



Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: Petroleum Engineer Reservoir Engineering	Spring semester, 2014 Open
Writer: Alireza Roostaei (Writer's signature)
Faculty supervisor: Skule Strand	
Thesis title: Enhanced Oil Recovery (EOR) by "Smart Water" in Carbonates Reservoir	
Credits (ECTS): 30	
Key words: Enhanced Oil Recovery Carbonates Reservoir SEM and EDAX Smart Water Wettability Alteration PHREEQC simulator	Pages: 63 Stavanger, 30.May.2014

Acknowledgment

Foremost, I would like to show my deepest gratitude to Associate Professor Skule Strand for offering me a really interesting thesis topic. This thesis would not have been possible without his supervision, patience, guidance and support.

I would like to especially thank Phd student, Ivan Piñerez for his excellent guidance and advice during my thesis.

I would also like to thank Hossein Akhlaghi, Zahra Aghaeifar and Paul Hopkins for their help and best suggestions in the laboratory.

I would like to acknowledge the technical and academic support of the Stavanger University and Petroleum engineering department.

Last but not the least, my appreciation especially to my adorable wife, Zahra Salimi, for her unconditional support, patience and understanding.

Alireza Roostaei

Abstract

Characterization of the reservoir limestone cores has to be specified to obtain possible solution (designed water) based EOR technique to enhance the oil production. In this project a parametric study was performed to observe the effects of 3 different brines that contained phosphate, sulfate and borate ions on chalk cores and deciding, which brine is the best candidate to use as imbibing brine for limestone cores. The phosphate brine was not suitable due to precipitation of phosphate with brines containing divalent ions. Borate brine had lower and slower oil production compare to sulfate brine. Finally it was decided to select the sulfate brine for the limestone cores experiment.

Reservoir cores based on same properties, were divided in three different groups. The chromatography wettability tests were used to study the potential of wettability alteration and specify if there is any water-wet surface in limestone cores for the smart water to be active. SEM and EDAX of cores were done to show the mineralogy, physical and chemical characteristics of cores. The heterogeneity and homogeneity of pores can be observed clearly. EDAX can shows the type of core that, if it is dolomitic or limestone (pure calcite). The information from surface reactivity test, SEM and EDAX of cores was important for the selection of the brines. For dolomitic and limestone cores, it was decided to select SWd₂₀ and SW0NaCl x 4SO₄²⁻ respectively as imbibing brines.

Initially the cores were imbibed by formation brine to establish an initial level of production. Core 10E (group 1) and 14C (group 2) had the highest and lowest oil recovery in this step. After that, the imbibing brines were changed to SWd₂₀ for core 10E and SW0NaCl x 4SO₄²⁻ for cores 14C and 37C as smart water. Increment in oil recovery of core 10E by SWd₂₀, was more than cores 14C and 37C by SW0NaCl x 4SO₄²⁻.

The core 37C was placed in to the steel cell at high temperature with the same imbibing fluid. By starting the steel cell spontaneous imbibition at high temperature, a small amount the oil recovery of core 37C increased mainly due to thermal expansion.

PHREEQC simulator predicted that, the sulfate concentration decreases by increasing the temperature in atmospheric and reservoir pressure for both brines. The analysis of sulfate concentration of the imbibing brine by ion chromatography after the experiment showed that there was no sulfate precipitation.

Table of Contents

Acknowledgment.....	I
Abstract.....	II
List of Tables.....	VI
List of Figures.....	VI
1. Introduction.....	1
2. Project Objective.....	3
3. Theory and Fundamental.....	3
3.1 Carbonates.....	3
3.1.1 Chalk.....	3
3.1.2 Limestone.....	3
3.1.3 Dolomite.....	3
3.2 Oil Recovery.....	3
3.2.1 Primary Recovery.....	4
3.2.2 Secondary Recovery.....	4
3.2.3 Tertiary Recovery / EOR Process.....	4
3.3 Fluid Displacement Forces.....	5
3.3.1 Gravity Forces.....	5
3.3.2 Capillary Forces.....	6
3.3.3 Viscous Forces.....	6
3.4 Wettability.....	7
3.4.1 Classification of Wettability.....	7
3.4.2 Mechanisms of Wetting Alteration.....	7
3.4.3 Wettability of Carbonate Reservoirs.....	8
3.4.4 Methods of Wettability Measurement.....	8
3.4.5 Sea water as a Wettability Alteration in Carbonate Reservoirs.....	12
4. Material and Experimental Method.....	13
4.1 Materials.....	13
4.1.1 Core Materials.....	13
4.1.2 Oil preparation.....	14
4.1.3 Brines.....	15
4.2 Analytical Methods.....	17
4.2.1 <i>pH</i> Measurement.....	17

4.2.2 Density Measurement	17
4.2.3 Scanning Electron Microscope (SEM)	17
4.2.4 Energy Dispersive Analysis X-Ray (EDAX)	18
4.2.5 PHREEQC Simulator	18
4.3 Experimental Methods	18
4.3.1 Limestone Core Cleaning	18
4.3.2 Chalk Core Cleaning	19
4.3.3 Surface Reactivity Tests	19
4.3.4 Core Saturation with Formation Water and Establish S_{wi}	20
4.3.5 Oil Saturation and Aging	20
4.3.6 Spontaneous Imbibition Methods	20
4.3.7 Spontaneous Drainage	21
4.3.8 Brine Composition Analysis	21
5. Result	22
5.1 Catalytic Effect of "smart water"	22
5.1.1 The effect of phosphate on wettability and oil recovery of carbonate cores	22
5.1.2 Borate and sulfate effects on chalk cores (IA1 and IA2)	22
5.2 Smart water in reservoir limestone cores	23
5.2.1 Core 10D	23
5.2.2 Core 14B	27
5.2.3 Core 37A	31
5.2.4 Oil recovery test on core 10E	34
5.2.5 Oil recovery test on core 14C	34
5.2.6 Oil recovery test on core 37C	35
5.3 Predicting the concentration of SO_4^{2-} in limestone and dolomitic cores by PHREEQC simulator	36
6. Discussion	39
6.1 The effects of phosphate, borate and sulfate on wettability alteration and oil recovery of chalk cores (parametric study)	39
6.2 Limestone cores	40
6.3 PHREEQC Simulator	45
7. Conclusions	47
8. Future Work	48
9. Symbols and Abbreviation	49

10. References	50
11. Appendix	53
11.1 Explanation of Ion Chromatography System	53
11.2 Input data of PHREEQC simulator	59
11.3 Materials and Instruments Pictures	60

List of Tables

Table 4.1. General observation of the reservoir limestone cores plugs	13
Table 4.2. Characterization of the reservoir limestone cores plugs	13
Table 4.3. Characterization of the reservoir Chalk cores plugs	14
Table 4.4. Oil Characterizations	14
Table 4.5. Brines composition for chalk cores.....	16
Table 4.6. Brines composition for surface reactivity test.....	16
Table 4.7. Brines composition for limestone cores.....	17
Table 11.1. Simulation brine properties (SW0NaCl x 4SO ₄ ²⁻) at atmospheric pressure.....	59
Table 11.2. Limestone (pure calcite) at atmospheric pressure.....	59
Table 11.3. Simulation brine properties (SW d ₂₀) at atmospheric pressure	59
Table 11.4. Limestone (dolomitic) at atmospheric pressure	59
Table 11.5. Simulation brine properties (SW0NaCl x 4SO ₄ ²⁻) at reservoir pressure	59
Table 11.6. Limestone (pure calcite) at reservoir pressure	59
Table 11.7. Simulation brine properties (SW d ₂₀) at reservoir pressure	59
Table 11.8. Limestone (dolomitic) at reservoir pressure	60

List of Figures

Figure 3.1. Wettability of the oil/water/rock system.....	9
Figure 3.2. USBM wettability measurement	10
Figure 3.3. Schematic illustration of the chromatographic separation of sulfate and thiocyanate for oil-wet core. Completely water-wet conditions are assumed using heptane as oil or at 100% water saturated conditions.....	11
Figure 3.4. Mechanism of wettability alteration by sea water. A: Proposed when Ca ²⁺ and SO ₄ ²⁻ are active ions at lower temperature B: Proposed when Ca ²⁺ , Mg ²⁺ and SO ₄ ²⁻ are active ions at high temperature ..	12
Figure 4.1. Rotational (Viscosity versus Temperature)	15
Figure 4.2. Oscillation (Storage Modulus, Loss Modulus and Phase Angle versus Temperature).....	15
Figure 4.3. Limestone Cleaning by Kerosene.....	19
Figure 4.4. Chalk Cleaning Process by Distillated Water.....	19
Figure 4.5. Surface Reactivity System.....	20
Figure 4.6. Spontaneous imbibition by Steel Cell at high temperature.....	21
Figure 5.1. Oil recovery versus days of spontaneous imbibition test by steel cell at 90°C for chalk cores IA1 & IA2	23
Figure 5.2. SEM Core 10D-1	24
Figure 5.3. EDAX Core 10D-1	24
Figure 5.4. SEM Core 10D-2.....	24
Figure 5.5. EDAX Core 10D-2	24
Figure 5.6. SEM Core 10D-3.....	25
Figure 5.7. EDAX Core 10D-3	25
Figure 5.8. First surface reactivity test, before hot sea water flooding for core 10D.....	26
Figure 5.9. Second surface reactivity test, after hot sea water flooding for core 10D	26
Figure 5.10. Spontaneous imbibition test, core 10D.....	26
Figure 5.11. Spontaneous drainage test, core 10D.....	27
Figure 5.12. SEM Core 14B-1	27
Figure 5.13. EDAX Core 14B-1	27

Figure 5.14. SEM Core 14B-2	28
Figure 5.15. EDAX Core 14B-2	28
Figure 5.16. SEM Core 14B-3	28
Figure 5.17. EDAX Core 14B-3	28
Figure 5.18. First Surface reactivity tests before hot sea water flooding for core 14B.....	29
Figure 5.19. Second Surface reactivity tests after hot sea water flooding for core 14B	29
Figure 5.20. Spontaneous Imbibition Tests, Core 14B	30
Figure 5.21. Spontaneous Drainage Test, Core 14B.....	30
Figure 5.22. SEM Core 37A-1	31
Figure 5.23. EDAX Core 37A-1	31
Figure 5.24. SEM Core 37A-2.....	31
Figure 5.25. EDAX Core 37A-2	31
Figure 5.26. First surface reactivity tests before hot sea water flooding for core 37A	32
Figure 5.27. Second surface reactivity tests after hot sea water flooding for core 37A.....	32
Figure 5.28. Spontaneous Imbibition Tests, Core 37A.....	33
Figure 5.29. Spontaneous Drainage Test, Core 37A.....	33
Figure 5.30. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for core 10E.....	34
Figure 5.31. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for core 14C.....	35
Figure 5.32. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C and 100°C for core 37C.....	36
Figure 5.33. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone cores at atmospheric pressure.....	37
Figure 5.34. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in dolomitic cores at atmospheric pressure.....	37
Figure 5.35. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone cores at reservoir pressure	38
Figure 5.36. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in dolomitic cores at reservoir pressure	38
Figure 6.1. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for different reservoir groups	45
Figure 6.2. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone and dolomitic cores at atmospheric and reservoir pressure.....	46
Figure 11.1. The position of the samples in the sampler of IC system.	53
Figure 11.2. The containers of Anion and Cation eluent DI.....	54
Figure 11.3. An example of the list of sample data, containing their names and positions in the sampler.....	54
Figure 11.4. Venting the air from pumps.....	55
Figure 11.5. Preparing the instruments in the program of the IC software for a) Anion and b) Cation.	56
Figure 11.6. Adding and starting the measurement in IC system.	57
Figure 11.7. Analyzing the obtained results after IC measurements.	58
Figure 11.8. Limestone Core	60
Figure 11.9. Chalk Core.....	60
Figure 11.10. IEC Model 2K-Centrifuge	60
Figure 11.11. Filtration Process	60
Figure 11.12. A Mettler Toledo DL55 Autotitrator	61
Figure 11.13. Modular Compact Rheometer MCR 302.....	61
Figure 11.14. METTLER TOLEDO pH meter.....	61
Figure 11.15. DMA 4500 Anton Paar Density Meter.....	61

Figure 11.16. ZEISS SUPRA 35VP, SEM & EDAX system.....	62
Figure 11.17. Core Cleaning Setup.....	62
Figure 11.18. Ion Chromatography System.....	62
Figure 11.19. Water Saturation Setup.....	62
Figure 11.20. Desiccator.....	63
Figure 11.21. Imbibition Amott cell.....	63
Figure 11.22. Drainage Amott cell.....	63
Figure 11.23. Phosphate Precipitation.....	63

1. Introduction

Carbonate rocks mainly comprised of dolomites and limestones. Huge amount of oil close to 50% in the world was reserved in these rocks but the percentage of ultimate oil recovery from carbonate reservoirs is less than 30%, principally because of natural fractured and wettability of this kind of reservoir (Høgnesen et al., 2005; E. J. Manrique et al., 2007). Injected fluids will flow through the fractures and bypassing the oil in the rock matrix and the early breakthrough will happen, because of high permeability in the fractures and its low porous volume (E. Manrique et al., 2004).

Oil recovery has been split into three stages: primary, secondary and tertiary recovery. In many situations, oil recovery are not conducted in this order and tertiary recovery process might be used as secondary recovery, therefore tertiary recovery is replaced by the more satisfactory term “Enhanced Oil Recovery” (EOR). (Green & Willhite, 1998). Water was injected in to the reservoir as a secondary recovery to support the pressure for displacement of oil toward the production well, (Baviere, 1991).

Oil recovery from carbonate reservoirs is dependent on wetting condition of the reservoir. Contrary to sandstone reservoirs, around 90% of the carbonate reservoirs are believed to be neutral to oil-wet. Acid and base number of oil plays an important role in determining the wetting state and wetting mechanism. Polar components, especially the carboxylic material in crude oil, are known to have great impact on the wetting conditions of carbonates. As the acid number, AN, of crude oil increases, the water-wetness decreases. The achievement of enhanced oil recovery by water flooding in fractured carbonates is strongly dependent on wetting conditions of formation. Modifying the wetting conditions of various carbonates is possible where the wetting conditions are dictated by the AN, and improved oil recovery was acquired by spontaneous water injection. This was done by adding surface active chemicals to injection water or adjusting the injected fluid for potential determining ions towards the carbonate surface (Tor Austad, 2004; Puntervold et al., 2007).

Water-wetness decreases by increasing the acid number. Carbonate surface is generally positively charged and will adsorb negatively charged acidic groups, but sandstone is negatively charged and is able to adsorb positively charged basic components in oil (Menezes et al., 1989; Standnes & Austad, 2003; Treiber & Owens, 1972). Temperature is another important parameter influencing the wettability alteration process, (Hjelmeland & Larrondo, 1986; Wang & Gupta, 1995; Yu & Buckley, 1997). The chemistry of formation brine and presence of multivalent cations in the brine can affect the rock wettability (W. G. Anderson, 1986a).

That sulfate ions in the imbibing fluid catalyzed the wettability alteration process. Seawater contains a significant amount of sulfate; therefore seawater is used as the imbibing fluid. It was shown by spontaneous imbibition that seawater was able to change the wettability of chalk and increase oil recovery (Strand et al., 2006). When seawater which contains SO_4^{2-} is injected in to the chalk reservoir, SO_4^{2-} will adsorb on the positive surface of chalk and will reduce the

positively of chalk, then Ca^{2+} will co-adsorb and the concentration of Ca^{2+} will increase close to the chalk surface. As Ca^{2+} reacts with negatively charged carboxylic group, some of adsorbed carboxylic material is desorbed from the surface. At high temperature, Mg^{2+} can substitute Ca^{2+} at chalk surface, therefore organic material can be removed from the surface and making the chalk surface to be less oil-wet (Zhang, 2006).

Gupta et al. recognized other commercially available salts which can potentially improve water flood oil recovery. Several salts were tested on Middle Eastern limestone. Borate and phosphate were two ions which performed better than sulfate. They found that enhanced oil recovery was significantly higher for the modified brine containing borate ions than for the modified brine containing sulfate ion and addition of borate or phosphate salt to seawater enhanced oil recovery more than seawater softening did, and during the first pore volume of modified brine injection, most of the oil was recovered, (Gupta et al., 2011).

2. Project Objective

General properties of the reservoir limestone cores has to be characterize to test the potential of a designed water based EOR technique with the purpose of enhancing the oil production. The possibility to increase the production is evaluated through different techniques such as surface reactivity tests, spontaneous imbibition, drainage tests and oil recovery experiments.

3. Theory and Fundamental

3.1 Carbonates

Carbonate rocks mainly comprised of dolomites and limestones. Huge amount of oil close to 50% in the world was reserved in these rocks but the percentage of ultimate oil recovery from carbonate reservoirs is less than 30%, principally because of natural fractured and wettability of this kind of reservoir (Høgnesen et al., 2005; E. J. Manrique et al., 2007). Pore distributions in carbonate rocks are heterogeneous. Limestone and dolomite contain more than 50% of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) minerals respectively. Chalk is also a special type of limestone (Skule Strand, 2005).

3.1.1 Chalk

One of the special kinds of carbonates is chalk. It was created by small single-cell algae that are called coccoliths (Cossé, 1993). The microstructure of the chalk is very important. The organic coating on chalk particles has a big influence on wetting behavior of chalk (Andersen, 1995). Chalk is one of the important reservoir rocks in North Sea (Zhang, 2006). The permeability of chalk is low, about 1 *mD* but the porosity is high (Cossé, 1993).

3.1.2 Limestone

Limestone is a kind of carbonate rock that constitute of calcite mineral. The chemical composition of calcite (calcium carbonate) is $CaCO_3$. Limestone is categorized related to its geological, structure and chemical composition (Siagi et al., 2007). Many of the giant oil reservoirs in the Middle East and other big oil and gas reservoirs in Canada, Mexico, USA and China are form in limestone and dolomites (Gluyas, 2004).

3.1.3 Dolomite

Dolomite is a kind of carbonate rock that contain dolomite ($CaMg(CO_3)_2$) minerals (Skule Strand, 2005). Dolomitization will happen due to weathering. Dolomite is created when magnesium ions replace calcium ions in calcite and this process is dolomitization. "Dolomite formation is thermodynamically favored in solutions of (a) low Ca^{2+}/Mg^{2+} ratios, (b) low Ca^{2+}/CO_3^{2-} (or Ca^{2+}/HCO_3^-) ratios, and (c) high temperatures." (Machel & Mountjoy, 1986).

3.2 Oil Recovery

Oil recovery has been split into three stages: primary, secondary and tertiary recovery. In many situations, oil recovery are not conducted in this order and tertiary recovery process might be used as secondary recovery, therefore tertiary recovery is replaced by the more satisfactory term "Enhanced Oil Recovery" (EOR). "Improved Oil recovery" (IOR) is another ordinarily

expression term, has used that contain EOR but also a broader range of activities, e.g., reservoir characterization, improved reservoir management and infill drilling" (Green & Willhite, 1998).

3.2.1 Primary Recovery

Primary recovery is the initial production of reservoir that resulting from simple pressure depletion where the only reservoir energy is used to produce the oil (Castor et al., 1981; Farouq-Ali & Stahl, 1970). Reservoir energy sources comes from solution gas drive, natural water drive, gas-cap drive, fluid and rock expansion and gravity drainage (Green & Willhite, 1998). The recovery factor of this stage is comparatively low, about 5-30% of original oil in place (Baviere, 1991).

3.2.2 Secondary Recovery

Secondary recovery is applied when the reservoir energies are not enough to produce oil and gas. Water or gas was injected in to the reservoir to support the pressure for displacement of oil toward the production well. After the secondary recovery around 30-70% of OOIP is remained in the reservoir (Baviere, 1991).

