<td>85,50</td>
<td>71,75</td>
</tr>
<tr>
<td>Water Saturation (%)</td>
<td>23,95</td>
<td>16,95</td>
<td>32,39</td>
<td>21,00</td>
<td>14,50</td>
<td>28,25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Core FR8</th>
<th>Core FR9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenght [mm]</td>
<td>59,77</td>
<td>60,12</td>
</tr>
<tr>
<td>Diameter [mm]</td>
<td>29,46</td>
<td>29,39</td>
</tr>
<tr>
<td>Area [mm²]</td>
<td>681,29</td>
<td>678,06</td>
</tr>
<tr>
<td>Volume [mm³]</td>
<td>40721</td>
<td>40765,03</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>25,97</td>
<td>28,20</td>
</tr>
<tr>
<td>Permeability [D]</td>
<td>0,25</td>
<td>0,14</td>
</tr>
<tr>
<td>Pore Volume [mm³]</td>
<td>10 575,24</td>
<td>11 495,74</td>
</tr>
<tr>
<td>Volume of Oil [mm³]</td>
<td>7 000</td>
<td>8 000</td>
</tr>
<tr>
<td>Volume of Water [mm³]</td>
<td>3 575,24</td>
<td>3 495,74</td>
</tr>
<tr>
<td>Oil Saturation (%)</td>
<td>66,19</td>
<td>69,59</td>
</tr>
<tr>
<td>Water Saturation (%)</td>
<td>33,81</td>
<td>30,41</td>
</tr>
</tbody>
</table>
4. Methodology

The methodology is proposed to study the objectives of this thesis, figure 21. The Amott Harvey Test measure the oil recovery by spontaneous imbibition and rocks wettability by brine imbibition. It is used Brine or a Non-ionic surfactant in Sandstone and Carbonate rock. The Two-Phase Separation Method is a method that measure the wettability of the rock by observing the rock grains preference by a fluid. All the procedures are explained at front.

Sample dry and clean

Saturate the sample with brine

Saturate the Sample with oil

Crush the rock into powder

Wash with solvent

Dry the sample into an oven

Amott Harvey Test

Two-Phase Separation Method

Imbibide the sample with synthetic oil

Figure 21 Experimental Design
4.1. Amott-Harvey test

The objectives of the Amott test is to measure the wettability by water imbibition and the oil recovery by spontaneous imbibition of water over time. The main mechanism of the spontaneous imbibition is the interaction between rock and aqueous phase, brine or surfactant. The capillary forces will attract the aqueous phase and displace the oil out of the rock, without any external forces. It will be executed with different brine salinities, different composition of the surfactant and different types of rocks for study the different environment and the mechanism of different recovery.

Figure 22 Amott Harvey Preparation Steps
4.1.1. Measure the Pore Volume
The fluids like oil, surfactant and brine for the experiments are prepared before. It is used a core dry and clean, with porosity and permeability measured. It is calculated the pore volume of the cores that is the total volume occupied by the fluids and it is important to know the volume of which fluid in the core. The steps to calculate the water and oil saturation are observed in figure 23.

4.1.2. Saturating a sample with brine
The sample is placed into an empty vial. It is closed a capsule that keeps inside a sample and a vial, figure 22 (2 left image). The capsule is bond to a pump figure 22 (2 right image) by a vial. The pump is turned on and the pressure inside the capsule starts to decrease to vacuum pressure, $7 \cdot 10^{-1}$ hPa. At this pressure all the pores will be filled with brine. So, the valve in the pipe bonded to a vial filled with brine is opened and the vial with the sample starts to fill with brine due to pressure difference. In this process the brine migrates through the pores of the sample and saturates the sample 100%. The sample continues for some minutes in this environment and then the pump is turned off. This process represents the cores before the oil migration into the reservoir rock.

4.1.3. Saturating a sample with oil
Firstly, it is necessary to clean the pipes of the coreflooding system with a solvent, in this case isopropanol, before starting to inject oil into the core sample. A sample fully filled with brine is placed into a hassler core holder of the coreflooding. The flow rate of the pump is set in 2 ml/m and the confining pressure is set in 50 bars. Then the system is closed with open valves for the oil flows through the sample. The pump is turned on and the injection of the oil starts until $S_{wi}$. This procedure is analysed by the pressure difference of the core system, and it allows analyse the equilibrium of the fluids in the system. When the system reaches an equilibrium ($S_{wi}$), difference pressure equal to 0, the fluids did not move inside the core and the volume of water and oil in the core are constant after that point. The pump is turned off and it is determined the volume of oil and water in the core by the volume of water recovery observing a vial with a scale. The volume of the oil in the core is the subtraction of the volume of water recovery less 0.05 ml that is the water inside the pipes of the system before the experiment starts. Volume of water is the volume to reach 1, and then it is possible calculate the saturation in the core. This process represents the oil migration and it is to gives a real saturation with oil and water in a reservoir before a waterflooding. Possible to observe in figure 23. After this step the core should submit to aged time but it is not possible. Aging the core will allow study the real wettability and environment of a reservoir.

4.1.4. Amott Harvey test measurement
An Amott Harvey cell is clean and it is placed in a safe place, figure 22 (4). A sample saturated with oil and water is placed inside the Amott Harvey cell, then the cell is filled with brine or surfactant. After this moment, the cell is closed and then it is recorded the time and the recovery over time.
4.2. Two-Phase Separation Method

This process determines the wettability of the rock by a qualitative measurement. The wettability is measured by the interaction between the rock grains saturated with oil and brine or oil. The rock grains will stand in the phase that have high interactions. If the rock grains are in oil phase, the rock is oil-wet, if the rock grains sink to water phase then the rock is water-wet, and if the rock grains are in the interface of the two phases the rock is intermediate wet, observed in figure 25. This phenomenon happens due to the chemical attraction between the rock and the fluids. It shows us the real behaviour of the reservoir in the presence of the two fluids. The preparation is observed in figure 24.
4.2.1. Crushing the rock into powder
The rock is milt by a hummer or a special apparatus. The size of the grains should be between 53 to 300 µm, to analyse only the interactions between the water or oil and rock grains, without count the weight of them.

4.2.2. Washing with a solvent
Before starting the wettability measurement of the rock, the grains are cleaned to restore the wettability. This process has the objective to eliminate all the fluids present in the rock grains. So, the grains are introduced into a vial filled with a solvent, in this case, isopropanol is used.

4.2.3. Drying a sample in an oven
The sample is placed into an oven to evaporate all the solvent used to clean the core sample. After some minutes, the sample is taken from the oven dry and clean from other fluids and waste.

4.2.4. Imbibide the sample with synthetic oil
In this step, the objective is to restore the wettability equal to reservoir wettability. It was not possible to imbibe the sample and then aging with the same environment at the reservoir. Therefore, the only procedure to try restore the wettability is by imbibing the rock grains with synthetic oil. The oil used during all the experiments.

4.2.5. Two Phase Saturation analyse
0.2g of crushed rock, 10ml of oil and 10ml of brine is placed in a vial with 20ml. The vial is gently shaken and then is placed in a structure to settle the compounds. The wettability is measured by observing where the rocks grains are when the compounds settle.

![Figure 25 Two Phase Separation Method Apparatus (Salehi, 2009)](image-url)
5. Results and Discussions

In this chapter, it is present the results from the experiments mentioned before. This experiment is based on the study of the wettability and oil recovery by spontaneous imbibition of aqueous phase at different salinities (brine or surfactant) in different cores, carbonates and sandstones. The wettability is measured by observing the preference of the rock by brine and/or oil.

5.1. Wettability Measurement

The analysis of wettability was executed by analysing the spontaneous imbibition of brine in Amott Harvey Test and observing the preference of the rock grains by a fluid in the Two-Phase Separation Method.

The results are equal for all the cores (carbonates and sandstones) measure the wettability by Amott Harvey Test. The carbonates and sandstones imbibe spontaneously water between 15 to 30% of OOIP, so the rocks are water-wet. This happens due to the positive capillary pressure that drives the brine into the core by attraction of the rock to the fluid.

The result of Two-Phase Separation Method indicates that all the cores are water-wet. The rock grains sink to aqueous-phase due to the high molecular interaction between water and the rock grains.