3.2.3 Tertiary Recovery / EOR Process

The target of the EOR process is the oil that is remained in the reservoir after the secondary oil recovery. Increasing the lifetime of oil reservoirs and approaching economical limit is the purpose of tertiary oil recovery processes (Skule Strand, 2005). After the secondary recovery, tertiary processes use chemicals, miscible gases and thermal energy to mobilize and displace the extra oil (Green & Willhite, 1998).

- **Mobility Control Process**

Mobility control processes are based on maintaining favorable mobility ratios to improve the displacement efficiency. Polymer solutions are used to maintain favorable mobility ratios between displacing polymer solutions and the oil that being displaced. More uniform volumetric sweep of the reservoir is the target of this process. An unfavorable mobility ratio is the cause of water fingering in the shortest path to the production well (Green & Willhite, 1998).

- **Chemical Process**

Two of chemicals that can be applied in EOR process are surfactants and alkaline agents, which are injected to use a combination of phase behavior and reduction of interfacial tension (IFT) to displace oil (Green & Willhite, 1998).

- **Miscible Process**

In miscible process the purpose is to inject fluids same as hydrocarbon solvents or carbon dioxide, CO₂ that are miscible directly with the oil or that produce miscibility through composition alteration in the reservoir (Green & Willhite, 1998).

- **Thermal Process**

Injection of thermal energy or in-situ generation of heat same as steam injection or in-situ combustion to reduce the viscosity of the oil so it flows easier towards the production wells, are thermal processes (Green & Willhite, 1998).

- **MEOR Process**

Several mechanisms same as reduction of interfacial tension (IFT) have been applied to describe the effects if bacterial growth on the recovery of oil reservoirs (Soudmand-asli et al., 2007).

Biosurfactants, due to their structures and functional variety, are able to divide at the oil/water interface and decrease the interfacial tension (Satpute et al., 2010).

- **Smart Water in carbonates**

Water chemistry has a strongly effect on desorption of organic oil components and stability of water film from the surfaces of minerals in water-based enhanced oil recovery (EOR) process. By knowing the chemical interaction between active ions in seawater, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , “Smart Water” can be made in terms of salinity and ionic composition as an EOR-fluid (Fathi et al., 2012).

3.3 Fluid Displacement Forces

Several forces apply on the fluid flowing through porous medium same as oil reservoir. Viscous forces, gravity forces and capillary forces are the most important forces that specifying the flow of oil or water in porous medium (Morrow, 1979).

3.3.1 Gravity Forces

One of the very important forces in oil production is gravity force, particularly in oil/gas systems with high difference between fluid phases. Differences in density of fluids are the cause of gravity force. In the presence of a more dense fluid, the fluid with lowest density will have a tendency to flow upwards (Murty et al., 1987). The gravity force can be expressed by formula 3.1 (Cole, 1969).

$$\Delta P_g = \Delta \rho \cdot g \cdot H \quad (3.1)$$

Where:

ΔP_g Pressure difference between oil and water due to gravity

$\Delta \rho$ Density difference between oil and water

g Acceleration due to gravity

H Height of the liquid column

3.3.2 Capillary Forces

Capillary pressure described as the pressure difference across a curved interface between two immiscible fluids or as the pressure difference between the non-wetting phase and the wetting phase (Zolotukhin & Ursin, 2000). The capillary pressure can be calculated by the following equation (Green & Willhite, 1998):

$$P_c = P_o - P_w = \frac{2\sigma_{ow} \cdot \cos \theta}{r} \quad (3.2)$$

Where:

- P_c Capillary pressure
- P_o Oil-Phase pressure at a point just above the oil-water interface
- P_w Water-phase pressure just below the interface
- r Radius of cylindrical pore channel
- σ_{ow} Interfacial tension between oil and water
- θ Contact angle measured through the wetting phase (water)

3.3.3 Viscous Forces

The viscous forces are the amount of pressure drop that happens as a result of flowing of a fluid through the porous medium. By assuming that a porous medium is a bundle of parallel capillary tube, the pressure drop is given by Poiseuille's law.

$$\Delta P = - \frac{8\mu L \bar{v}}{r^2 gc} \quad (3.3)$$

Where:

- ΔP Pressure across the capillary tube
- μ Viscosity of flowing fluid
- L Capillary tube length
- \bar{v} Average velocity in capillary tube
- r Capillary tube radius
- gc Conversion factor

Dimensionless grouping of variables which show the ratio of viscous to capillary forces is Capillary number (N_{ca}). From the equation 3.4, capillary number increases by increasing the viscosity or flow rate of displacing fluid or by decreasing IFT between displacing and displaced fluids (Green & Willhite, 1998).

$$N_{ca} = \frac{F_v}{F_c} = \frac{v\mu_w}{\sigma_{ow}} \quad (3.4)$$

Where:

- F_v Viscous forces
- F_c Capillary forces
- v Interstitial pore velocity
- μ_w Viscosity of water
- σ_{ow} Interfacial tension between oil and water

3.4 Wettability

The tendency of one fluid to distribute on or stick to a solid surface in the presence of other immiscible fluids is wettability (W. G. Anderson, 1986a). Wettability is an important specifying factor in a multiphase flow in reservoir rock, trapping and fluid distribution (Skule Strand, 2005).

3.4.1 Classification of Wettability

Wettability can be categorized as strongly water-wet, strongly oil-wet, and intermediate-wet.

For strongly oil-wet rock, water is in the middle of the larger pores and the oil will contact most of the rock surface and occupy the smallest pores. In water flooding process, the oil will remain in the smallest pores and as a film on the rock surface where the water does not penetrate.

On the other hand, when the oil will be in the middle of the larger pores and the water will contact most of the rock surface and occupy the smallest pores, the rock is strongly water-wet. During water flooding, a snapping phenomenon may happen, leaving oil in the middle of larger pores.

If both fluid phases tend to wet the solid surface, but one of them is slightly more attracted than other, intermediate wettability occurs in the reservoir (Green & Willhite, 1998).

3.4.2 Mechanisms of Wetting Alteration

Primitively, all reservoir rocks are considered to be water-wet. By adsorption of polar compounds or deposition of organic matter in the oil on rocks surface, the wettability could be altered to oil-wet (W. G. Anderson, 1986a).

Adsorption of polar compounds from the crude oil results in a less water-wet rock (Punternvold, 2008). Asphaltenes and resins are the important crude oil fractions that affecting the wettability in rocks (Buckley, 1996; Xie et al., 2000). Resins are generally more polar than the asphaltenes (Speight, 1999; Skule Strand, 2005). Also proved that both acid and base number increased with increasing asphaltene content (Skauge et al., 1999). The ability of different polar compounds to alter the wettability depended on rock type (Punternvold, 2008). The acid number of oil is one of the most important factors that effect on wettability of carbonate rocks (Standnes & Austad,

2000). Water-wetness decreases by increasing the acid number. Carbonate surface is generally positively charged and will adsorb negatively charged acidic groups, but sandstone is negatively charged and is able to adsorb positively charged basic components in oil (Menezes et al., 1989; Standnes & Austad, 2003; Treiber & Owens, 1972). The main reason of oil-wetness of carbonate reservoirs is because of carboxylic material in crude oil that is the most strongly adsorbed polar components on the carbonate surface (Thomas et al., 1993). Another important parameter influencing the wettability alteration process is temperature (Hjelmeland & Larrondo, 1986; Wang & Gupta, 1995; Yu & Buckley, 1997). The chemistry of formation brine because of pH and salinity of the brine that affect the surface charge of rock and fluid interfaces is also an important factor that influences rock wettability. The presence of multivalent cations in the brine can affect the rock wettability (W. G. Anderson, 1986a).

3.4.3 Wettability of Carbonate Reservoirs

Literature data indicate that around 80-90% of the world's carbonate reservoirs are oil-wet (Høgnesen et al., 2005). The natural fractured of carbonate reservoirs is one of the biggest challenges during production since injected water will pass through fractures and will not imbibe in to the matrix blocks because of negative capillary pressure, therefore earlier water production will happen and huge amount of oil will remain in matrix blocks (Skule Strand, 2005). Ions in the injected Sea water chemically react with the solid surface of chalk and change the wettability to more water-wet, therefore secondary recovery, water injection will change the wettability of chalk (T. Austad et al., 2005; Tweheyo et al., 2006; Zhang & Austad, 2005).

3.4.4 Methods of Wettability Measurement

Many different methods have been applied for measuring the wettability. The quantitative methods consist Contact angles, Amott (imbibition and forced displacement) and USBM wettability method. The qualitative methods includes, imbibition rates, microscopic examination, flotation, glass slide method, relative permeability curve, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance and dye adsorption (W. Anderson, 1986b).

Chromatographic separation between sulfate ions, SO_4^{2-} , and thiocyanate, SCN^- , as a tracer is a new quantitative wettability test method for carbonates (S Strand et al., 2006).

- **Contact Angle**

When artificial cores and pure fluids are used, the contact angle method is the best measure of wettability (W. Anderson, 1986b). Contact angle is a direct measure of wettability of flat surfaces; however it is not a good method to measure the wettability in porous media with different minerals (Skule Strand, 2005). One of the generic systems to measuring the wettability is shown in figure 3.1. Surface energies are related to the Young's equation (W. Anderson, 1986b).

$$\sigma_{ow} \cdot \cos \theta = \sigma_{os} - \sigma_{ws} \quad (3.5)$$

Where:

σ_{ow} Interfacial tension between oil and water

θ Contact Angle

σ_{os} Interfacial tension between oil and solid

σ_{ws} Interfacial tension between water and solid

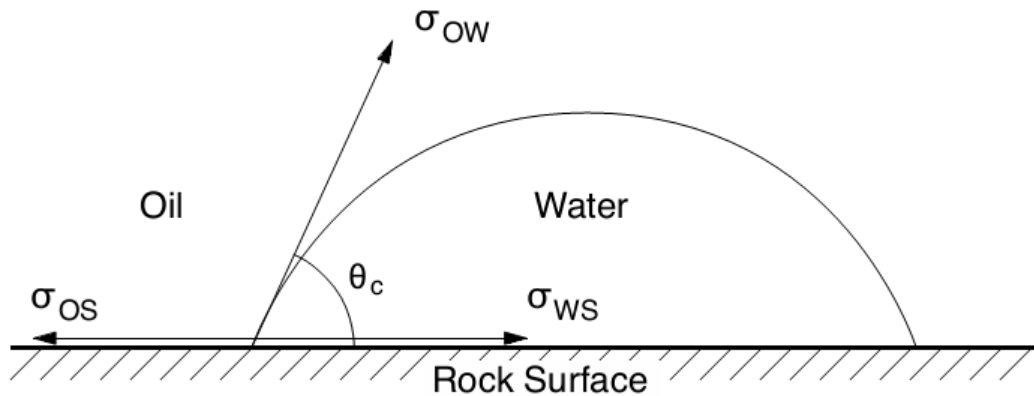


Figure 3.1. Wettability of the oil/water/rock system. After (Raza, Treiber, & Archer, 1968).

- **Amott cell Method**

One of the usual methods of determining wettability of porous medium is Amott test (Ma et al., 1999).

This method combines forced displacement (water and oil) and imbibition to measure the average wettability of core (W. Anderson, 1986b). In fact in this method, wetting fluid imbibes spontaneously in to the pores of core and displaces the non-wetting fluid.

- **USBM Method**

USBM method compares the work for one fluid to displace the other. The work that required displacing the non-wetting fluid by wetting fluid is less than the work that needed for opposite displacement. It has been depicted that the needed work to displace one fluid by another one is related to area under the capillary pressure curve, therefore the area under brine-drive capillary pressure for water-wet core is less than the area under the capillary pressure curve for the opposite displacement (W. Anderson, 1986b).

As shown in equation 3.6 the USBM method uses the ratio of areas under the two capillary pressure curves to calculate the wettability index.

$$W = \log\left(\frac{A_1}{A_2}\right) \quad (3.6)$$

A_1 Area under the secondary water-drainage curve, shown in figure 3.2.

A_2 Area under the imbibition curve falling below the zero- P_c axis, shown in figure 3.2.

When W is bigger or less than zero the core is water-wet and oil wet respectively. The core is neutrally wet when the W is close to zero (W. Anderson, 1986b).

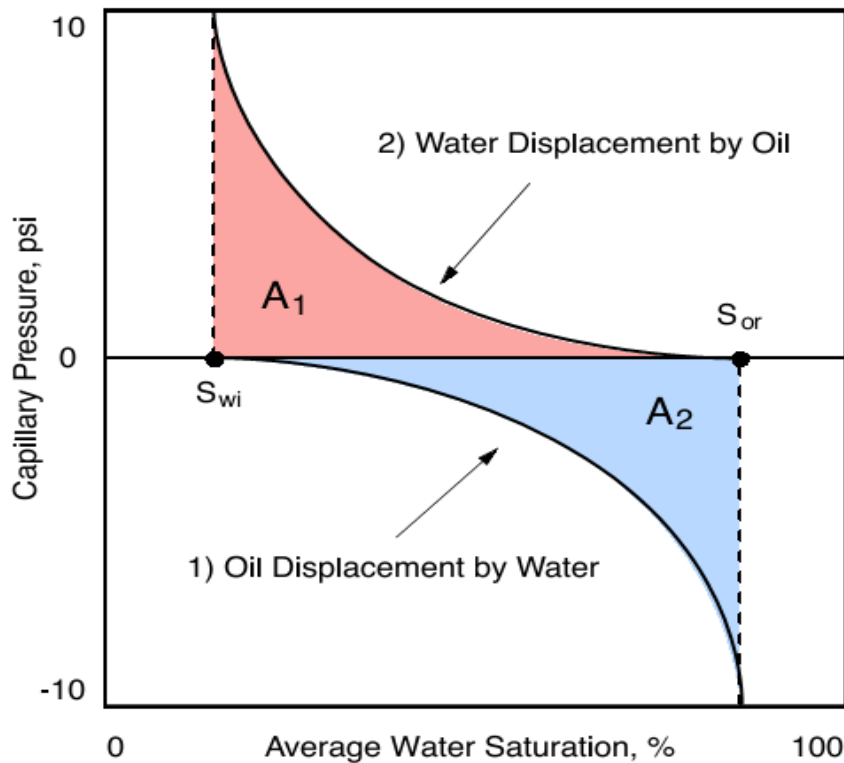


Figure 3.2. USBM wettability measurement (Donaldson et al., 1969).

- **Chromatography wettability test**

This method is based on chromatographic separation between sulfate ions, SO_4^{2-} and a non-adsorbing tracer, thiocyanate (SCN^-). The core firstly is flooded until residual oil saturation, S_{or} by brine without tracer and sulfate. Then the core is flooded with brine containing sulfate (SO_4^{2-}) and tracer (SCN^-). Tracer breaks through sooner than the sulfate because of adsorption of sulfate on the chalk surface. Effluent is collected and is analyzed for the amount of sulfate and tracer. The relative ions concentration is calculated and plotted against the pore volume injected. The area between the effluent curves for SCN^- and SO_4^{2-} is directly proportional to the water-wet surface area in the porous medium (S Strand et al., 2006).

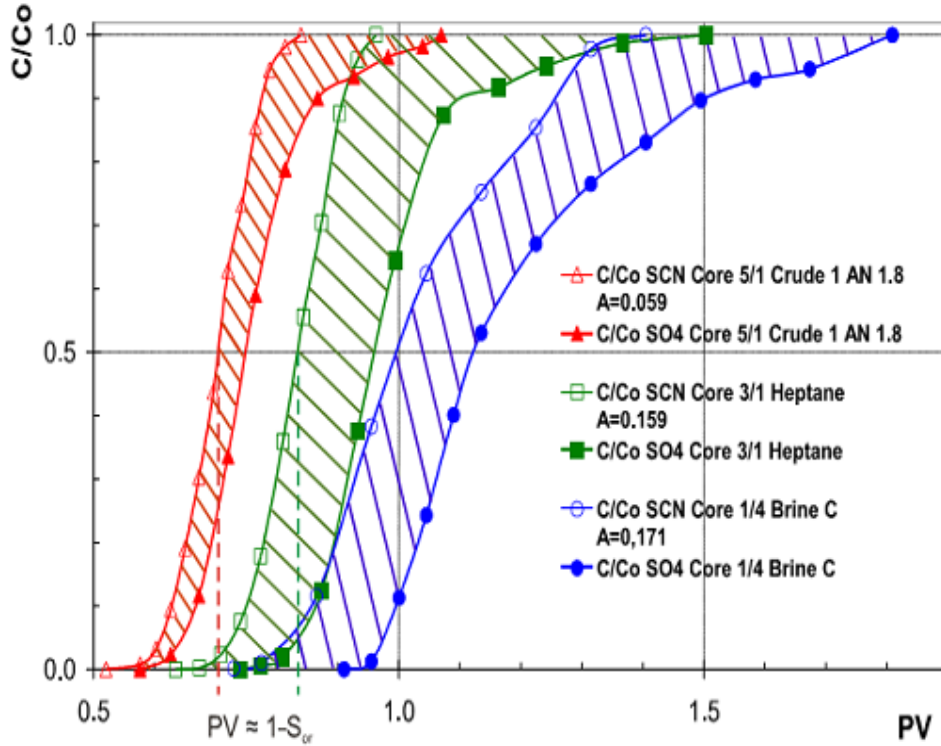


Figure 3.3. Schematic illustration of the chromatographic separation of sulfate and thiocyanate for oil-wet core. Completely water-wet conditions are assumed using heptane as oil or at 100% water saturated conditions (Strand, 2005).

Wetting index (WI_{NEW}) is described as:

$$WI_{NEW} = \frac{A_{wett}}{A_{Heptane}} \quad (3.7)$$

Where:

WI_{NEW} Fraction of water-wetness

A_{wett} The area between the thiocyanate and sulfate curves generated by flooding a core at S_{or}

$A_{Heptane}$ The reference area between the thiocyanate and sulfate curves, generated by flooding a core assumed to be completely water-wet

When WI_{NEW} is equal to 1, the system is completely water-wet and if WI_{NEW} is equal to 0, represents a completely oil-wet system. The system is neutral wettability, when the WI_{NEW} is 0.5.

3.4.5 Sea water as a Wettability Alteration in Carbonate Reservoirs

Strand et al., (2003) detected that sulfate ions in the imbibing fluid catalyzed the wettability alteration process. Seawater contains a lot of sulfate; therefore seawater is used as the imbibing fluid. It was shown by spontaneous imbibition that seawater was able to change the wettability of chalk and increase oil recovery (S Strand et al., 2006).

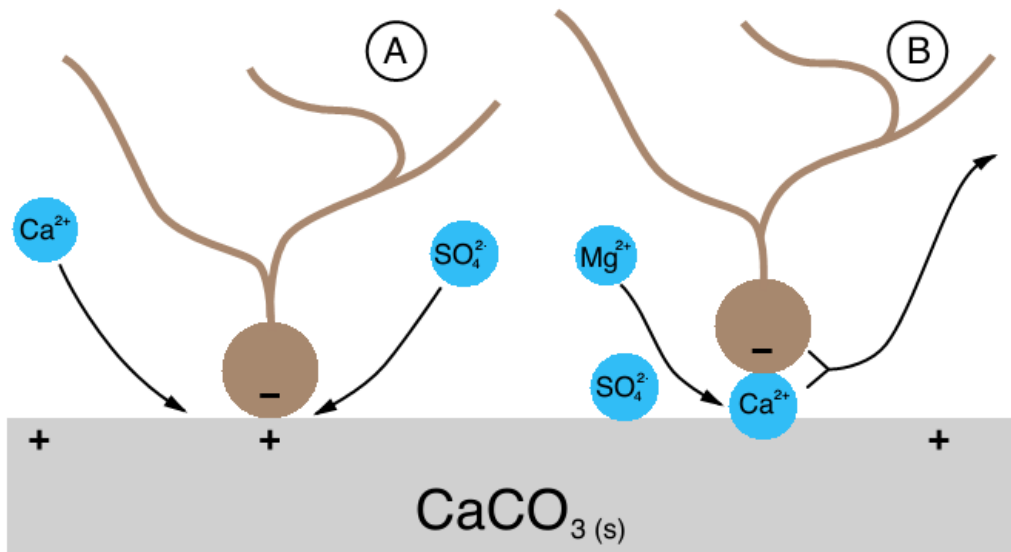


Figure 3.4. Mechanism of wettability alteration by sea water. A: Proposed when Ca^{2+} and SO_4^{2-} are active ions at lower temperature B: Proposed when Ca^{2+} , Mg^{2+} and SO_4^{2-} are active ions at high temperature (Zhang, 2006).