It is possible conclude that the rock used in this study are Water-Wet. Measure the real wettability of the rocks in this experiments, the cores should aged in the same environment of the reservoir. This step will change the wettability of the rocks toward more oil-wet by the oil-rock interaction and mechanism resulting by the high pressure and high temperature.

5.2. Spontaneous Imbibition

The results of the experiments by spontaneous imbibition are present at next. These experiments are executed with all faces open of the cores, at room temperature for carbonates and sandstones, at different salt environment and using brine or non-ionic surfactant of different concentrations. The experiments for recovery the oil by brine are studied in carbonate at low salinity and in sandstone at low and high salinity. The recovery of the oil by surfactant are studied in carbonate at low salinity and in sandstone at low and high salinity. It is used different surfactant concentration in the experiments with surfactant. The variations in surfactant is in same cases it is used 1 wt%, 2wt% or 4w% of Calamide.
5.2.1. Comparison of the oil recovery by surfactant and brine at high salinity in sandstone

The first experiment of spontaneous imbibition is to compare the imbibition of brine and surfactant at high salinity in sandstones. The Core N1 was immersed in surfactant while the Core N2 was immersed in brine. The $S_w$ of Core N1 is 23.95% of $P_v$ and the Core N2 is 16.95% of $P_v$. The brine used has 95 000 ppm of salt and the surfactant used with a mixture of 2wt% of calamide + 1wt% of isopropanol + 97wt% of brine with 95 000 ppm of salt. The pH of the Brine is 7, so it is neutral.

![Figure 26 Oil Recovery with brine and surfactant at High Salinity in Sandstone](image)

By analysing the figure 26, it is possible to visualize that the oil recovery by surfactant (N1) is recovered mostly in the first hour and then start stabilized. In brine (N2) the oil recovery continued to increase slightly over the time.

The oil recovery in surfactant (N1) in the first hour is 80% of OOIP, while in brine (N2) it is 20% of OOIP. A huge difference shows that the surfactant has a large impact on spontaneous imbibition in the first hour due to some unknown mechanism in this environment. The recovery after 200 hours in surfactant (N1) is 96% of OOIP, while in brine (N2) it is 32% of OOIP.

The cores are water-wet, because they imbibe brine spontaneously until 30% of OOIP (N2) only by capillary forces. The surfactant recovery almost all the oil in the core and it shows that the capillary forces has more strong than using brine. This result show that the rock has high interaction with the water phase.

The surfactant used has a good performance in high salinity. The surfactant increases the oil recovery by some mechanism, low interfacial tension and/or change the wettability of the rock toward more water-wet.
The microemulsion described in this case was possibly formed during the delay in the introduction of surfactant, which allowed for the occurrence of some reaction with the oil. The experiment was not done according the planned because the lack of sufficient volume of surfactant to fill all the Amott cell. So, it was necessary to obtain more surfactant and fill the Amott cell. With the additional injection of surfactant the microemulsion was generated.

It is possible to analyse that the emulsion decreases over time by observe the figure 27, and the density and colour are similar to the surfactant of that microemulsion. Due to high salinity at this point, the microemulsion was not formed.

It can be concluded that the main mechanism of this surfactant was to change the wettability and interfacial tension in this environment, because the microemulsion was not formed and it is difficult to conclude one mechanism.
5.2.2. Comparison of the oil recovery by surfactant and brine at low salinity in sandstone

The second experiment of spontaneous imbibition is to compare the imbibition brine and surfactant in sandstones at low salinity and at room temperature. The Core N5 was immersed in brine while the Core N6 was immersed in surfactant. The \( S_w \) of Core N5 is 21% of \( P_v \) and the \( S_w \) of Core N6 is 14.5% of \( P_v \). The brine used has 3 400 ppm of salt and the surfactant used with a mixture of 2wt% of calamide + 1wt% of isopropanol + 97wt% of brine with 3 400 ppm of salt. The pH of the Brine is 8.5, so it is basic.

![Comparison of Oil Recovery by Brine and Surfactant in Sandstone at Low Salinity](image)

*Figure 28 Oil Recovery with Brine and Surfactant at Low Salinity in Sandstone*

Analysing the figure 28, the spontaneously imbibition of aqueous phase determine that both cores are water-wet because the driven force for imbing water phase was the capillary pressure. It is possible to analyse that the surfactant has a good performance in low salinity.

The core imbibed in surfactant (N6) until the first hour recovered the twice the amount of the oil recovery of the core imbibed in brine (N5). With the oil recovery of 20% of OOIP in surfactant solution (N6). After the first hour the core imbibed in surfactant (N6) has a high rate of oil recovery, while in brine the oil recovery has a very low rate. This should be because the mechanism of the surfactant that recovery more oil.

The oil recovery by surfactant represented in the figure 28 is combination of the oil phase and the microemulsion phase. Therefore, the recovery is high than 100% of OOIP, because it has in the mixture oil, surfactant and brine.
This system (N6) is constituted by three phases: Surfactant (brine and surfactant), Microemulsion (brine, surfactant and oil) and Oil. The surfactants near the optimum salinity form a microemulsion due to the solubility of the surfactant at brine and oil. The main compound of this microemulsion formed is oil, identified by the green colour, and the minor compound water.

![Comparison between the Volume of Oil and Microemulsion Recovery in Core N6](image)

*Figure 29 Comparison of the volume of oil and microemulsion recovery in Core N6*

Analyse the figure 29, it is observed that the microemulsion described in this experiment increases over time. The recovery of oil increases in the first hours by oil phase but after that, the oil is recovered in the microemulsion. The system equilibrates after 148 hours and after that the oil is not recovered.

Analysing the recovery of oil and the phases involved, it can be concluded that the main oil recovery mechanism in this environment is the low interfacial tension between water and oil. At this salinity, the surfactant gain solubility to oil and form a mixture of 3 compounds between the water and oil phase. This new phase decrease the interfacial tension and a capillary pressure between water and oil phases and allows the recovery of more oil.
5.2.3. Comparison of the oil recovery by surfactant and brine at low salinity in carbonate

This Experiment of spontaneous imbibition is to compare the imbibition of brine and surfactant in carbonates at low salinity and at room temperature. The Core FR9 was immersed in brine while the Core FR8 was immersed in surfactant. The $S_{wi}$ of Core FR8 is 33.81% of $P_v$ and the Core FR9 is 30.41% of $P_v$. The brine used has 3 400 ppm of salt and the surfactant used with a mixture of 2wt% of calamide + 1wt% of isopropanol + 97wt% of brine with 3 400 ppm of salt. The pH of the Brine is 8.5, so it is basic.

![Comparison of Oil Recovery by Brine and Surfactant in Carbonate at Low Salinity](image)

*Figure 30 Oil Recovery with brine and surfactant at Low Salinity in Carbonates*

After one hour, the oil recovered by brine (FR9) was 10% of OOIP. Over time the oil recovered by brine (FR9) reached a maximum of 25% of OOIP. The rate of oil recovery is low compared with the surfactant. During the first hour using surfactant (FR8), the oil recovery is 22% of OOIP, after that the oil recovery rate increases over time with a maximum recovery of 92% of OOIP after 168 hours.

By analysing the figure 30, it is possible to understand that the cores analysed in this are water-wet because they imbibe water phase spontaneously. The surfactant has a good performance in low salinity like in the second experiment.
The surfactant (FR8) recovered more oil than the brine (FR9) by lowering the interfacial tension and/or changing the wettability. The curve of oil recovery by surfactant (FR8) is split into two phases, the oil phase and the microemulsion phase that contains oil. The different recovery volumes by phase using surfactant are shown in figure 31.

![Comparison between the Volume of Oil and Microemulsion Recovery in Core FR8](image)

*Figure 31 Comparison of the volume of oil and microemulsion recovery in Core FR8*

In this system (FR8), it is possible to observe 2 different phases that the oil was recovery: Microemulsion phase and Oil phase. The microemulsion described in this case increases over time and it is constituted by water, surfactant and oil. It is a water in oil emulsion because the colour of the microemulsion is green like the colour of the synthetic oil used that shows that the oil is the compound with higher percentage in the mixture. This is the justification for the oil recovery is higher than the OOIP.

The recovery of oil increases in the first hour but after 72 hours stabilizes. The oil after 72 hours is recovered in a microemulsion and stabilizes after 192 hours of the beginning of the experiment.