When seawater which contains a lot of SO_4^{2-} is injected in to the chalk reservoir, SO_4^{2-} will adsorb on the positive surface of chalk and will reduce the positivity of chalk, then Ca^{2+} will co-adsorb and the concentration of Ca^{2+} will increase close to the chalk surface. As Ca^{2+} reacts with negatively charged carboxylic group, some of adsorbed carboxylic material is desorbed from the surface (figure 3.4. A). At high temperature, Mg^{2+} can substitute Ca^{2+} at chalk surface (figure 3.4. B), therefore organic material can be removed from the surface and making the chalk surface to be less oil-wet (Zhang, 2006).

4. Material and Experimental Method

4.1 Materials

4.1.1 Core Materials

- Limestone cores

A previous characterization of the cores was done through a visual inspection; the cores were classified according to an overall punctuation based on how layered they are, the presence of fractures, vugs and their general mineral homogeneity. A description of the single characteristics of each core and the picture of one of them are shown respectively in tables 4.1, 4.2 and figure 11.8.

Table 4.1. General observation of the reservoir limestone cores plugs

Code	Layers	Fractures	Vugs	Homogeneity
10-D	None	None	None	Very-High
10-E	None	None	None	Very-High
14-B	Low	None	Low	High
14-C	Medium	None	None	High
37-A	Low	None	Low	Medium
37-C	Medium	None	Low	Medium-High

In order to characterize the main properties of the reservoir and to be able to replicate experiments, different groups of similar cores with high degree of heterogeneity and characteristic in common were identified. The main groups were:

- 10A, 10B, 10C, 10D, 10E.
- 14A, 14B, 14C.
- 37A, 37B, 37C.

Table 4.2. Characterization of the reservoir limestone cores plugs

Group	Core	Length, cm	Diameter, cm	Test	Pore volume, ml	Φ (Porosity)	K (Permeability), Md	Initial Water Saturation (%)
1	10D	7.1	3.82	Surface Reactivity Test	10.234	13%	1.05	100
1	10E	7.1	3.82	Oil Recovery	8.73	11%	26.3	10
2	14B	7.09	3.8	Surface Reactivity Test	9.069	11%	0.89	100
2	14C	7.1	3.71	Oil Recovery	8.44	11%	2.45	10
3	37A	7.01	3.81	Surface Reactivity Test	8.002	10%	0.87	100
3	37C	7.05	3.88	Oil Recovery	12.17	15%	15.46	10

- **Chalk Cores**

During this experiment, outcrop chalk cores from Stevns Klint nearby Copenhagen, Denmark, with porosity and permeability around 44% and 1-2mD, respectively, were used. The properties of these chalk cores are similar to the North Sea chalk oil reservoirs. Characteristics of cores and the picture of one of them are shown respectively in table 4.3 and figure 11.9.

Table 4.3. Characterization of the reservoir Chalk cores plugs

Core	Length, cm	Diameter, cm	Core Cleaning	Pore volume, ml	Φ (Porosity)	K (Permeability), Md	Initial Water Saturation (%)
I-A-1	6.5	3.8	DIW (5PV)	31.1	42%	1.86	10
I-A-2	6.5	3.8	DIW (5PV)	31.7	43%	0.92	10
I-A-3	6.5	3.8	DIW (5PV)	32.15	44%	1.25	10

4.1.2 Oil preparation

Two kinds of oil after centrifuge and filtration for separating water and particles were used during this experiment in the lab. One of the oil was RES 40 with acid number 0.5 and another one was reservoir oil with acid number 0.37. They were used for oil saturation of chalk and limestone cores respectively. Two kind of oil with high and zero AN, were needed for preparing RES40 with AN, 0.5. Acidic crude oil was diluted by 40 volume % n-heptane. 20 wt. % Active silica gel for adsorbing the polar component added to oil during 6 days stirring. The AN, of oil was measured after filtration. The oil with 0 AN, was obtained. At last by adding the oil with high AN, to the oil with 0 AN, the oil RES 40 with 0.5 AN, was acquired. The characterizations of oils are illustrated in table 4.4.

Table 4.4. Oil Characterizations

Oil Type	AN (mg KOH/g oil)	BN (mg KOH/g oil)	Density (g/cm ³)	Viscosity (cp)
RES 40	0.5	0.3	0.806	2.6
Reservoir Oil	0.37	0.27	0.825	4

- **Centrifuge and Filtration**

Reservoir oil contains brine and particles that are not useful for our experiment. Oil should be centrifuged for separating brine and particles. Small particles cannot be separated by centrifuge system; therefore those particles that are bigger than 3 μ m can be filtrated by filtration system, figure 11.10 and 11.11.

- **Acid and Base Number Determination**

As shown in figure 11.12, a Mettler Toledo DL55 autotitrator was used to measure the AN, and BN, for the different crude oils. The method involves potentiometric titrations using an internal standard. The method developed by Fan and Buckley, which are modified variations of

American Society for Testing Materials (ASTM) D2896 For BN titration and ASTM D66a for AN titration (ASTM, 1988, 1989; Fan & Buckley, 2006).

- **WAX Precipitation Point Measurement**

The wax precipitation point was performed by Modular Compact Rheometer MCR 302 shown in figure 11.13. Plotting the viscosity versus temperature and storage modulus, loss modulus and phase angle versus temperature were 2 different methods for measuring the point. As shown in figure 4.1 and 4.2, the deviation point started at 35°C, therefore this point is wax precipitation point.

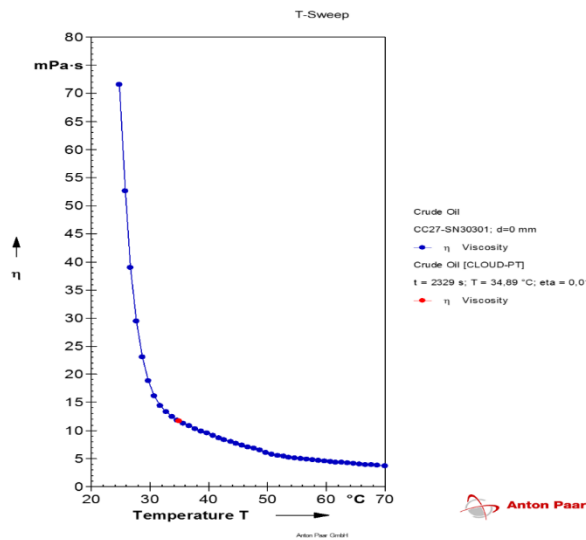


Figure 4.1. Rotational (Viscosity versus Temperature)

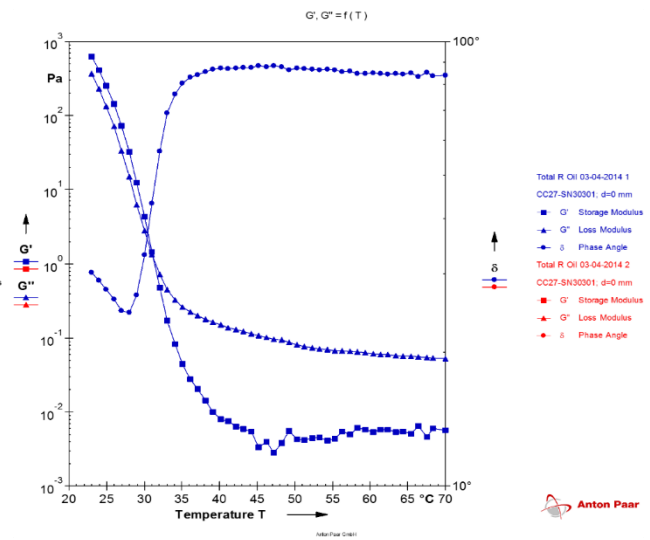


Figure 4.2. Oscillation (Storage Modulus, Loss Modulus and Phase Angle versus Temperature)

4.1.3 Brines

All the reagents used to prepare the brines were reagent grade and were purchased from Merck laboratories. Deionized water was used for the brine preparation, the D.I water was obtained from the Milli-Q device Integral-5 from Millipore with T.O.C <5 ppb and a resistivity of 18.2 MΩ cm. Artificial formation brine (VB) and limestone reservoir formation brine similar to Valhall and limestone field were used. $SW_0NaCl \times 1SO_4^{2-}$, $SW_0NaCl \times 4SO_4^{2-}$, $SW_0NaCl \times 1Borate$ and SW_{d20} ; were used as imbibing brines during spontaneous imbibition by steel and Amott cell.

The overall description of the concentration, compositions and properties of brines are presented in the tables 4.5, 4.6 and 4.7.

Table 4.5. Brines composition for chalk cores

Ion	Units	VB	SW0NaCl x1[B ₄ O ₅ (OH) ₄] ²⁻	SW0NaCl x1Phosphate	SW0NaCl x1SO ₄ ²⁻
[Na ⁺]	mol/L	0.966	0.002	0.074	0.026
[K ⁺]	mol/L	0.005	0.010	0.010	0.010
[Ca ²⁺]	mol/L	0.029	0.012	0.013	0.012
[Mg ²⁺]	mol/L	0.008	0.044	0.045	0.044
[Cl ⁻]	mol/L	1.065	0.125	0.125	0.125
[SO ₄ ²⁻]	mol/L	-	-	-	0.024
[SCN ⁻]	mol/L	-	-	-	-
[PO ₄ ³⁻]	mol/L	-	-	0.024	-
[B ₄ O ₅ (OH) ₄] ²⁻	mol/L	-	0.024	-	-
TDS	mg /L	62830	11431	10536.427	10011
pH	-	7.30	8.76	-	8.08
Density	g/cm ³	1.047	1.007	-	1.006

Table 4.6. Brines composition for surface reactivity test

Ion	Units	SW	SW 0T	SW 1/2T
[Na ⁺]	mol/L	0,4501	0.460	0.427
[K ⁺]	mol/L	0,0101	0.010	0.022
[Ca ²⁺]	mol/L	0,013	0.013	0.013
[Mg ²⁺]	mol/L	0,0445	0.045	0.045
[Cl ⁻]	mol/L	0,5251	0.0583	0.538
[SO ₄ ²⁻]	mol/L	0,024	-	0.012
[SCN ⁻]	mol/L	-	-	0.012
[HCO ₃ ⁻]	mol/L	-	-	-
TDS	mg /L	33360	33390	33390
pH	-	7.61	7.73	7.55
Density	g/cm ³	1.022	1.021	1.022

Table 4.7. Brines composition for limestone cores

Ion	Units	SW d ₂₀	FW	FW 0 SO ₄ ²⁻	SW0NaCl x4SO ₄ ²⁻
[Na ⁺]	mmol/L	22.5	1516	1516	194.1
[K ⁺]	mmol/L	0.5	89	89	10.0
[Ca ²⁺]	mmol/L	0.6	305	305	12.9
[Mg ²⁺]	mmol/L	2.2	90	90	44.5
[Cl ⁻]	mmol/L	26.2	2369	2382	125.0
[SO ₄ ²⁻]	mmol/L	1.2	6.2	0	96.0
[SCN ⁻]	mmol/L	-	-	-	-
[HCO ₃ ⁻]		-	13.66	13	-
TDS	mg /L	1668	138214	138058	20240.8
pH	-	7.05	6.2	6.02	8.01
Density	g/cm ³	0.999	1.093	1.094	1.015

4.2 Analytical Methods

4.2.1 pH Measurement

The pH of brines was measured by a METTLER TOLEDO *pH* meter, figure 11.14. For measuring the pH, 2 ml of brine is needed. To prevent any error the electrode should be cleaned completely by distilled water before putting in to the brine, and then it was stirred in the brine until the pH was stabilized.

4.2.2 Density Measurement

All the oil and brines densities were measured by DMA 4500 Anton Paar Density Meter as shown in figure 11.15.

Density meter instrument should be completely cleaned and free of air. Oily liquid was cleaned by white sprit and acetone. For cleaning the previous brines, distilled water was used. 2 ml of sample were injected in to the system for measuring the density.

4.2.3 Scanning Electron Microscope (SEM)

Scanning of samples with beams of electrons to produce very high resolution images. Surely one of the most important beam technology inventions is scanning Electron Microscopic (SEM). Although the first SEM instrument appeared in the early 1960s, but its' design has been constantly developing and improving. Identifying that the SEM is much more than a powerful microscope came. In addition to producing high resolution images of a samples' surface, SEM could also provide diversity of different contrast modes, where information relating to things like surface voltage is enclosed in its output signals. In many cases, in order to specify these contrast mechanisms, electron energy spectrometers are required (Khursheed, 2011).

4.2.4 Energy Dispersive Analysis X-Ray (EDAX)

EDAX is an analytical method that is used for chemical characterization or elemental analysis of samples. It relies on an interaction of source of X-ray stimulation and a sample. Each element allowing unique set of peaks on its X-ray spectrum because each of them has a unique atomic structure. A high energy beam of charged particles such as electrons or protons or a beam of X-rays is concentrated in to the sample to excite the emission of characteristic X-ray from a sample, therefore the energy of the X-rays emitted from the sample can be measured by an energy-dispersive spectrometer. This allows the elemental composition of the sample to be measured (Goldstein et al., 2003). The ZEISS SUPRA 35VP SEM and EDAX tool that was used during this experiment is showed in figure 11.16.

4.2.5 PHREEQC Simulator

PHREEQC is a computer program written in the C programming language for accomplishing a large diversity of low-temperature aqueous geochemical calculations or simulating transport processes and chemical reactions in polluted or natural water. PHREEQC is relying on equilibrium chemistry of aqueous solutions interacting with gases, minerals, solid solutions and sorption surfaces, but also consist the sufficiency to model kinetic reactions with rate equations (Parkhurst & Appelo, 1999).

PHREEQC applying many abilities, consisting:

- Ion-exchange equilibria
- Surface-complexation equilibria
- Fixed-pressure gas-phase equilibria
- Advective transport
- Kinetically controlled reactions
- Solid-solution equilibria
- Fixed-volume gas-phase equilibria
- Variation of the number of exchange or surface sites in proportion to a mineral or kinetic reactant
- Diffusion or dispersion in 1D transport
- 1D transport coupled with diffusion into static zones, and
- Isotope mole balance in inverse modeling

4.3 Experimental Methods

4.3.1 Limestone Core Cleaning

Reservoir cores should be cleaned completely by Mild Cleaning procedure. As shown in figure 11.17, the cleaning procedure was carried out in a hassler core holder subjected to a confining pressure of 15 bars to assure the axial flow of the cleaning fluids and avoid the bypassing of injected fluid. A mild cleaning was performed for each core; such procedure consists of Kerosene as a first cleaning fluid followed by Heptane and Distilled water. The flooding rate is constant for each fluid 0.1 ml/min.

The Kerosene was flooded until obtaining a clear effluent or until the outlet samples be similar to each other. During the kerosene cleaning a fraction of crude oil was coloring the effluent as it is shown in figure 4.3, then the Heptane was flooded to displace the Kerosene, 3 PV in average were flooded for each core, subsequently a minimum of 4 PV of distilled water were injected into the core. During the cleaning stage and after displacing the Heptane with water a qualitative analysis of sulfate presence was carried out, a group of effluent samples containing water were collected and then tested with BaCl_2 or Ion Chromatography for sulfate presence.

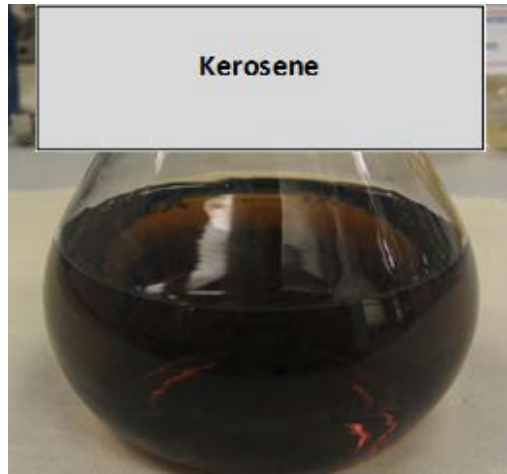


Figure 4.3. Limestone Cleaning by Kerosene

4.3.2 Chalk Core Cleaning

Initial solvable salts, especially sulfate, which could affect the wetting properties in the chalk cores, should be removed by injecting 5 PV of distilled water. As illustrated in figure 4.4, the solvable salts and sulfate coloring the effluent.

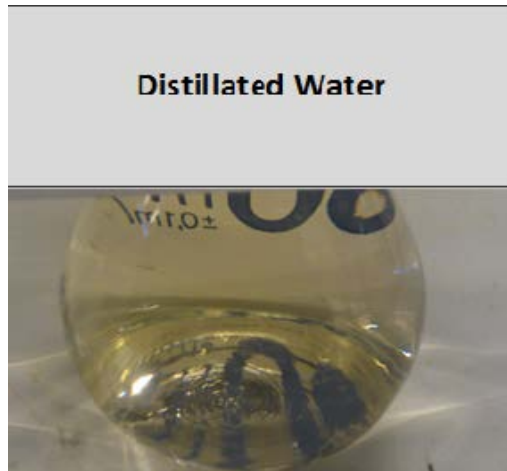


Figure 4.4. Chalk Cleaning Process by Distilled Water

4.3.3 Surface Reactivity Tests

As shown in figure 4.5, the cores were introduced into a hassler core holder, a confining pressure of 20 bars was held over the experiment, the system had a constant back pressure of 10 bars, the

injection rate of the SW0T, SW1/2T and SW were 0.05 ml/min, 0.1 ml/min and 3PV/Day respectively, and the experiment was performed at room temperature for SW0T and SW1/2T but 130°C for SW.

Two brines were based on the compositions of sea water to study the surface reactivity of the cores. One of the brines was prepared containing sulfate and thiocyanate ions (Tracer) and the other one having a complete absence of them. Prior to the injection of the brine with the tracer and the sulfate the core was flooded for 3 PV with sea water without tracer and sulfate (SW 0T) and then 3 PV of the brine with the tracer and sulfate (SW 1/2T) were injected; effluent samples were collected and analyzed for sulfates and thiocyanate in a ion chromatography system, figure 11.18.

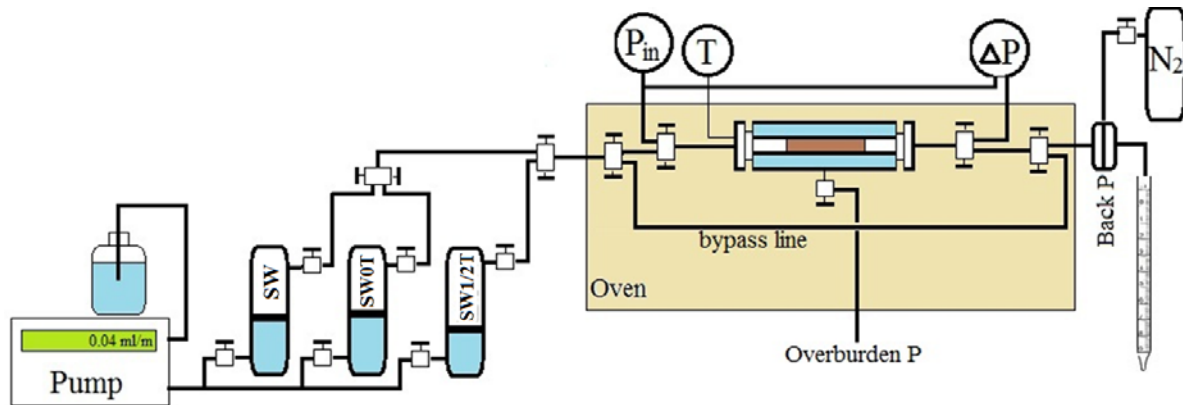


Figure 4.5. Surface Reactivity System

4.3.4 Core Saturation with Formation Water and Establish S_{wi}

As depicted in figure 11.19, the core was evacuated and saturated by 10 times diluted formation brine. The initial water saturation, $S_{wi} \approx 10\%$, was established after several days by desiccator technique (evaporation and desorption of water) using silica gels, figure 11.20.