It can be concluded based on the results presented by figure 31 that the main mechanism in this environment is the decrease of the interfacial tension and the capillary pressure by forming a new phase.
5.2.4. Comparison of the oil recovery by different surfactants at low salinity in sandstone

This Experiment of Spontaneous imbibition, it is to compare the imbibition of different concentrations of surfactants in sandstones at low salinity and at room temperature. The Core N4 was immersed in surfactant with 4 wt% of calamide while the Core U1 was immersed in surfactant with 1% of Calamide. The $S_{wi}$ of Core N4 is 32.38% of $P_v$ and the Core U1 is 28.25% of $P_v$. The brine used has 3 400 ppm of salt and the surfactant used is a mixture of 4 wt% of calamide + 1wt% of isopropanol + 95wt% of brine with 3 400 ppm of salt and 1 wt% of calamide + 1wt% of isopropanol + 98wt% of brine with 3 400 ppm of salt. The pH of the Brine is 8.5, so it is basic.

![Comparison of Oil Recovery by different Surfactants in Sandstone at Low Salinity](image)

Figure 32 Oil Recovery at Low Salinity in Sandstones with different concentration of surfactants

By analysing the figure 32, it is possible to understand that the surfactant with different concentration has a different performance.

Until the first 10 minutes the surfactant with 4% of calamide (N4) has a better performance than the 1% calamide (U1), but after that, the 1% calamide has the best performance. After one hour of the experiment starting, the oil recovered by the surfactant with 1% calamide (U1) is more than the oil recovery by the surfactant with 4% calamide (N4). This may be explain by from a microemulsion in 1% calamide (U1).

The surfactant with 1% calamide (U1) continues with a high rate of oil recovery with a final recovery of about 110% of OOIP after 168 hours of the experiment starting. This value (U1) over 100% means that this oil recovery is accounting for a proportion of water and surfactant present in the microemulsion, and not exclusively oil. This value is a mixture of the oil phase and microemulsion phase. While the surfactant with 4% calamide (N4), continues recovering oil with a low rate over time. The last recovery is 36% of OOIP, with oil phase and microemulsion after 48 hours of the experiment starting.
In figure 33 it is observed the surfactant with 4 wt% calamide (N4) increases the oil recovery over time. This surfactant needs some time to start forming a microemulsion compared with the surfactant with 1 wt% calamide (U1). The microemulsion formed by this surfactant is small compared with the total volume recovery. In this case, recovery percentage is initially very fast but then it stabilizes.

The concentration of 1 wt% of calamide in surfactant (U1) tends to form more microemulsion compared with 4 wt% of calamide (N4), observed in figure 33 and 34. Most of the oil is recovered through the microemulsion in 1 wt% calamide (U1). Both microemulsion are water in oil because the colour of microemulsions are mainly the colour of the oil. It can be concluded that the main mechanism of 1 wt% and 4 wt% of calamide are to lower interfacial tension caused by the formation of the microemulsion.
5.2.5. Comparison of the performance of different surfactants with viscosity and their concentrations

Comparison of the different surfactant concentration in the surfactant solution by analysing the viscosity of the surfactant is possible by analysing figure 35.

![Rheology of Surfactants](image)

*Figure 35 Comparison of the viscosity of the different concentration of surfactant*

All the concentration of the surfactant reduces the viscosity by the application of the shear rate, observing the figure 35.

The viscosity of the surfactant is not linear depending on the surfactant concentration, because the 2 wt% calamide has a higher viscosity than the 4wt% and 1wt%. The 1wt% calamide has a lower viscosity than the 4wt% and 2wt%. 
5.2.6. Comparison of the performance of different surfactants on sandstone and carbonate

Compare the performance of different environments and different concentrations of surfactants in figure 36.

![Comparison of Oil Recovery by Surfactants](image)

**Figure 36 Comparison of the Oil Recovery by Surfactants**

Until the first hour the surfactant with 2wt% of calamide (N1) at high salinity has the best performance of all tests. Over time, the surfactant with 1wt% of calamide (U1) at low salinity has a higher volume of microemulsion.

The surfactant on the carbonate and sandstone at low salinity has similar performance, it is possible conclude by observing the recovery in N6 and FR8. They have a similar performance over the time. The surfactant with 4wt% calamide (N4) has the lowest recovery of oil, but most of the oil is recovery exclusively in oil phase.