4.3.5 Oil Saturation and Aging

After establishing of S_{wi} , the cores were flooded with 2 PV of crude oil in each direction at 50°C using a Hassler core holder with confining pressure 20 bars. At last the cores were wrapped with Teflon tape completely to prevent unrepresentative adsorption of polar components on the surface and they were aged in the aging cell for 2 weeks at 90°C.

4.3.6 Spontaneous Imbibition Methods

- Spontaneous Imbibition by Amott cells

The spontaneous imbibition tests were carried out in two steps at room temperature using standard Amott cells made of glass, figure 11.21. The first step was done after mild cleaning and before injection of brines for checking the surface reactivity test. A previous saturation of the

core with Heptane was done and then the core was placed in the Amott cell, distilled water was used as imbibition fluid, the tests were carried out for 5 days.

The second step was done after injection of brines, the main reason is to compare if there was presence of induced capillary forces after the sea water injection.

- **Spontaneous Imbibition by Steel Cell**

As shown in figure 4.6, the aged cores were immersed in the imbibing fluids in steel cells. The spontaneous imbibition tests were done at different temperatures, 90 and 65 °C with 10 bar back pressure for preventing boiling of fluids. Produced oil was collected during test and oil recovery was calculated as a percentage of original oil in place (OOIP) and plotted versus time.

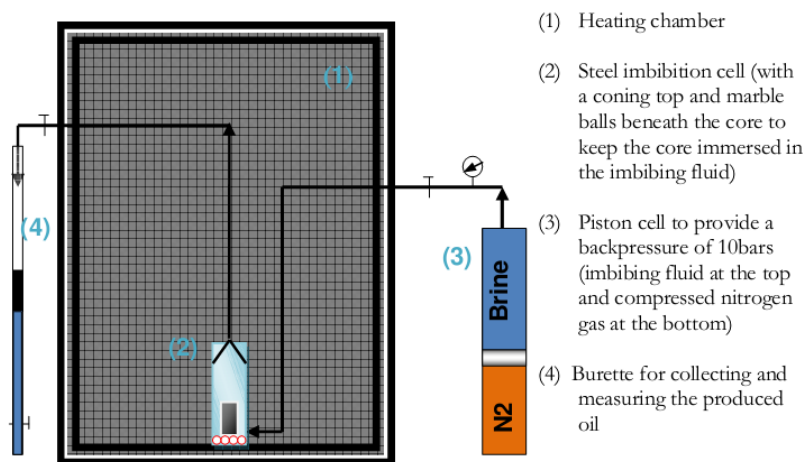


Figure 4.6. Spontaneous imbibition by Steel Cell at high temperature (Fathi, 2012).

4.3.7 Spontaneous Drainage

The spontaneous drainage tests were carried out at room temperature using standard Amott cells made of glass, figure 11.22. Spontaneous drainage test was done after spontaneous imbibition by Amott cell for checking if there is any production due to spontaneous drainage. A previous saturation of the core with distilled water was done and then the core was placed in the Amott cell, Heptane was used as imbibition fluid, the tests were carried out for 5 days.

4.3.8 Brine Composition Analysis

A fraction of the samples collected during the flooding stages were stored at 4 °C and diluted with DI water prior to analysis with the assistance of the trilution™ LH system from Gilson, afterwards the samples were analyzed with an ion chromatograph DIONEX ICS-3000 for $[Ca^{2+}]$, $[Mg^{2+}]$, $[Cl^-]$, and $[SO_4^{2-}]$. A further analysis of the data obtained was made using the software Chromeleon™.

5. Result

The results from this experiment are mainly divided in three parts. The first part is the effects of phosphate, borate and sulfate brines on outcrop chalk cores (parametric study) to select the best brine for limestone cores experiment. The second part is wettability study by surface reactivity test, spontaneous imbibition and drainage test on cores 10D, 14B and 37A. The oil recovery tests by spontaneous imbibition on reservoir limestone and dolomitic cores, 10E, 14C and 37C were done in this part and the last part is PHREEQC simulator for simulating and predicting the SO_4^{2-} concentration in brines containing limestone and dolomitic minerals versus different temperatures.

5.1 Catalytic Effect of "smart water"

Water chemistry has a strongly effect on desorption of organic oil components in water-based enhanced oil recovery (EOR) process. By knowing the chemical interaction between active ions in seawater, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , "Smart Water" can be made in terms of salinity and ionic composition as an EOR-fluid (Fathi et al., 2012).

Strand et al., (2003) detected that sulfate ions in the imbibing fluid catalyzed the wettability alteration process. Seawater contains a lot of sulfate; therefore seawater is used as the imbibing fluid.

Gupta et al. recognized other commercially available salts which can potentially improve water flood oil recovery. They found that enhanced oil recovery was significantly higher for the modified brine containing borate ions than for the modified brine containing sulfate ion and addition of borate or phosphate salt to seawater enhanced oil recovery more than seawater softening did (Gupta et al., 2011).

5.1.1 The effect of phosphate on wettability and oil recovery of carbonate cores

As shown in figure 11.23, a quick precipitation in presence of divalent ions happened after adding phosphate to the brine, therefore this brine was not used during limestone cores experiment. The compositions of phosphate brine is shown in table 4.5.

5.1.2 Borate and sulfate effects on chalk cores (IA1 and IA2)

Core cleaning by injecting 5 PV of distilled water was performed for cores IA1 and IA2 to remove initial dissolvable salts, especially sulfate. The cores (established of S_{wi}) were saturated with crude oil (RES40) at 50°C. At last the cores were wrapped with Teflon tape completely and they were aged in the aging cell for 2 weeks at 90°C. After aging period, the cores were brought out of the aging cells and were placed in to the steel cells at 90°C for spontaneous imbibition.

- **Spontaneous Imbibition Test by Steel Cell (90°C)**

Two brines containing different chemical composition were tested with spontaneous imbibition tests; one had the presence of Sulfate and the second one contained Borate ions, the tests were performed at 90°C using spontaneous imbibition, the concentration of ions of these brines are shown in table 4.5.

As shown in figure 5.1, the brine containing Sulfate had a faster production of oil, after 10 days the Sulfate brine produced 46% of the OOIP, for the brine that contains borates the production after 10 days was 28% of the OOIP. After 31 days the ultimate oil recovery of IA2 that was imbibed by SW0NaCl x 1Borate brine reached to the plateau at 35.6 % of OOIP, but the core IA1 that was imbibed by SW0NaCl x 1SO₄²⁻ after 44 days, the ultimate oil recovery reached to the plateau at 58.2 % of OOIP.

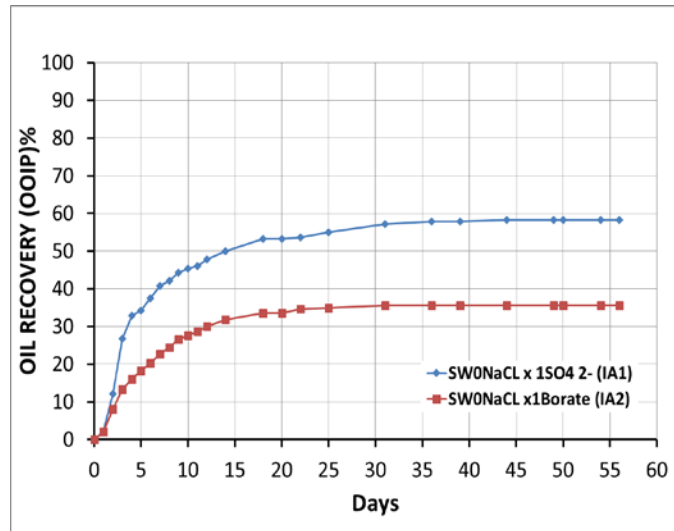


Figure 5.1. Oil recovery versus days of spontaneous imbibition test by steel cell at 90°C for chalk cores IA1 & IA2

5.2 Smart water in reservoir limestone cores

SEM, EDAX and wettability study on cores 10D, 14B and 37A were done during this experiment to observe the chemical properties and wettability alteration and deciding which smart brine is better to use for the oil recovery tests on reservoir limestone and dolomitic cores (10E, 14C and 37C).

5.2.1 Core 10D

SEM & EDAX

Small piece of the core was prepared for SEM and EDAX to see the mineralogy, physical and chemical characteristics of this core. The results are shown in figure 5.2 to 5.7.

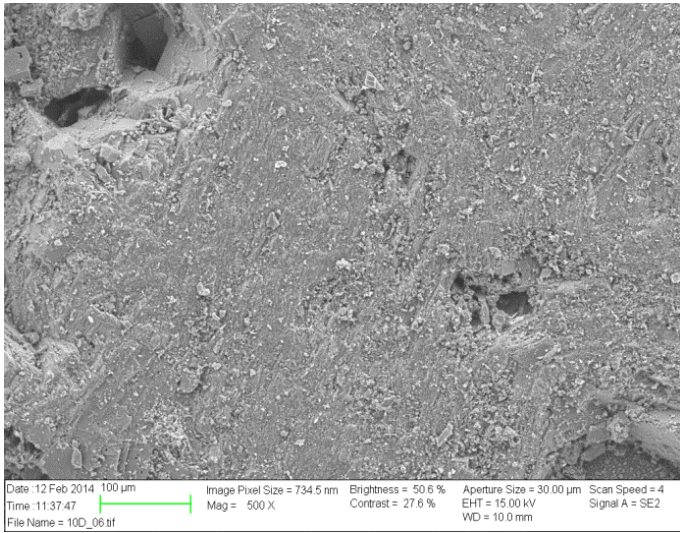


Figure 5.2. SEM Core 10D-1

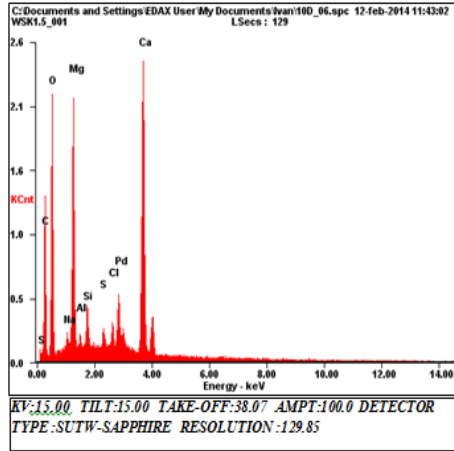


Figure 5.3. EDAX Core 10D-1

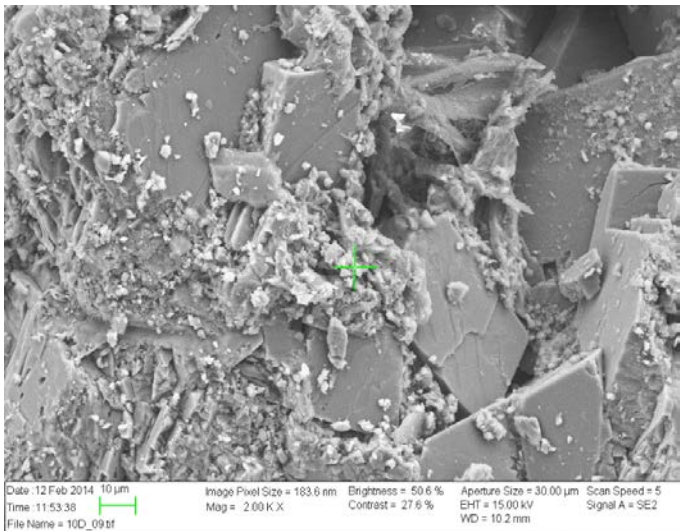


Figure 5.4. SEM Core 10D-2

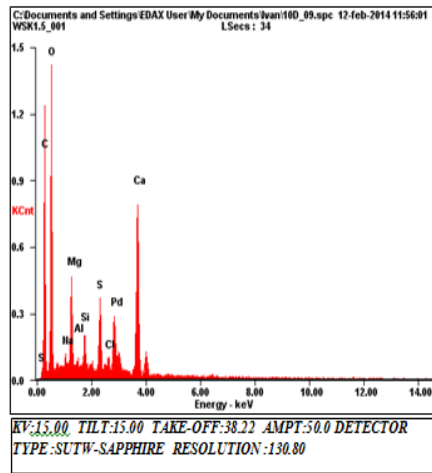


Figure 5.5. EDAX Core 10D-2

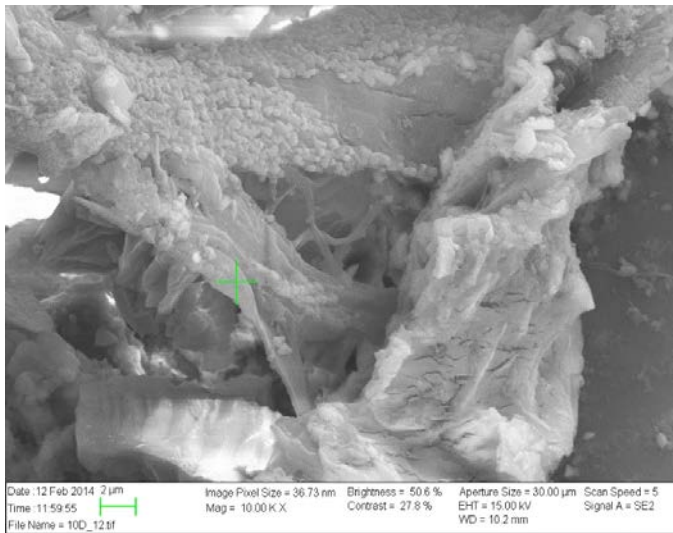
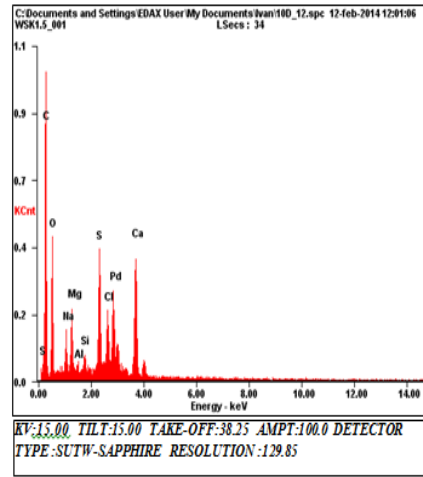


Figure 5.6. SEM Core 10D-3



Element	Wt %	At %
MgK	10.99	15.60
AlK	01.05	01.34
SiK	03.21	03.94
SK	28.42	30.60
CaK	56.34	48.52

Figure 5.7. EDAX Core 10D-3

Wettability study for core 10D

Mild cleaning was performed to clean the core completely. During the kerosene cleaning a fraction of crude oil was coloring the effluent. The kerosene injection was stopped when a clear effluent was reached. Then the injection of Heptane took place followed by the flooding with distilled water, the water was sampled for checking the sulfate concentration. The water effluent of the last cleaning stage was tested with BaCl_2 for sulfate presence, the test was positive for the first 3 pore volumes collected in the effluent.

- **First spontaneous imbibition**

Prior the surface reactivity test a spontaneous imbibition test was carried out and core 10D did not produce any heptane during 5 days of test, figure 5.10.

- **Surface reactivity test**

After the spontaneous imbibition test a surface reactivity test was done, it was expected to have lower concentrations of sulfate after the initial flooding with sea water without sulfate, however when the sulfate concentrations were evaluated they were very high to quantify a chromatographic separation of the thiocyanate and sulfate ions, figure 5.8.

After the flooding with sea water at 130°C a new tracer test was carried out and the levels were slightly higher. No separation of sulfate and thiocyanate was possible to be quantified, figure 5.9.

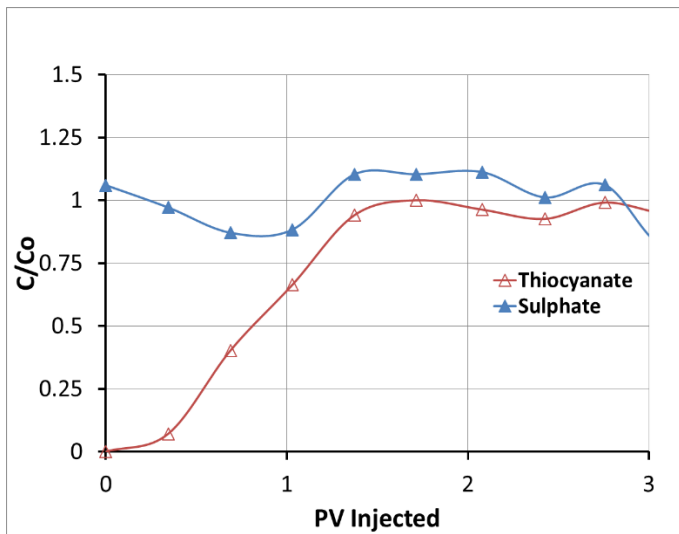


Figure 5.8. First surface reactivity test, before hot sea water flooding for core 10D

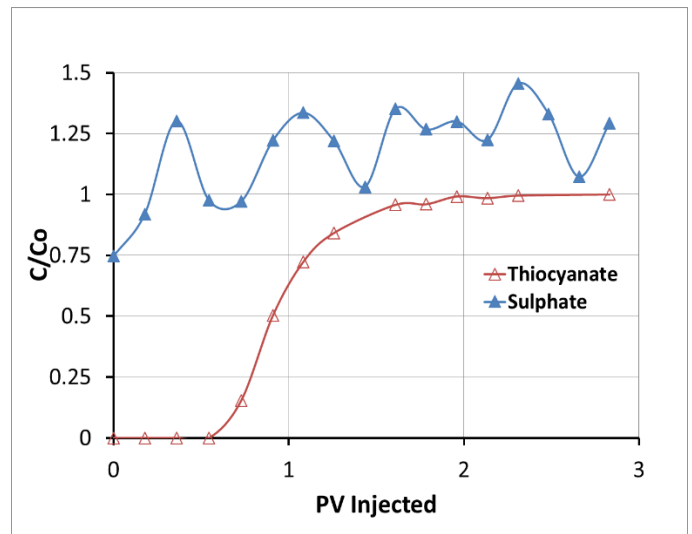


Figure 5.9. Second surface reactivity test, after hot sea water flooding for core 10D

More over the constant concentration of sulfate indicates a high amount of this ion during the flooding, it is important to note that in between each tracer test 9 PV of hot sea water were injected and the sulfate concentration still being high.

- **Second spontaneous imbibition test**

After the flooding with hot sea water a new spontaneous imbibition test was carried out, the core 10D did not produce any heptane during 5 days of test.

A graphic including the initial and the second spontaneous imbibition tests for the core 10D is presented in figure 5.10.