In the range of concentration used in this study, it is possible to understand that by decreasing the surfactant concentration the oil recovery increases by microemulsion. This means that it was not possible to find the optimal surfactant concentration. The volume of microemulsion is inversely proportional with the weight percentage of calamide present on the surfactant. Decreasing the calamide allows to form more volume of microemulsion and to decrease the interfacial tension in the system.

Thus, the main mechanism of this surfactant is lower the interfacial tension and change the rock wettability. Because all the scenarios except at high salinity the main mechanism is low the interfacial tension. At high salinity is difficult understand the mechanism so it is change the rock wettability and low the interfacial tension.
5.2.7. Comparison of the performance of different brines on sandstone and carbonate

In figure 37, it is possible to analyse the different oil recoveries by brine in different environments.

![Comparison of the Oil Recovery by Brines](image)

*Figure 37 Comparison of the Oil Recovery by Brine*

It is possible to understand that the rocks have the same wettability. They are water-wet, because they imbibe brine spontaneously only by capillary forces. At high salinity (N2), the recovery of oil is greater than at low salinity (N5) in sandstones. This is possible due to the low pH of the brine that forms an acid surface at the sandstone that adsorbs only the basic compounds of crude oil or due to some salt compound in the brine. By this way, a more water-wet reservoir is formed because it is more difficult to change oil wettability of the rock.

The brine at low salinity with pH equal to 8.5 has a better performance in carbonate (FR9) than in sandstones (N5). Brine with pH higher than 8 allows the carbonate to form an acid surface adsorbing only the basic compounds of the oil, while in sandstones form a basic surface adsorbing only the acid compounds of the oil.

So, decreasing the pH of the brine can be the main mechanism to recovery oil in this type of sandstone, while in other hand, increasing the pH can be the main mechanism to recovery oil in this type of carbonate.
6. Conclusions

The carbonate and sandstone were both water-wet in this study. The cores were taken from an outcrop and in these experiments they were not submitted to aging with crude oil. Both rocks imbibed an amount of brine spontaneously that allowed to determine that they were water-wet rocks. The two-phase separation method also confirmed that the rocks were water-wet because the crushed rock sank into the water-phase. The results showed that there was a larger interaction between rock and water than between oil and rock.

Analysing the oil recovery results using brine, it was possible to conclude that the brine at high salinity recovered more oil in sandstones than the brine at low salinity. This might be explained by the specific chemical composition of the brines or due to a low pH that created an acid surface with the sandstones which adsorbs only the basic compounds of crude oil. For the carbonates was the opposite because in order to create an acid surface that adsorbs only the basic compounds of the crude oil it was necessary to increase the pH.

The viscosity of the surfactants did not influenced the spontaneous imbibition, because it was not linearly dependent on the concentration of the surfactant. However, the oil recovery by microemulsion had an inverse linear dependence on the surfactant concentration. Decreasing the concentration of the surfactant, increased the oil recovery by forming a microemulsion. The microemulsion had intermediate density between oil and water phase that allowed both interfacial tension and capillary forces to decrease. These resulted on an easier water imbibition by the rock and consequently a larger oil recovery.

The used non-ionic surfactant increased the oil recovery by the alteration of the wettability and by lowering the interfacial tension. At high salinity, the surfactant did not form a microemulsion, leading to the conclusion that the main mechanism was the Wettability alteration and lower the interfacial tension. While using the surfactant with 1wt% and 2wt% of calamide at low salinity the main mechanism of surfactant was by form the microemulsion that low the interfacial tension. Therefore, using the surfactant with 4wt% of calamide at low salinity it was difficult to understand the mechanism because the microemulsion formed was insignificant compared with other surfactant concentrations, but the main mechanism was the decrease of interfacial tension too.