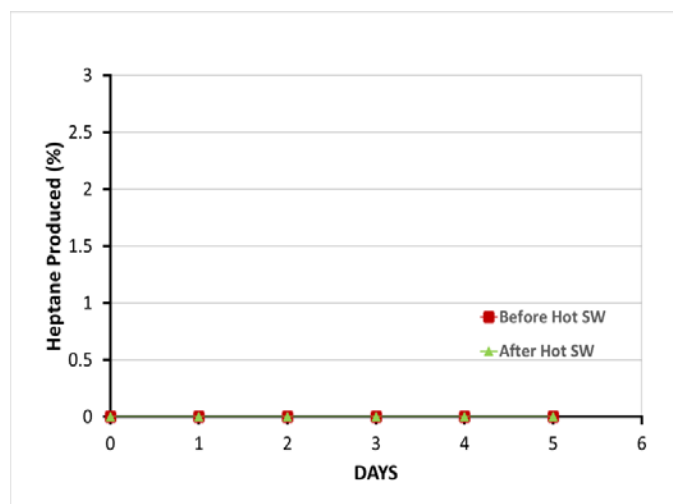


Figure 5.10. Spontaneous imbibition test, core 10D

- **Spontaneous Drainage Test**

After the second spontaneous imbibition test, the spontaneous drainage test was carried out, the core 10D did not produce any water during 5 days of test, figure 5.11.

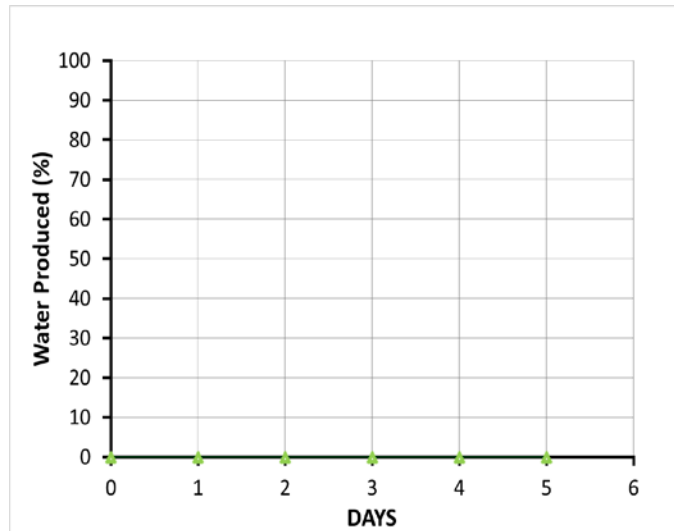


Figure 5.11. Spontaneous drainage test, core 10D

5.2.2 Core 14B SEM & EDAX

Small piece of the core 14B was prepared for SEM and EDAX to evaluate mineralogy, physical and chemical characteristics of this core. The results are shown in figure 5.12 to 5.17.

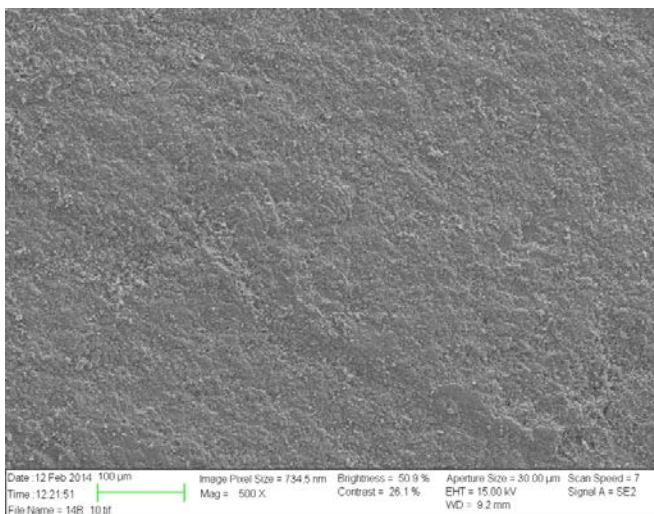
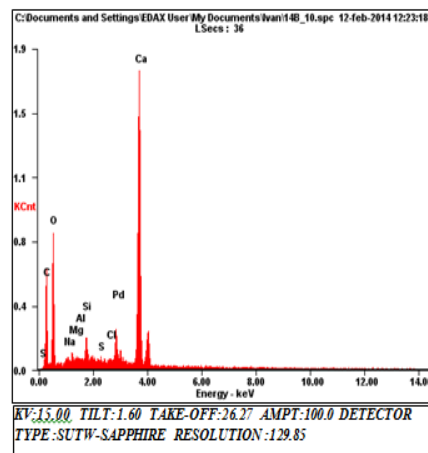


Figure 5.12. SEM Core 14B-1



Element	Wt %	At %
MgK	01.27	02.03
AlK	00.60	00.87
SiK	04.09	05.67
SK	00.00	00.00
CaK	94.04	91.43

Figure 5.13. EDAX Core 14B-1

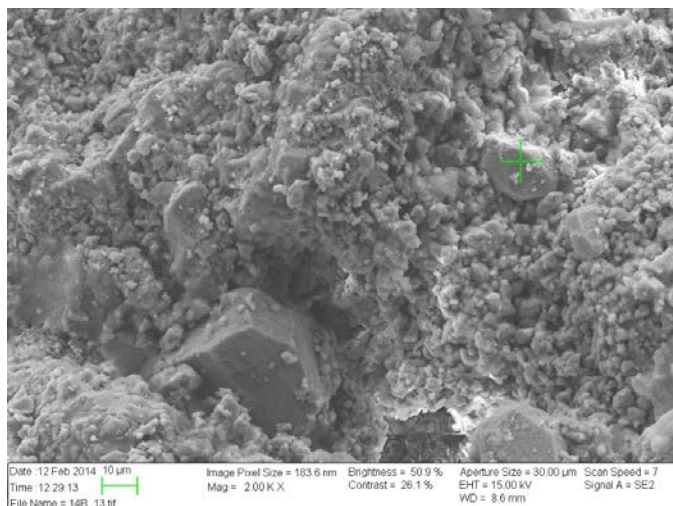
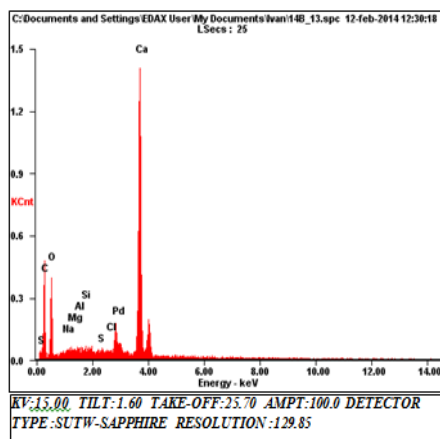


Figure 5.14. SEM Core 14B-2



Element	Wt %	At %
MgK	01.78	02.86
AlK	01.17	01.69
SiK	01.14	01.59
SK	00.75	00.91
CaK	95.17	92.95

Figure 5.15. EDAX Core 14B-2

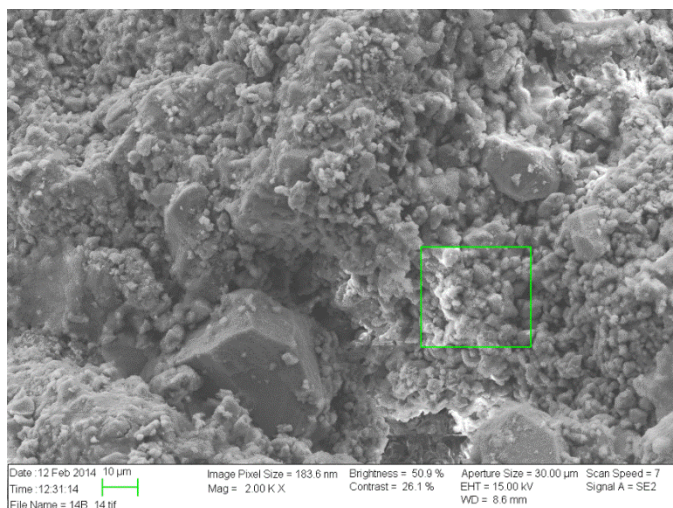
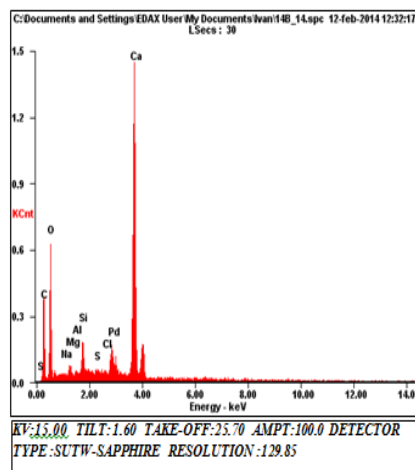


Figure 5.16. SEM Core 14B-3



Element	Wt %	At %
MgK	02.51	03.96
AlK	00.61	00.87
SiK	05.57	07.61
SK	00.51	00.61
CaK	90.80	86.95

Figure 5.17. EDAX Core 14B-3

Wettability study for core 14B

During the kerosene cleaning a fraction of crude oil was coloring the effluent, a lighter color compared with the core 10D was observed. The kerosene injection was stopped when a clear effluent was reached. Then the injection of Heptane took place followed by the flooding with distilled water, the water was sampled for checking sulfate concentration. The water effluent of

the last cleaning stage was tested with BaCl_2 for sulfate presence, the test was positive for the first 3 pore volumes collected in the effluent.

- **First spontaneous imbibition**

Prior the surface reactivity test a spontaneous imbibition test was carried out the core 14B did not produce any heptane during 5 days of test, figure 5.20.

- **Surface reactivity test**

The first surface reactivity test was done after the spontaneous imbibition test, it was hardly possible to observe a chromatographic separation between the sulfate and the thiocyanate as the sulfate concentration was around a tenth of the concentration of sulfate after flooding with the sea water without tracer. As shown in figure 5.18, the effluent concentration was started to increase around 0.3 PV and it reached to plateau about 2.5 PV.

After the flooding with sea water at 130°C , a new tracer test was carried out and the sulfate concentration was a tenth of the sulfate concentration of the tracer, but in here the area between sulfate and the thiocyanate a little increased. As illustrated in figure 5.19, the effluent concentration was started to increase around 0.4 PV and it reached to plateau about 2.5 PV.

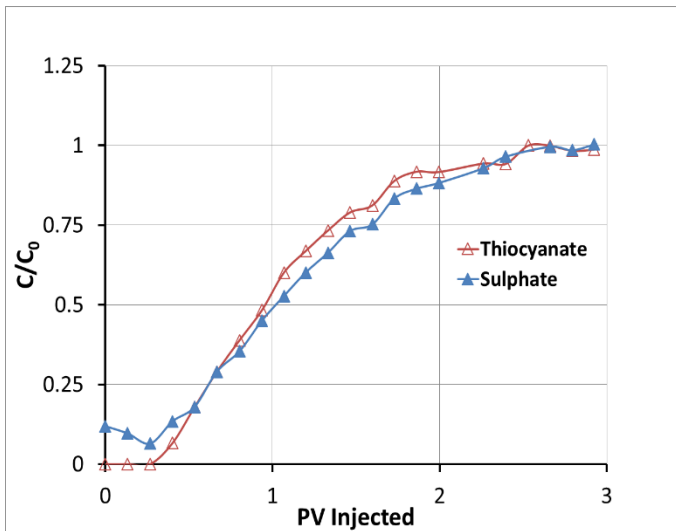


Figure 5.18. First Surface reactivity tests before hot sea water flooding for core 14B

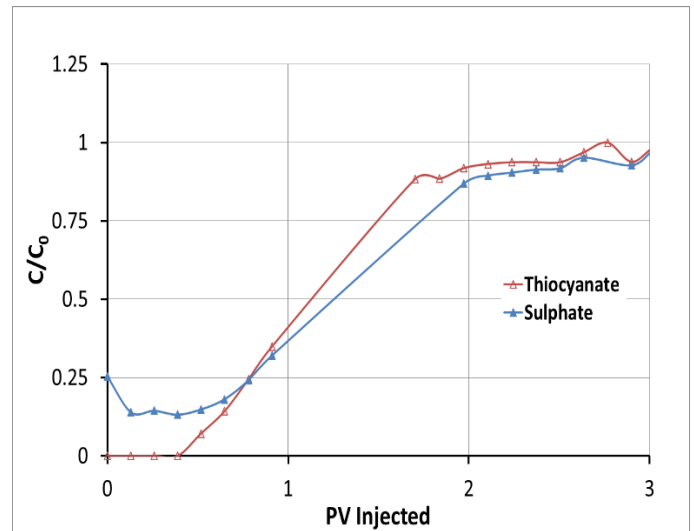


Figure 5.19. Second Surface reactivity tests after hot sea water flooding for core 14B

A lower concentration of sulfate in the effluent allowed performing the surface reactivity test in both cases; regardless the absence of variation in the area of separation between the sulfate and thiocyanate ions. However the presence of sulfate in the effluents analyzed was constant.

- **Second spontaneous imbibition test**

A new spontaneous imbibition test was carried out after the flooding with hot sea water, the core 14B produced a little amount of heptane (3.5% OOIP) during 5 days of test.

A graphic including the initial and the second spontaneous imbibition tests for the core 14B is presented in figure 5.20.

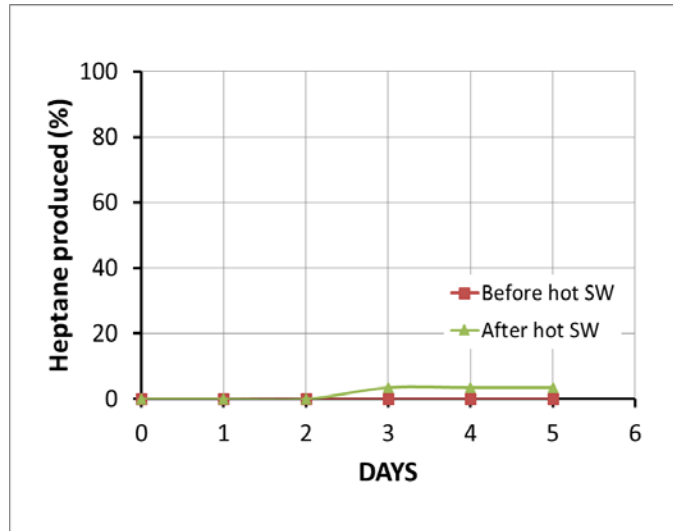


Figure 5.20. Spontaneous Imbibition Tests, Core 14B

- **Spontaneous Drainage Test**

The spontaneous drainage test was carried out after the second spontaneous imbibition test, the core 14B did not produce any water during 5 days of test, figure 5.21.

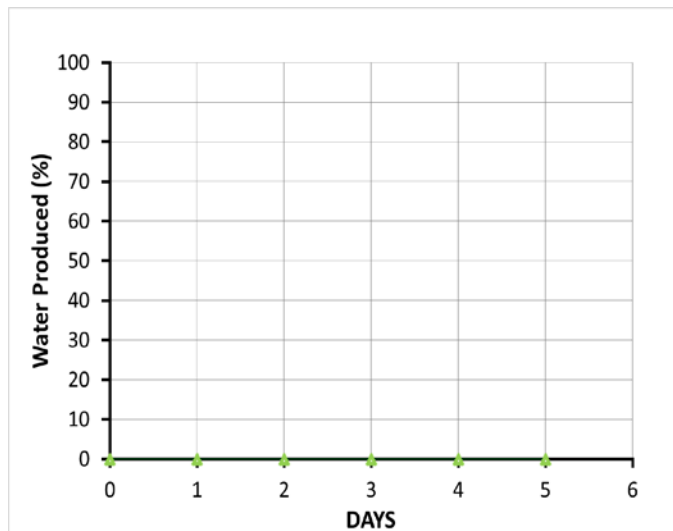


Figure 5.21. Spontaneous Drainage Test, Core 14B

5.2.3 Core 37A SEM & EDAX

To see the mineralogy, physical and chemical characteristics of core 37A, Small piece of the core was prepared for SEM and EDAX. The results are shown in figure 5.22 to 5.25.

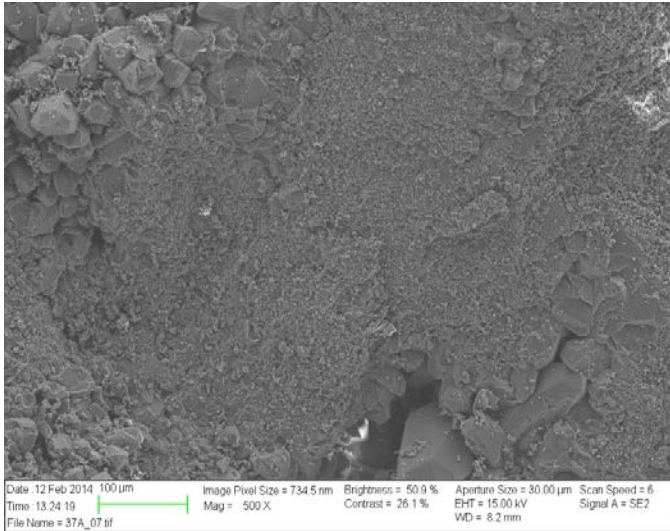
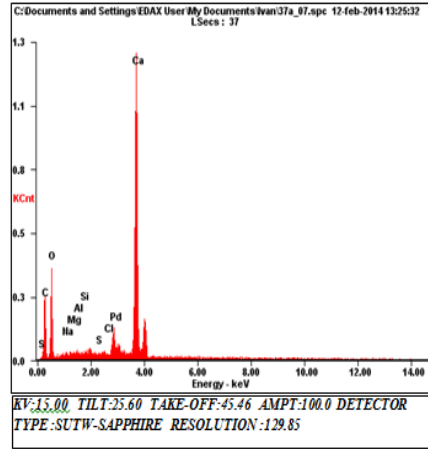


Figure 5.22. SEM Core 37A-1



Element	Wt %	At %
MgK	00.64	01.05
AlK	00.70	01.03
SiK	00.41	00.58
SK	00.28	00.35
CaK	97.96	96.99

Figure 5.23. EDAX Core 37A-1

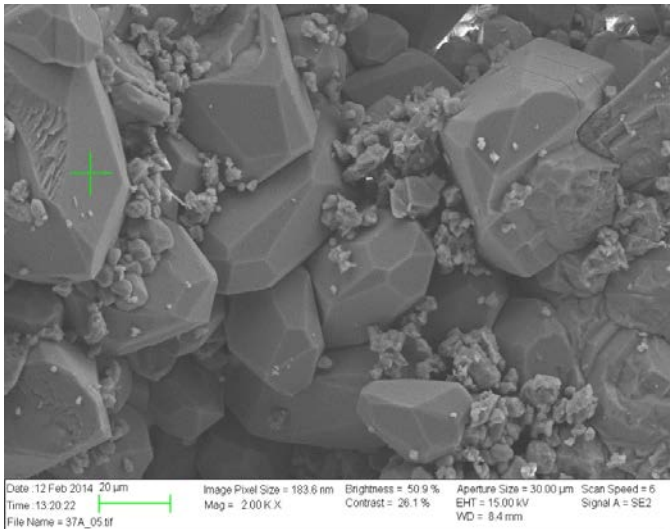
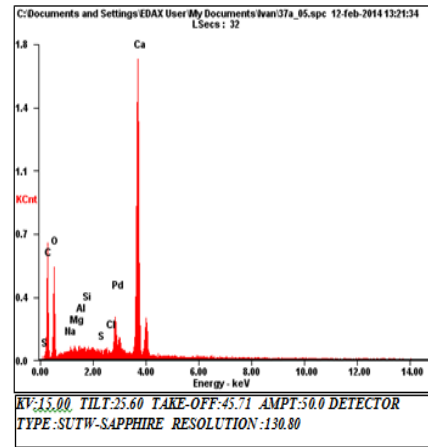


Figure 5.24. SEM Core 37A-2



Element	Wt %	At %
MgK	00.73	01.18
AlK	00.73	01.07
SiK	00.58	00.81
SK	00.53	00.66
CaK	97.44	96.28

Figure 5.25. EDAX Core 37A-2

Wettability study for core 37A

Same as previous cleaning cores, during the kerosene cleaning a fraction of crude oil was coloring the effluent. When the effluent was clarified, the injection of kerosene was stopped. Then the injection of Heptane took place followed by the flooding with distilled water, the water was sampled for checking sulfate concentration. The BaCl_2 was used to test the sulfate presence in effluent water. For the first 3 pore volumes, the test was positive, therefore the presence of sulfate in core 37A was clear.

- **First spontaneous imbibition**

A spontaneous imbibition test was carried out before the surface reactivity test, but 37A did not produced any heptane during 5 days of test, figure 5.28.

- **Surface reactivity test**

After the spontaneous imbibition test, the first surface reactivity test was done, it was impossible to observe a chromatographic separation between the sulfate and the thiocyanate as the sulfate concentration was around a tenth of the concentration of sulfate after flooding with the sea water without tracer. The effluent concentration was started to increase around 0.25 PV and it reached to plateau about 2.5 PV, as shown in figure 5.26.

A new tracer test was carried out after the flooding with hot seawater at 130°C and the sulfate concentration was a tenth of the sulfate concentration of the tracer and it was impossible to see a chromatographic separation between the sulfate and the thiocyanate. As depicted in figure 5.27, the effluent concentration was started to increase around 0.2 PV and it reached to plateau about 2.5 PV.

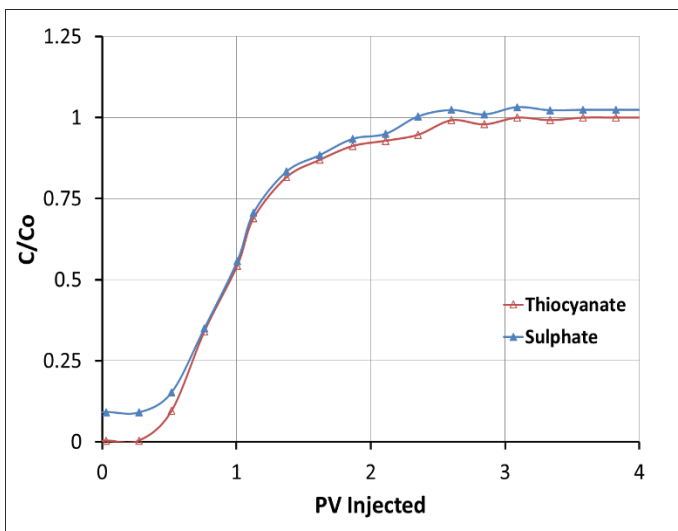


Figure 5.26. First surface reactivity tests before hot sea water flooding for core 37A

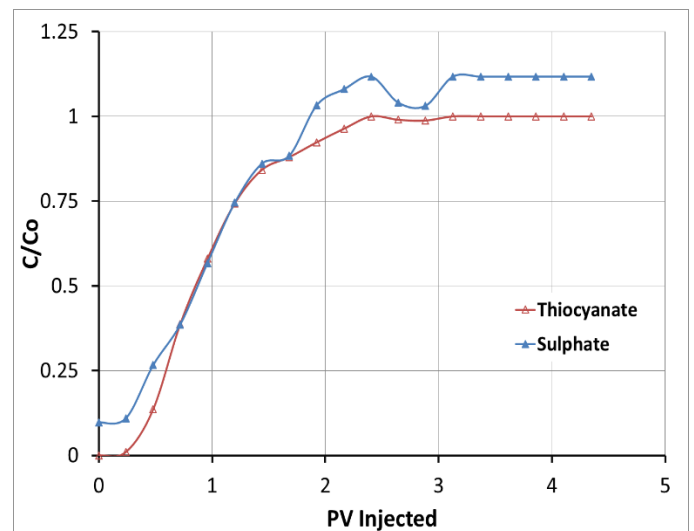


Figure 5.27. Second surface reactivity tests after hot sea water flooding for core 37A

- **Second spontaneous imbibition test**

After the flooding with hot sea water a new spontaneous imbibition test was carried out, the core 37A produced a little amount of heptane (2.5% OOIP) during 5 days of test.

A graphic including the initial and the second spontaneous imbibition tests for the core 37A is presented in figure 5.28.

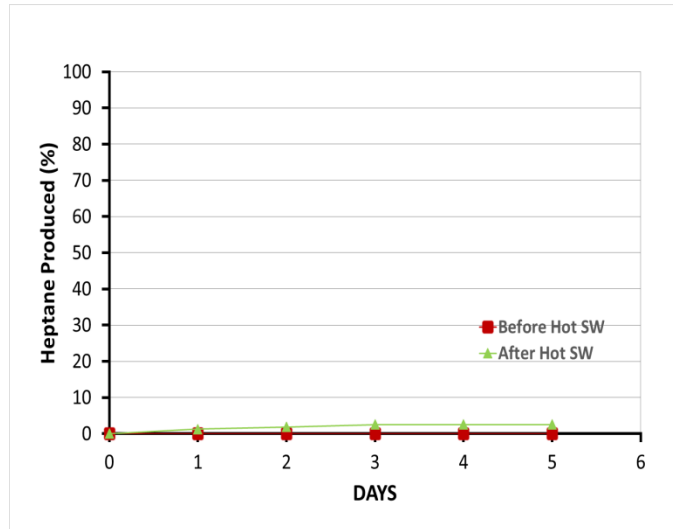


Figure 5.28. Spontaneous Imbibition Tests, Core 37A

- **Spontaneous Drainage Test**

The spontaneous drainage test was carried out when the second spontaneous imbibition test was done, but the core 37A did not produce any water during 5 days of test, figure 5.29.

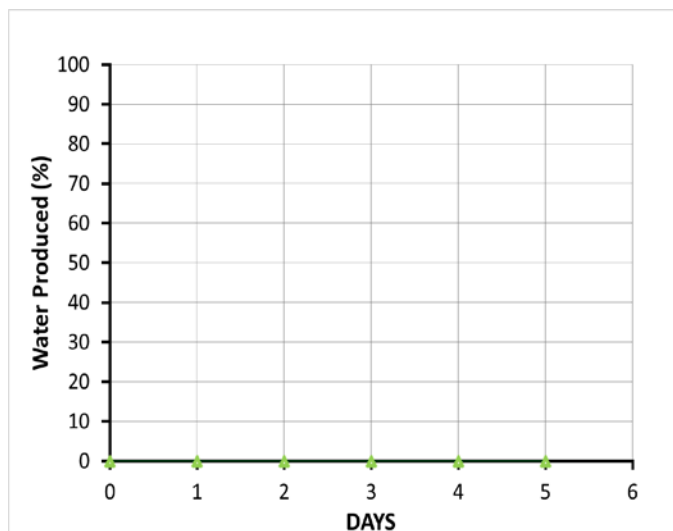


Figure 5.29. Spontaneous Drainage Test, Core 37A

5.2.4 Oil recovery test on core 10E

Mild core cleaning was performed for core 10E to clean the crude oil that was remained in reservoir core and the water was sampled for checking sulfate concentration. After establishing of S_{wi} , the core was saturated with reservoir crude oil at 50°C, then the core was wrapped with Teflon tape completely and it was aged in the aging cell for 2 weeks at 90°C. After aging period, the core was brought out of the aging cell and was placed in to the Amott cell at 65°C. This is a dolomitic limestone core with anhydrite and SWd₂₀ based on surface reactivity test and EDAX was chosen as spontaneous imbibition brine.

- **Spontaneous Imbibition Test by Amott Cell at 65°C (Reservoir Temperature)**

Core 10E was placed in to Amott cell for spontaneous imbibition at 65°C to see the wettability alteration and recovery of this core. The recovery curve (%OOIP) versus days of core 10E at different steps is shown in figure 5.30. Initially the core was imbibed by FW0SO₄²⁻ as a formation brine. After 1 day the oil recovery reached to the plateau at 5.7% of OOIP and when no more oil produced during 3 days, the imbibing formation water was changed to SWd₂₀ as a smart water. Finally the ultimate oil recovery reached to the plateau at 15.9% of OOIP after 29 days.

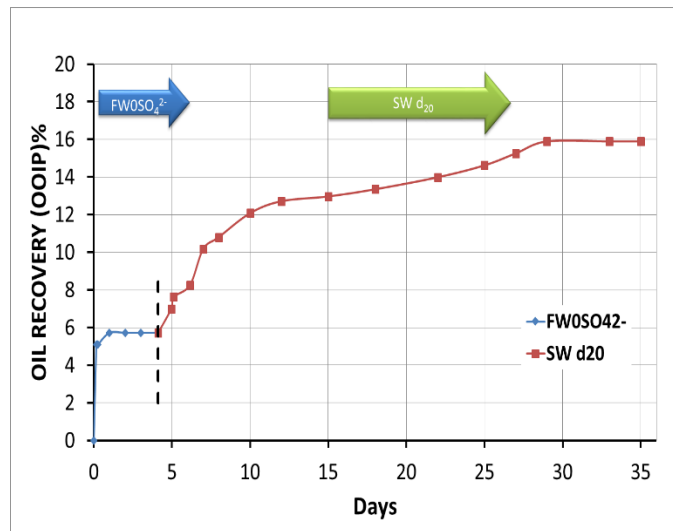


Figure 5.30. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for core 10E

5.2.5 Oil recovery test on core 14C

The core 14C was not clean and it contained a fraction of crude oil that by injecting of kerosene, a clean core was prepared. The water was sampled for checking sulfate concentration. The core was saturated with reservoir crude oil at 50°C, after establishing of S_{wi} . Then the core was wrapped with Teflon tape and it was aged in the aging cell for 2 weeks at 90°C. After aging period, the core was brought out of the aging cell and was placed in to the Amott cell at 65°C.

This is a limestone (pure calcite) core and $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ based on surface reactivity test and EDAX was chosen as spontaneous imbibition brine.

- **Spontaneous Imbibition Test by Amott Cell at 65°C (reservoir temperature)**

After aging period, core 14C was placed in to the Amott cell for spontaneous imbibition at 65°C to see the recovery and wettability alteration of this core. The recovery curve (%OOIP) versus days of core 14C at different steps is presented in figure 5.31. At the beginning the core was imbibed by FW0SO_4^{2-} as a formation brine. After 2 days the oil recovery reached to the plateau at 4.6% of OOIP and when no more oil produced during 2 days, the imbibing formation water was changed to $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ as a smart water. The ultimate oil recovery reached to the plateau at 12.9% of OOIP after 27 days.

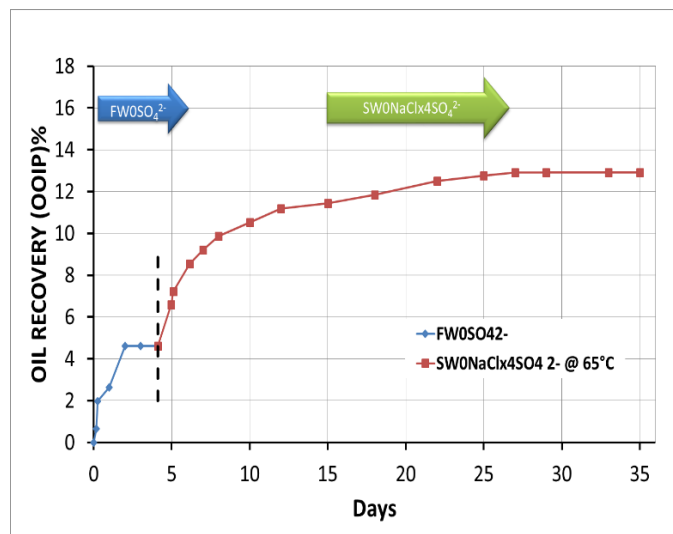


Figure 5.31. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for core 14C

5.2.6 Oil recovery test on core 37C

A fraction of crude oil was remained in core 37C that should be cleaned by injecting kerosene (mild cleaning). The water was sampled for checking sulfate concentration. After establishing of S_{wi} , the core was saturated with reservoir crude oil at 50°C. Then the core was wrapped with Teflon tape and it was aged in the aging cell for 2 weeks at 90°C. The core after aging period, was brought out of the aging cell and was placed in to the Amott cell at 65°C and steel cell at 100°C for spontaneous imbibition. Same as core 14C, this core is a limestone (pure calcite) core and based on surface reactivity test and EDAX, $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ was chosen as spontaneous imbibition brine.

- **Spontaneous Imbibition Test by Amott Cell at 65°C (reservoir temperature) and by steel cell at 100°C**

Same procedure as core 14C, after aging period, core 37C was placed in to the Amott cell for spontaneous imbibition at 65°C to see if there is any wettability alteration and recovery of this core. Figure 5.32 shows the recovery curve (%OOIP) versus days of core 37C at different steps. In the first step the core was imbibed by FW0SO_4^{2-} as a formation brine. After 2 days the oil recovery reached to the plateau at 5% of OOIP and when no more oil produced during 2 days, the imbibing formation water was switched to $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ as a smart water. The oil recovery reached to the plateau at 6.8% of OOIP after 7 days and no more oil produced until 11 days, then the core was placed in to the steel cell at 100°C with the same imbibing fluid. By starting the steel cell spontaneous imbibition, after 10 days the ultimate oil recovery reached to the plateau at 8.6% of OOIP.

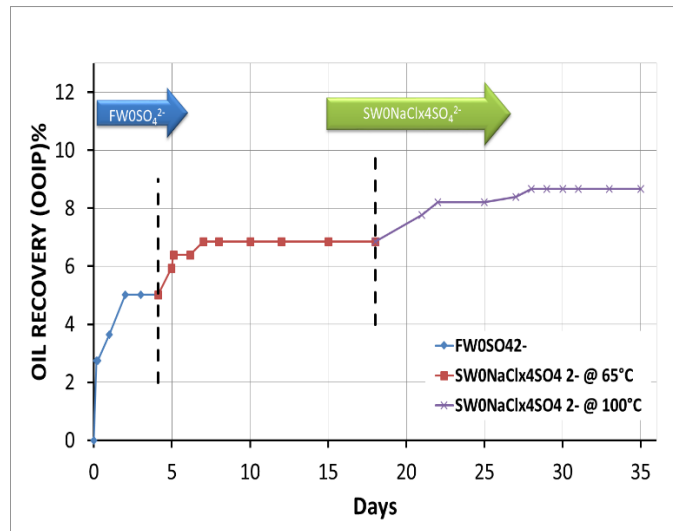


Figure 5.32. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C and 100°C for core 37C

5.3 Predicting the concentration of SO_4^{2-} in limestone and dolomitic cores by PHREEQC simulator

PHREEQC simulator was used in this experiment to simulate and predict the concentration of SO_4^{2-} in aqueous solution in a system containing limestone and dolomitic minerals, the simulation were made at atmospheric and reservoir pressure using different temperatures to equilibrate the brine (20°C to 130°C).

EDAX analysis were used to design the mineralogical phases of the system, atmospheric CO_2 was added to the brine, calcite and anhydrite were included for the limestone cores simulation, calcite, anhydrite and dolomite were representative of dolomitic cores.

The previous phases were added to a kg of mentioned brine ($\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ for limestone cores and SW d_{20} for dolomitic cores) and let reach equilibrium. PHREEQC predicted the amount of SO_4^{2-} after a few seconds. The ions concentration of simulation brines and the amount of limestone and dolomitic minerals are shown in tables 11.1 to 11.8. All results of simulation are mentioned as following steps:

- **Concentration of sulfate (SO_4^{2-}) in limestone and dolomitic cores at atmospheric pressure in different temperatures (20°C to 130°C)**

Figure 5.33 and 5.34 depict the concentration of SO_4^{2-} in aqueous solution in a system containing limestone and dolomitic minerals versus different temperatures at atmospheric pressure. In both cases the concentration of SO_4^{2-} decreases by increasing the temperature.

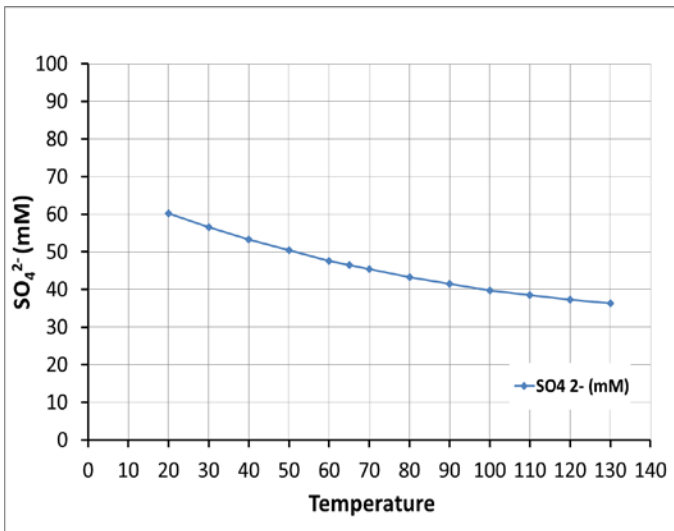


Figure 5.33. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone cores at atmospheric pressure

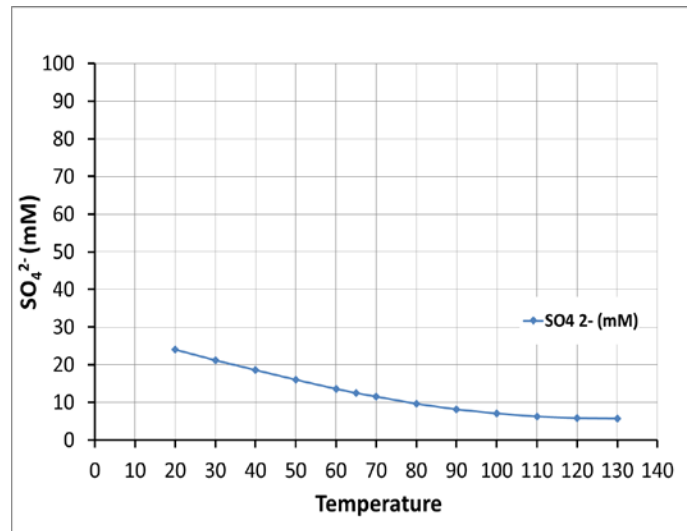


Figure 5.34. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in dolomitic cores at atmospheric pressure

- **Concentration of sulfate (SO_4^{2-}) in limestone and dolomitic cores at reservoir pressure in different temperatures (20°C to 130°C)**

Figure 5.35 and 5.36 show the concentration of SO_4^{2-} in aqueous solution in a system containing limestone and dolomitic minerals versus different temperatures at reservoir pressure. Same as atmospheric pressure, in both cases the concentration of SO_4^{2-} decreases by increasing the temperature.