Analysing the results, it was possible to determine that the surfactant had a good performance either in high salinity and low salinity. In low salinity the surfactant forms microemulsion by achieving the Windsor type III, with three different phases. It was a good indicator of the decrease of interfacial tension between oil-water phases.
7. Future Work

This study has some very important points that need further development in the future to complement this analysis. The more important points are described as follows:

- Analyse the oil recovery at high salinity by different concentrations of surfactant, to compare with the experiments at low salinity and understand if have the same behaviour.
- Determine if the different concentrations of salts influence the recovery of oil.
- Execute a spontaneous imbibition with carbonate at high salinity to understand if the pH of the brine changes the properties of the carbonate.
- Execute the spontaneous imbibition at high temperature and high pressure to approximate the experiment to reality and analyse the results.
- Measure the wettability of the rocks but in the preparation of the core, they need to submit to aging time.
8. References


Behrens, E.J. (2013). *Investigation of loss surfactants during enhance oil recovery applications-adsorption of surfactants onto clay materials*. Norwegian University of Science and Technology


ElMofty, O (2012). *Surfactant enhance oil recovery by wettability alteration in sandstones reservoirs*. Missouri University of Science and Technology

Engler, T. W. (2010). *Multiphase Phenomena*. Research University, Faculty of New Mexico Tech


Mosayed, A. and Abedini, R. (2012). *The effect of non-ionic surfactants on the interfacial tension between crude oil and water*. Department of Petroleum Engineering, Mahallat Branch, Islamic Azad University, Mahallat, Iran


Olsen, M. (2007). *Enhanced oil recovery in limestone. Chemical effects of seawater injection on the rock surface at different temperatures*. Faculty of Science and Technology, Stavanger


Tangen, M. (2012). *Wettability Variations within the North Sea Oil Field Frøy*. Trondheim: Norwegian University of Science and Technology


9. Appendix

It is presented here the different images taken during the spontaneous imbibition of the different environments.

9.1. Spontaneous imbibition in Bentheimer at high salinity using surfactant

Figure 38 After 1 hour

Figure 39 After 1 hour and 30 minutes

Figure 40 After 2 hours and 30 minutes

Figure 41 After 3 hours and 30 minutes
9.2. Spontaneous imbibition in Bentheimer at high salinity using brine
Figure 46 After 2 hours and 30 minutes

Figure 47 After 48 hours

Figure 48 After 168 hours

Figure 49 After 552 hours
9.3. Spontaneous imbibition in Bentheimer at low salinity using Surfactant

Figure 50 After 2 hours

Figure 51 After 20 minutes

Figure 52 After 48 hours

Figure 53 After 120 hours
9.4. Spontaneous imbibition in Bentheimer at low salinity using Brine

*Figure 54 After 20 minutes*

*Figure 55 After 24 hours*

*Figure 56 After 48 hours*
9.5. Spontaneous imbibition in Carbonate at low salinity using Surfactant

Figure 57 After 10 minutes

Figure 58 After 1 hour

Figure 59 After 22 hours

Figure 60 After 3 hours
Figure 61 After 24 hours

Figure 62 After 168 hours

Figure 63 After 366 hours
9.6. Spontaneous imbibition in Carbonate at low salinity using Brine

*Figure 64 After 10 minutes*
*Figure 65 After 24 hours*

*Figure 66 After 168 hours*
*Figure 67 After 366 hours*
9.7. Spontaneous imbibition in Bentheimer at low salinity with 4% Calamide in Surfactant

Figure 68 After 10 minutes

Figure 69 After 30 minutes

Figure 70 After 2 hours

Figure 71 After 24 hours
9.8. Spontaneous imbibition in Bentheimer at low salinity with 1% Calamide in Surfactant

Figure 72 After 10 minutes

Figure 73 After 30 minutes

Figure 74 After 1 hour

Figure 75 After 24 hours
9.9. Tables of the results from spontaneous imbibition realized in this study at EOR laboratory.

**Table 9 Results of Oil Recovery by spontaneous imbibition in Sandstones at high salinity**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Core N1 (Surfactant)</th>
<th>Core N2 (Brine)</th>
<th>Oil Recovery % from OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>After (h)</td>
<td>Oil (ml)</td>
<td>Microemulsion (ml)</td>
<td>Core N1 joint (ml)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>1,5</td>
<td>5,5</td>
</tr>
<tr>
<td>2</td>
<td>4,7</td>
<td>1,3</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1,2</td>
<td>6,2</td>
</tr>
<tr>
<td>24</td>
<td>5,4</td>
<td>1,2</td>
<td>6,6</td>
</tr>
<tr>
<td>48</td>
<td>5,9</td>
<td>0,7</td>
<td>6,6</td>
</tr>
<tr>
<td>168</td>
<td>6,6</td>
<td>0</td>
<td>6,6</td>
</tr>
<tr>
<td>216</td>
<td>6,6</td>
<td>0</td>
<td>6,6</td>
</tr>
</tbody>
</table>