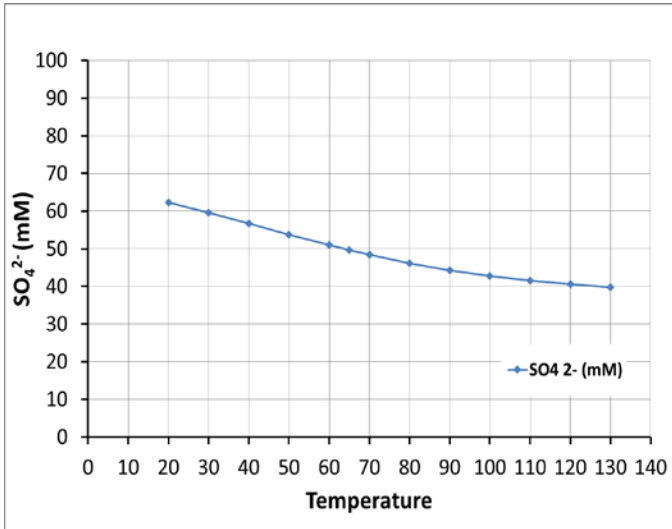


Figure 5.35. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone cores at reservoir pressure

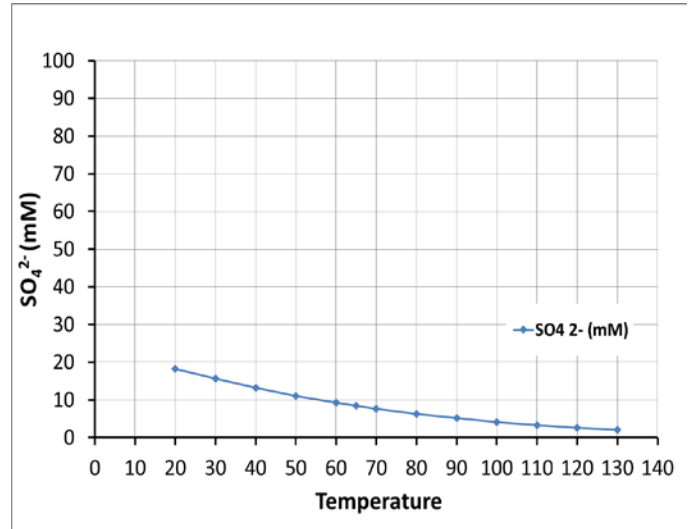


Figure 5.36. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in dolomitic cores at reservoir pressure

6. Discussion

In this work, the effects of 3 different brines that contain phosphate, sulfate and borate ions, as a parametric study were tested on chalk cores to decide, which brine is a good candidate to use as imbibing brine for limestone and dolomitic cores. Additionally PHREEQC simulator was used to simulate and predict the SO_4^{2-} concentration in brines containing limestone and dolomitic minerals versus different temperatures.

6.1 The effects of phosphate, borate and sulfate on wettability alteration and oil recovery of chalk cores (parametric study)

Gupta et al. 2011, recognized borate and phosphate were two ions which performed better than sulfate and they can potentially improve water flood oil recovery. They found that enhanced oil recovery was significantly higher for the modified brine containing borate ions than for the modified brine containing sulfate ion.

Parametric study was performed during this test. Three brines containing different chemical composition were prepared for spontaneous imbibition tests for chalk cores. The one that contain phosphate, was not a suitable brine, since quick precipitation happened after adding phosphate to the brine, figure 11.23. By adding the phosphate brine to the cores or reservoir, because of precipitation, plugging of pores will happen. The reason of this precipitation is the low solubility of calcium and magnesium in presence of the phosphate ion. Another one had the presence of Borate ions and the last brine contained Sulfate ions. Borate and sulfate solutions were completely clear and without any precipitation. Two bottles of these brines were put in the oven at reservoir temperature (65°C) during experiment to observe if there is any precipitation, but no precipitation happened at reservoir temperature and both were clear. As shown in figure 5.1, borate brine had lower and slower oil production compare to sulfate brine and finally the oil recovery by sulfate brine was almost 22% of OOIP more than borate brine.

In here spontaneous imbibition is dominated by capillary forces, since the shape of the oil recovery curve is mostly curved not linear. The slope of the graph in figure 5.1 after 25 days becomes almost linear. This change in the curve indicates that the gravity force is the main imbibition forces not the capillary forces. The effect of “smart water” can be observed by increasing 22% in oil recovery compared to the borate brine.

This experiment was done same conditions as Fathi’s work (2012) and the spontaneous imbibition oil recovery by VB and SW brines in his work were 17% and 38% of OOIP respectively, however the oil recovery by borate brine is more than VB and less than SW, therefore the brine that contains sulfate ions (smart water) was the best brine for spontaneous imbibition. Finally it was decided to select the sulfate brine for the limestone cores experiment. The compositions of phosphate, borate and sulfate brines are shown in table 4.5.

6.2 Limestone cores

- **Core 10D**

The batch test of core 10D was done. The water effluent of the last cleaning stage was tested with BaCl_2 for sulfate presence, the test was positive for the first 3 pore volumes collected in the effluent. This may imply presence of anhydrite.

Prior and after the surface reactivity test (flooding with hot sea water) a spontaneous imbibition test was carried out and core 10D did not produce any heptane during 5 days of test, figure 5.10. It is important to note that no capillary forces were induced after the flooding with hot sea water and after the second spontaneous imbibition test, the spontaneous drainage test was carried out, the core 10D did not produce any water during 5 days of test, figure 5.11. This core was not water-wet nor oil-wet, it did not produce any oil during spontaneous imbibition and any water during spontaneous drainage test. The wettability did not change after hot sea water flooding, so the sulfate ions in the sea water did not catalyzed the wettability alteration process.

After the first spontaneous imbibition test a surface reactivity test was done, it was expected to have lower concentrations of sulfate after the initial flooding with sea water without sulfate, however when the sulfate concentrations were evaluated they were very high to quantify a chromatographic separation of the thiocyanate and sulfate ions, figure 5.8. After the flooding with sea water at 130°C a new tracer test was carried out and the levels were slightly higher, probably due to the contribution of sulfate present during the hot sea water flooding. No separation of sulfate and thiocyanate was possible to be quantified, figure 5.9. Note that the sulfate concentration is due to dissolution of a mineral containing sulfate and the contribution of the brine containing sulfate. In the second test the higher level can be explained by the presence of sulfate derived from the sea water flooded at high temperature. Finally the chromatographic separation of the thiocyanate and sulfate ions was not achieved to observe any wettability alteration after hot sea water flooding.

However as the thiocyanate ion does not interact with the limestone surface, is possible to use it to get an information about the pore distribution; a profile of this concentration describes that in about 2 PV a full flood of the core is carried out, this can be translated into an even distribution of pores. The “S” shape of thiocyanate profile shows that this core is a kind of homogeneous core.

More over the constant concentration of sulfate indicates a high amount of this ion during the flooding, it is important to note that in between each tracer test 9 PV of hot sea water were injected and the sulfate concentration still being high.

SEM and EDAX of core 10D were performed after experiment to see the physical and chemical characteristics of this core. The results are shown in figure 5.2 to 5.7. The pores are very heterogeneous, figures 5.3 and 5.5 depict the high content of Magnesium in core 10D, concentrations from 15% to 38% in weight percentage were observed. It shows that core is

dolomitic. Figure 5.6 shows the presence of CaSO_4 , which is confirmed in the sulfate levels observed in the surface reactivity test.

The surface reactivity test, SEM and EDAX of core 10D were important for the selecting imbibing brine for core 10E in spontaneous imbibition at reservoir temperature. By recognizing that core 10D is a dolomitic core, it was decided to select SWd_{20} that has lower concentration of SO_4^{2-} as imbibing brine for core 10E that is in same group of core 10D.

- **Core 14B**

The batch test of core 14B was done. The water effluent of the last cleaning stage was tested with BaCl_2 for sulfate presence, the test was positive for the first 3 pore volumes collected in the effluent. The color of the samples containing BaCl_2 was not as intense as in the core 10D, so a lower concentration of sulfates is expected in the IC analysis; however the presence of them is clear.

Prior the surface reactivity test (flooding with hot sea water) a spontaneous imbibition test was carried out and core 14B did not produce any heptane during 5 days of test, but after flooding with hot sea water (surface reactivity test), the second spontaneous imbibition was done and core 14B produced a little amount of heptane (3.5% OOIP) during 5 days of test, figure 5.20. The little production of heptane in the second tests can be due to wettability alteration or gravitational forces. The spontaneous drainage test was carried out and the core 14B did not produce any water during 5 days of test, figure 5.21. This core was not water-wet nor oil-wet, however it produced a little amount of oil during spontaneous imbibition and no water during spontaneous drainage test. Maybe the wettability had a small change because of a little production of heptane after hot sea water flooding (surface reactivity test), therefore the sulfate ions in the sea water could catalyzed the wettability alteration process.

The first surface reactivity test was done after the spontaneous imbibition test, it was hardly possible to observe a chromatographic separation between the sulfate and the thiocyanate as the sulfate concentration was around a tenth of the concentration of sulfate after flooding with the sea water without tracer, figure 5.18. As shown in figure 5.19, after the flooding with sea water at 130°C a new tracer test was carried out and the sulfate concentration was a tenth of the sulfate concentration of the tracer, but in here the area between sulfate and the thiocyanate a little increased and this could be because of change in wettability and it was demonstrated by second spontaneous imbibition that had a minor oil production.

However as the thiocyanate ion does not interact with the limestone surface, is possible to use it to get an information about the pore distribution. After observing the profile, during the first and second surface reactivity test, 2.5 PV were required to obtain to displace completely the tracer. The reason could be because of micro porosity that this core may has and it takes 0.5 PV more to remove all the thiocyanate. The “S” shape thiocyanate profile shows that this core is a kind of homogeneous core, but it is less homogenous than core 10D, figure 5.18 and 5.19.

A lower concentration of sulfate in the effluent allowed performing the surface reactivity test in both cases; regardless the little of variation in the area of separation between the sulfate and thiocyanate ions. However the presence of sulfate in the effluents analyzed was constant.

SEM and EDAX of core 14B were performed after experiment to evaluate physical and chemical characteristics of this core. The results are shown in figure 5.12 to 5.17. Figures show the heterogeneity of core 14B, since the grain sizes were variable. Figures 5.13, 5.15 and 5.17 show high content of CaCO_3 in core 14B. This core was mainly formed of CaCO_3 and no CaSO_4 was found during this analysis.

Same as core 10D, the surface reactivity test, SEM and EDAX of core 14B were important for the selecting imbibing brine for core 14C in spontaneous imbibition at reservoir temperature. By recognizing that core 14B is a limestone core (almost pure calcite), it was decided to select $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ that has higher concentration of SO_4^{2-} as imbibing brine for core 14C that is in same group of core 14B.

- **Core 37A**

The batch test of core 37A was done. The water effluent of the last cleaning stage was tested with BaCl_2 for sulfate presence, the test was positive for the first 3 pore volumes collected in the effluent.

A spontaneous imbibition test was carried out prior the surface reactivity test (flooding with hot sea water) and core 37A did not produce any heptane during 5 days of test, but after surface reactivity test, the second spontaneous imbibition was done and core 37A produced a little amount of heptane (2.5% OOIP) during 5 days of test, figure 5.28. No relevant capillary forces were observed and the little production of heptane in the second tests can be due to gravitational forces. It also can be proved by surface reactivity test. The area before and after hot sea water flooding did not change and it means sulfate ions in the sea water could not catalyzed the wettability alteration process therefore wettability did not change in this process. The spontaneous drainage test was carried out and the core 37A did not produce any water during 5 days of test, figure 5.29. This core was not water-wet nor oil-wet, it produced a little amount of oil during spontaneous imbibition and no water during spontaneous drainage test.

After the first spontaneous imbibition test, the first surface reactivity test was done, it was impossible to observe a chromatographic separation between the sulfate and the thiocyanate as the sulfate concentration was around a tenth of the concentration of sulfate after flooding with the sea water without tracer, figure 5.26. A new tracer test was carried out after the flooding with hot seawater at 130°C and the sulfate concentration was a tenth of the sulfate concentration of the tracer and once again it was impossible to see a chromatographic separation between the sulfate and the thiocyanate, figure 5.27. There was no change in area after the flood with hot sea water (130°C), so no wettability alteration occurred during hot sea water flooding and no capillary forces were improved.

The thiocyanate ion is possible to use it to get an information about the pore distribution. After observing the profile, during the first and second surface reactivity test, 2.5 PV were required to obtain to displace completely the tracer. The reason could be because of micro porosity that this core may has and it takes 0.5 PV more to remove all the thiocyanate. The “S” shape thiocyanate profile shows that this core is a homogeneous core, figure 5.26 and 5.27.

To see the physical and chemical characteristics of core 37A, SEM and EDAX of this core were performed after experiment. The results are shown in figure 5.22 to 5.25. The grain sizes of core 37A were variable, the figures show the heterogeneity of this core. Figures depict high content of CaCO_3 in core 37A. This core was formed of CaCO_3 , no CaSO_4 was found during this analysis.

The surface reactivity test, SEM and EDAX of core 37A were also important for the selecting imbibing brine for core 14C and 37C in spontaneous imbibition at reservoir temperature. By recognizing that core 37A is a limestone core (almost pure calcite), it was decided to select $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ that has higher concentration of SO_4^{2-} as imbibing brine for core 37C that is in same group of core 37A.

- **Comparison oil recovery between reservoir groups (cores 10E, 14C, and 37C) by spontaneous imbibition test by Amott cell at 65°C (reservoir temperature) and by steel cell at 100°C**

Core 10E, 14C and 37C were placed in to the Amott cells for spontaneous imbibition at 65°C to see the wettability alteration and recovery. The recovery curve (%OOIP) versus days of these cores at different steps is shown in figure 6.1. Initially the cores were imbibed by FW0SO_4^{2-} as a formation imbibing brine. Since the concentration of SO_4^{2-} in reservoir (cores) was high, therefore FW0SO_4^{2-} was used instead of FW, therefore the FW0SO_4^{2-} will reach to equilibrium in these cores. Core 10E and 14C with 5.7% and 4.6% recovery of OOIP had the highest and lowest oil recovery in this step. From the shape of the figure it can be observed that almost half of this recovery was because of thermal expansion and another half was capillary forces.

After several days that no more oil production was observed, the imbibing brines were changed to SWd_{20} for core 10E and $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ for cores 14C and 37C as smart water. As explained in experimental materials, the cores 10E and 10D are in the same group and they have the same mineralogy and characterization. EDAX analysis showed that the cores in this group are dolomitic; therefore SWd_{20} that has lower SO_4^{2-} concentration than $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ was used for imbibing fluid. And also in the spontaneous imbibition process both Na^+ and Cl^- ions were the non-active ions. Reducing the concentrations of these ions, allow active ions (SO_4^{2-} and Ca^{2+}) to have easier access to the limestone surface (Udegbunam, 2011). But the main reason of choosing SWd_{20} as imbibing fluid is that, Romanuka et al. 2012, recognized that the adsorption of carboxylic materials on dolomitic cores is less than the limestone (pure calcite) cores, so the amount of SO_4^{2-} concentration that needs for reducing the positively of surface and prepare the rock surface for desorption of carboxylic materials and changing the wettability is less than for limestone (pure calcite) cores.

The cores 14B, 14C and 37A, 37C are in same groups (group 2 and 3) and they have same characterization. EDAX analysis showed that the cores in this group are limestone with high percentage of calcite and as described in section 3.4.5, Zhang 2006, showed that when sea water (which contains a lot of SO_4^{2-}) is injected in to the chalk reservoir, SO_4^{2-} will adsorb on the positive surface of chalk and will reduce the positively of chalk, then Ca^{2+} will co-adsorb and the concentration of Ca^{2+} will increase close to the chalk surface. As Ca^{2+} reacts with negatively charged carboxylic group, some of adsorbed carboxylic material is desorbed from the surface, therefore $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ that has higher SO_4^{2-} concentration than SWd_{20} was used for imbibing fluid and the adsorption of carboxylic materials is high for limestone (pure calcite) cores, so the amount of SO_4^{2-} concentration that needs for reducing the positively of surface and prepare the rock surface for desorption of carboxylic materials and changing the wettability is higher than dolomitic cores. Once again in this step the oil recovery of core 10E was the highest with 15.9% of OOIP and the oil recovery of cores 14C and 37C reached to the plateau at 12.9% and 6.8% of OOIP respectively. Increasing in oil recovery of core 10E by SWd_{20} , was 10.2% of OOIP and for cores 14C and 37C by $\text{SW0NaCl} \times 4\text{SO}_4^{2-}$ was 8.3% and 1.8% of OOIP.

The magnesium concentrations of group 1 was from 15% to 38% in weight percentage and for group 2 and group 3 was 3% and 1% in weight percentage respectively. It was observed from the ion chromatography that core 37A had the lowest response to wettability alteration and this effect could be observed in oil recovery of core 37C that had the lowest oil recovery.

For increasing the reactivity of sulfate, core 37C was placed in to the steel cell at 100°C with the same imbibing fluid. By starting the steel cell spontaneous imbibition at 100°C , the oil recovery of core 37C, 1.8% of OOIP increased and reached to 8.6% of OOIP. Increasing temperature did not have much effect on wettability alteration and oil recovery and this small production could be because of thermal expansion.

At the end of the test, several samples were taken from the Amott cells at reservoir temperature and atmospheric pressure for ion chromatography analysis. The analysis of sulfate concentration of the imbibing brine by ion chromatography showed that there was no sulfate precipitation.

Checking of SO_4^{2-} concentration by ion chromatography had a good result for experiment. It means that the concentration of SO_4^{2-} as a catalyst for changing wettability in experiment could be higher than $4 \times \text{SO}_4^{2-}$.

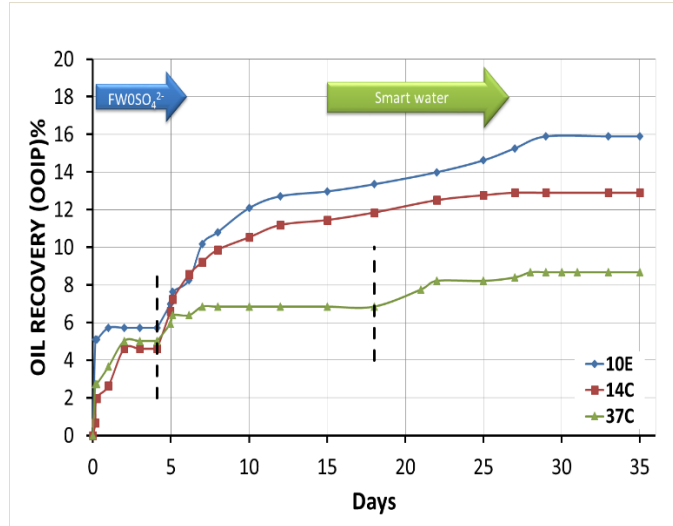


Figure 6.1. Oil recovery versus days of spontaneous imbibition by Amott cell at 65°C for different reservoir groups

6.3 PHREEQC Simulator

- **Comparison between limestone and dolomitic cores at different pressures and temperatures**

PHREEQC simulator was used in this experiment to simulate and predict the concentration of SO_4^{2-} in aqueous solution in a system containing limestone and dolomitic minerals. EDAX analysis were used to design the mineralogical phases of the system. The simulation were made at atmospheric and reservoir pressure using different temperatures to equilibrate the brine (20°C to 130°C).

Figure 6.2 shows the concentration of SO_4^{2-} versus different temperatures in atmospheric and reservoir pressure. In all cases the concentration of SO_4^{2-} decreases by increasing the temperature.

The SO_4^{2-} concentration reduction for limestone cores in reservoir pressure is less than atmospheric pressure, but SO_4^{2-} concentration reduction for dolomitic cores in reservoir pressure are higher than atmospheric pressure.

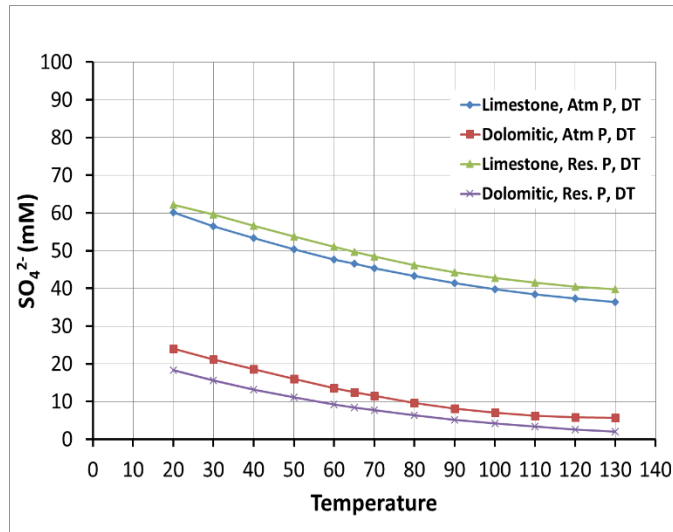


Figure 6.2. Concentration of SO_4^{2-} versus temperatures (20°C to 130°C) in limestone and dolomitic cores at atmospheric and reservoir pressure

7. Conclusions

The main objective of this project was to observe the effects of 3 different designed brines on chalk cores and choose the best brine as imbibing brine for limestone and dolomitic cores.