**Table 10 Results of Oil Recovery by spontaneous imbibition in Sandstones at low salinity**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Core N6 (Surfactant)</th>
<th>Core N5 (Brine)</th>
<th>Oil Recovery % from OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>After (h)</td>
<td>Oil (ml)</td>
<td>Microemulsion (ml)</td>
<td>Core N6 joint (ml)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0,166</td>
<td>0,6</td>
<td>0</td>
<td>0,6</td>
</tr>
<tr>
<td>0,33</td>
<td>1,1</td>
<td>0</td>
<td>1,1</td>
</tr>
<tr>
<td>0,5</td>
<td>1,4</td>
<td>0</td>
<td>1,4</td>
</tr>
<tr>
<td>1</td>
<td>1,8</td>
<td>0</td>
<td>1,8</td>
</tr>
<tr>
<td>24</td>
<td>2,4</td>
<td>3,8</td>
<td>6,2</td>
</tr>
<tr>
<td>48</td>
<td>2,4</td>
<td>4,7</td>
<td>7,1</td>
</tr>
<tr>
<td>120</td>
<td>2,4</td>
<td>5,9</td>
<td>8,3</td>
</tr>
<tr>
<td>148</td>
<td>2,4</td>
<td>6,1</td>
<td>8,5</td>
</tr>
<tr>
<td>168</td>
<td>2,4</td>
<td>6,1</td>
<td>8,5</td>
</tr>
</tbody>
</table>
### Table 11: Results of Oil Recovery by spontaneous imbibition in Carbonates at low salinity

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Core FR8 (Surfactant)</th>
<th>Core FR9</th>
<th>Oil Recovery % from OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil (ml)</td>
<td>Microemulsion (ml)</td>
<td>Core FR8 joint (ml)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0,166</td>
<td>0,8</td>
<td>0</td>
<td>0,8</td>
</tr>
<tr>
<td>0,33</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0,5</td>
<td>1,2</td>
<td>0</td>
<td>1,2</td>
</tr>
<tr>
<td>1</td>
<td>1,3</td>
<td>0,3</td>
<td>1,6</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>2,9</td>
<td>4,9</td>
</tr>
<tr>
<td>48</td>
<td>2,2</td>
<td>3,2</td>
<td>5,4</td>
</tr>
<tr>
<td>72</td>
<td>2,3</td>
<td>3,3</td>
<td>5,6</td>
</tr>
<tr>
<td>96</td>
<td>2,3</td>
<td>3,8</td>
<td>6,1</td>
</tr>
<tr>
<td>168</td>
<td>2,3</td>
<td>4,1</td>
<td>6,4</td>
</tr>
<tr>
<td>192</td>
<td>2,3</td>
<td>4,2</td>
<td>6,5</td>
</tr>
<tr>
<td>240</td>
<td>2,3</td>
<td>4,2</td>
<td>6,5</td>
</tr>
</tbody>
</table>

### Table 12: Results of Oil Recovery by spontaneous imbibition in Sandstones at low salinity with surfactantes with different wt% of calamide

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Core N4 (Surfactant 4%)</th>
<th>Core U1 (Surfactant 1%)</th>
<th>Oil Recovery % from OOIP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil (ml)</td>
<td>Microemulsion (ml)</td>
<td>Core N4 joint (ml)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0,166</td>
<td>1,3</td>
<td>0</td>
<td>1,3</td>
</tr>
<tr>
<td>0,33</td>
<td>1,5</td>
<td>0</td>
<td>1,5</td>
</tr>
<tr>
<td>0,5</td>
<td>1,8</td>
<td>0</td>
<td>1,8</td>
</tr>
<tr>
<td>1</td>
<td>2,3</td>
<td>0</td>
<td>2,3</td>
</tr>
<tr>
<td>2</td>
<td>2,6</td>
<td>0</td>
<td>2,6</td>
</tr>
<tr>
<td>24</td>
<td>2,7</td>
<td>0,3</td>
<td>3</td>
</tr>
</tbody>
</table>