From the experimental results and discussion of this study, the following conclusions were observed:

- Brine that contain phosphate ions due to precipitation in presence of divalent ions was not a proper brine. Borate brine had slower and lower production compare to sulfate brine, but the brine with sulfate ions (smart water) was the best brine with highest oil recovery and this brine was selected for spontaneous imbibition in limestone cores.
- The smart water increased the oil recovery of core 10E (group 1) by SWd₂₀, 10.2% of OOIP and for cores 14C (group 2) and 37C (group 3) by SW0NaCl x 4SO₄²⁻, 8.3% and 1.8% of OOIP respectively.
- Anhydrite presence was confirmed by using different techniques same as surface reactivity test, EDAX and batch test.
- SEM and EDAX can show the mineralogy, physical and chemical characteristics of cores. The heterogeneity and homogeneity of pores can be observed clearly. It shows that this kind of core is dolomitic or limestone (pure calcite) core. The SEM and EDAX of cores were important for the selecting imbibing brine in spontaneous imbibition. For dolomitic and limestone cores, it was decided to select SWd₂₀ and SW0NaCl x 4SO₄²⁻ respectively as imbibing brines.
- The chromatography wettability tests were used to study the potential of wettability alteration and specify if there is any water-wet surface in limestone cores.
- Information about the pore distribution was obtained by using the thiocyanate concentration from the surface reactivity test.
- Sulfate is a catalyst in wettability alteration and by increasing sulfate concentration the ultimate oil recovery will increase. Group 1 had the highest sulfate content and oil recovery between groups.
- Increasing temperature did not have effect on wettability alteration and oil recovery of limestone core 37C in group 3 and no wettability alteration was observed by ion chromatography of this group. The small production was because of thermal expansion.
- The analysis of sulfate concentration of the imbibing brine by ion chromatography showed that there was no sulfate precipitation. It means that the concentration of SO₄²⁻ as a catalyst for changing wettability in experiment could be higher than 4 x SO₄²⁻.
- PHREEQC simulator predicted the SO₄²⁻ concentration decreases by increasing the temperature in atmospheric and reservoir pressure and the SO₄²⁻ concentration reduction for limestone cores in reservoir pressure is less than atmospheric pressure, but SO₄²⁻ concentration reduction for dolomitic cores in reservoir pressure is higher than atmospheric pressure.

8. Future Work

Suggestion to future works:

- Surfactant C12TAB can help us to compare the performance of the smart water, therefore the next step of spontaneous imbibition could be checking the effects of brines with surfactant as an imbibing fluids on wettability alteration.
- As discussed in this study, it has been approved by ion chromatography that SW0NaCl x 4SO₄²⁻ did not have precipitation during experiment, therefore the brines with more concentration of SO₄²⁻ (more catalyst) could be used in future experiments to see their effects on limestone cores.
- SWd₂₀ worked for dolomitic core in this study, so it will be better to check more dolomitic cores from this or other reservoirs by diluted sea water.
- For comparison between groups, it will be better to use the same brine for three different groups.
- Force displacement (long time flooding with low rate) by brines was not done in this project, so it would be good to do this process and observe the results.

9. Symbols and Abbreviation

K	Absolute permeability, m^2 or mD
g	Acceleration due to gravity, m/s^2
AN	Acid number, mg KOH/g oil
$ASTM$	American Society for Testing and Materials
A_1	Area under the secondary water-drainage curve
A_2	Area under the imbibition curve falling below the zero- P_c axis
$A_{Heptane}$	Reference area between the thiocyanate and sulfate curves generated by flooding a core assumed to be strongly water-wet (saturated with heptane)
A_{wett}	Area between the thiocyanate and sulfate curves generated by flooding a core aged in crude oil
BN	Base number, mg KOH/g oil
P_c	Capillary pressure, Pa
C/C_0	Relative concentration of ions
θ	Contact angle, $^\circ$
D	Core diameter, cm
DIW	Distillated water
EOR	Enhanced oil recovery
IFT, σ	Interfacial tension, mN/m
σ_{os}	Interfacial tension oil-solid, mN/m
σ_{ws}	Interfacial tension water-solid, mN/m
σ_{ow}	Interfacial tension oil-water, mN/m
IOR	Improved oil recovery
L	Core length, cm
$OOIP$	Original oil in place.
PV	Pore volume cm^3
SW	Synthetic seawater
$SW0NaCl$	Modified synthetic seawater without NaCl
$SW0T$	Synthetic seawater without SO_4^{2-}
$SW1/2T$	Synthetic seawater in which the concentration of SCN^- and SO_4^{2-} is 0.012 mole/l respectively
$SW d20$	Seawater diluted 20 times
$SW4S0NaCl$	Modified synthetic seawater without NaCl and with 4 times the concentration of sulfate
S_{or}	Residual oil saturation, %
S_{wi}	Initial water saturation, %
TDS	Total dissolved solids, g/l
$USBM$	United state Bureau of Mines
VB	Valhall formation brine
WI	Chromatography wettability index
μ	Viscosity, cp
ϕ	Porosity, %
ρ	Density, g/cm^3
$\Delta\rho$	Density difference, g/cm^3

10. References

- Andersen, M. A. (1995). *Petroleum research in North Sea chalk*: RF-Rogaland Research.
- Anderson, W. (1986b). *Wettability literature survey-part 2: Wettability measurement*. Journal of Petroleum Technology, 38(11), 1,246-241,262.
- Anderson, W. G. (1986a). *Wettability literature survey-Part 1: Rock/oil/brine interactions and the effects of core handling on wettability*. J. Pet. Technol.:(United States), 38(11).
- ASTM. (1988). *ASTM 2896-88. Standard test method for base number of petroleum products by potentiometric perchloric acid titration*. Annual Book of ASTM Standards.
- ASTM. (1989). *ASTM 664-89. Standard test method for Acid number of petroleum products by potentiometric titration*. Annual Book of ASTM Standards.
- Austad, T. (2004). *Waterflooding of carbonate reservoirs - Optimization and improved oil recovery*. Norway: forskningsradet.
- Austad, T., Strand, S., Høgnesen, E., & Zhang, P. (2005, February 2-4). *Seawater as IOR fluid in fractured chalk*. Paper presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA.
- Baviere, M. (1991). *Basic concepts in enhanced oil recovery processes*. Critical Reports on Applied Chemistry, 33, 101.
- Buckley, J. S. (1996). *Mechanisms and consequences of wettability alteration by crude oils*. (Phd), Heriot-Watt, Edinburgh, UK.
- Castor, T., Somerton, W., & Kelly, J. (1981). *Recovery mechanisms of alkaline flooding Surface phenomena in enhanced oil recovery* (pp. 249-291): Springer.
- Cole, F. W. (1969). *Reservoir engineering manual*. Houston, Texas. Printed in USA: Gulf Pub. Co.
- Cossé, R. (1993). *Basics of reservoir engineering*: Editions OPHRYS.
- Donaldson, E., Thomas, R. D., & Lorenz, P. B. (1969). *Wettability determination and its effect on recovery efficiency*. SPE.
- Fan, T., & Buckley, J. S. (2006). *Acid Number Measurements Revisited*.
- Farouq-Ali, S., & Stahl, C. (1970). *Increased oil recovery by improved waterflooding*. Earth Miner. Sci.:(United States), 39(4).
- Fathi, S. J., Austad, T., & Strand, S. (2012). *Water-based Enhanced Oil recovery (EOR) by "Smart Water" in Carbonate Reservoirs*. Paper presented at the SPE EOR Conference at oil and Gas West Asia.
- Fathi, J. (2012). *Water-based enhanced oil recovery (EOR) in carbonate reservoirs: initial wetting condition and wettability alteration by "Smart Water"* (Vol. no. 149). Stavanger: UiS.
- Gluyas, J. a. S., Richard. (2004). *Petroleum Geoscience* Oxford: Blackwell Publishing.
- Goldstein, J., Newbury, D. E., Joy, D. C., Lyman, C. E., Echlin, P., Lifshin, E., . . . Michael, J. R. (2003). *Scanning electron microscopy and X-ray microanalysis*: Springer.
- Green, D. W., & Willhite, G. P. (1998). *Enhanced oil recovery*: Richardson, Tex.: Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers.
- Gupta, R., Smith, G. G., Hu, L., Willingham, T., Lo Cascio, M., Shyeh, J. J., & Harris, C. R. (2011). *Enhanced Waterflood for Carbonate Reservoirs - Impact of Injection Water Composition*.
- Hjelmeland, O., & Larrondo, L. (1986). *Experimental Investigation of the Effects of Temperature Pressure and Crude Oil Composition on Interfacial Properties*. SPE Reservoir Engineering, 1(04), 321-328.

- Høgenesen, E. J., Strand, S., & Austad. (2005). *Water flooding of Preferential Oil-Wet Carbonates: Oil recovery Related to Reservoir Temperature and Brine Composition*. SPE Europec/EAGE Annual
- Khursheed, A. (2011). *Scanning Electron Microscope optics and spectrometers*: World Scientific.
- Ma, S., Zhang, X., Morrow, N., & Zhou, X. (1999). *Characterization of wettability from spontaneous imbibition measurements*. *Journal of Canadian Petroleum Technology*, 38(13), 1-8.
- Machel, H.-G., & Mountjoy, E. W. (1986). *Chemistry and Environments of Dolomitization —A Reappraisal*. *Earth-Science Reviews*, 23(3), 175-222. doi: [http://dx.doi.org/10.1016/0012-8252\(86\)90017-6](http://dx.doi.org/10.1016/0012-8252(86)90017-6)
- Manrique, E., Gurfinkel, M., & Muci, V. (2004). *Enhanced oil recovery field experiences in carbonate reservoirs in the United States*. Paper presented at the 25th Annual Workshop and Symposium, International Energy Agency (IEA), Stavanger, Norway.
- Manrique, E. J., Muci, V. E., & Gurfinkel, M. E. (2007). *EOR Field Experiences in Carbonate Reservoirs in the United States*. doi: 10.2118/100063-PA
- Menezes, J., Yan, J., & Sharma, M. (1989). *The mechanism of wettability alteration due to surfactants in oil-based muds*. paper SPE, 18460, 8-10.
- Morrow, N. R. (1979). *Interplay of Capillary Viscous And Buoyancy Forces In the Mobilization of Residual Oil*. *Journal of Canadian Petroleum Technology*, 18(03).
- Murty, C., Al-Saleh, N., & Dakessian, B. (1987). *Forty-Seven Years' Gas Injection in a Preferentially Oil-Wet Low-Dip Reservoir*. *Journal of Petroleum Technology*, 39(03), 363-368.
- Parkhurst, D. L., & Appelo, C. (1999). *User's guide to PHREEQC (Version 2): Acomputer Program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*.
- Punternold, T. (2008). *Waterflooding of carbonate reservoirs: EOR by wettability alteration (Vol. no. 50)*. Stavanger: UiS.
- Punternold, T., Strand, S., & Austad, T. (2007). *Water flooding of carbonate reservoirs: Effects of a model base and natural crude oil bases on chalk wettability*. *Energy & fuels*, 21(3), 1606-1616.
- Raza, S., Treiber, L., & Archer, D. (1968). *Wettability of reservoir rocks and its evaluation*. *Prod. Mon.:(United States)*, 32(4).
- Romanuka, J.; Hofman, J.; Ligthelm, D. J.; Suijkerbuijk, B.; Marcelis, F.; Oedai, S.; Brussee, N.; Linde, H. v. d.; Aksulu, H.; Austad, T. *In Low salinity EOR in carbonates*, Paper SPE 153869 presented at the eighteenth SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 14-18 April, 2012.
- Satpute, S. K., Banat, I. M., Dhakephalkar, P. K., Banpurkar, A. G., & Chopade, B. A. (2010). *Biosurfactants, bioemulsifiers and exopolysaccharides from marine microorganisms*. *Biotechnology Advances*, 28(4), 436-450.
- Siagi, Z. O., Mbarawa, M., Mohamed, A. R., Lee, K. T., & Dahlan, I. (2007). *The effects of limestone type on the sulphur capture of slaked lime*. *Fuel*, 86(17-18), 2660-2666. doi: <http://dx.doi.org/10.1016/j.fuel.2007.03.034>
- Skauge, A., Standal, S., Boe, S., Skauge, T., & Blokhus, A. (1999, October 3-6). *Effects of organic acids and bases, and oil composition on wettability*. Paper presented at the SPE annual technical conference, Houston, TX, USA.
- Soudmand-asli, A., Ayatollahi, S. S., Mohabatkar, H., Zareie, M., & Shariatpanahi, S. F. (2007). *The in situ microbial enhanced oil recovery in fractured porous media*. *Journal of Petroleum Science and Engineering*, 58(1-2), 161-172.

- Speight, J. G. (1999). *Chemistry and Technology of Petroleum (3rd Edition)*. New York, NY, USA: CRC Press.
- Standnes, D. C., & Austad, T. (2000). *Wettability alteration in chalk: 1. Preparation of core material and oil properties*. *Journal of Petroleum Science and Engineering*, 28(3), 111-121.
- Standnes, D. C., & Austad, T. (2003). *Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions*. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 216(1), 243-259.
- Strand, S. (2005). *Wettability alteration in chalk: a study of surface chemistry* (Vol. no. 21). [Stavanger]: UiS.
- Strand, S., Standnes, D., & Austad, T. (2006). *New wettability test for chalk based on chromatographic separation of SCN and SO₄²⁻*. *Journal of Petroleum Science and Engineering*, 52(1), 187-197.
- Thomas, M. M., Clouse, J. A., & Longo, J. M. (1993). *Adsorption of organic compounds on carbonate minerals: 3. Influence on dissolution rates*. *Chemical geology*, 109(1), 227-237.
- Treiber, L., & Owens, W. (1972). *A laboratory evaluation of the wettability of fifty oil-producing reservoirs*. *Society of petroleum engineers journal*, 12(06), 531-540.
- Tweheyo, M. T., Zhang, P., & Austad, T. (2006, April 22-26). *The effects of temperature and potential determining ions present in seawater on oil recovery from fractured carbonates*. Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, U.S.A.
- Udegbumam, J.E. (2011). *EOR in Chalk: Optimized Oil Recovery with modified seawater*. Stavanger: UiS.
- Wang, W., & Gupta, A. (1995, October 22-25). *Investigation of the effect of temperature and pressure on wettability using modified pendant drop method*. Paper presented at the Society of Petroleum Engineers. Annual technical conference, Dallas, TX, USA.
- Xie, X., Morrow, N. R., & Buckley, J. S. (2000). *Contact angle hysteresis and the stability of wetting changes induced by adsorption from crude oil*. Paper presented at the 6th International Symposium on Reservoir Wettability and Its' Effect on Recovery Socorro, NM, USA.
- Yu, L., & Buckley, J. (1997). *Evolution of wetting alteration by adsorption from crude oil*. *SPE Formation Evaluation*, 12(01), 5-12.
- Zhang, P. (2006). *Water-based EOR in fractured chalk-Wettability and chemical additives*. (Phd), Stavanger, Norway.
- Zhang, P., & Austad, T. (2005, June 13-16). *Waterflooding in Chalk—Relationship between Oil Recovery, New Wettability Index, Brine Composition and Cationic Wettability Modifier (SPE94209)*. Paper presented at the 67th EAGE Conference & Exhibition, Madrid, Spain.
- Zolotukhin, A. B., & Ursin, J.-R. (2000). *Introduction to petroleum reservoir engineering*: Norwegian Academic Press (HøyskoleForlaget).

11. Appendix

11.1 Explanation of Ion Chromatography System

- **Sampler**

All the collected effluent samples are put in the sampler container (Figure 11.1), according to the positions (1 to 100) which will be specified in the data list through the software program.

Note: All the samples have to be diluted and filtered prior to putting them in the sampler of IC system. It is important to prepare several reference samples, which their compositions are known.



Figure 11.1. The position of the samples in the sampler of IC system.

- **Eluent containers**

Eluent helps the samples to pass the resin column during measurements. It is important to make sure that the Eluent DI (deionized water) containers (Figure 11.2) are full prior to starting the measurement.



Figure 11.2. The containers of Anion and Cation eluent DI.

- **Input Data**

As shown in Figure 11.3, in the data list of the software program all the prepared samples have to be named ('Name' column) and allocated ('Position' column) according to their positions in the sampler. For analyzing Anions and Cations in a group of samples it is necessary to prepare two different data files, which have to be saved in the related folders.

#	CD_1	Name	Type	Level	Position	Volume [µl]	Instrument Method	Processing Me	Status
1		Sw1/2T 1:200	Unknown		91	300.0	Anion SW-T 16 min	TestProcess	Finished
2		DI	Unknown		81	300.0	Anion SW-T 16 min	TestProcess	Finished
3		Sw1/2T 1:200	Unknown		91	300.0	Anion SW-T 16 min	TestProcess	Finished
4		Sw1/2T 1:200	Unknown		91	300.0	Anion SW-T 16 min	TestProcess	Finished
5		1.1.C SW/OT	Unknown		1	300.0	Anion SW-T 16 min	TestProcess	Finished
6		1.1.C SW/OT	Unknown		2	300.0	Anion SW-T 16 min	TestProcess	Finished
7		1.1.C SW/OT	Unknown		3	300.0	Anion SW-T 16 min	TestProcess	Finished
8		1.1.C SW/OT	Unknown		4	300.0	Anion SW-T 16 min	TestProcess	Finished
9		1.1.C SW/OT	Unknown		5	300.0	Anion SW-T 16 min	TestProcess	Finished
10		1.1.C SW/OT	Unknown		6	300.0	Anion SW-T 16 min	TestProcess	Finished
11		Sw1/2T 1:200	Unknown		92	300.0	Anion SW-T 16 min	TestProcess	Finished
12		1.1.C SW/OT	Unknown		7	300.0	Anion SW-T 16 min	TestProcess	Finished
13		1.1.C SW/OT	Unknown		8	300.0	Anion SW-T 16 min	TestProcess	Finished
14		1.1.C SW/OT	Unknown		9	300.0	Anion SW-T 16 min	TestProcess	Finished
15		1.1.C SW/OT	Unknown		10	300.0	Anion SW-T 16 min	TestProcess	Finished
16		1.1.C SW/OT	Unknown		11	300.0	Anion SW-T 16 min	TestProcess	Finished
17		1.1.C SW/OT	Unknown		12	300.0	Anion SW-T 16 min	TestProcess	Finished
18		Sw1/2T 1:200	Unknown		92	300.0	Anion SW-T 16 min	TestProcess	Finished
19		1.1.C SW/OT	Unknown		13	300.0	Anion SW-T 16 min	TestProcess	Finished
20		1.1.C SW/OT	Unknown		14	300.0	Anion SW-T 16 min	TestProcess	Finished
21		1.1.C SW/OT	Unknown		15	300.0	Anion SW-T 16 min	TestProcess	Finished
22		1.1.C SW/OT	Unknown		16	300.0	Anion SW-T 16 min	TestProcess	Finished
23		1.1.C SW1/2T	Unknown		21	300.0	Anion SW-T 16 min	TestProcess	Finished
24		Sw1/2T 1:200	Unknown		92	300.0	Anion SW-T 16 min	TestProcess	Finished
25		1.1.C SW1/2T	Unknown		22	300.0	Anion SW-T 16 min	TestProcess	Finished
26		1.1.C SW1/2T	Unknown		23	300.0	Anion SW-T 16 min	TestProcess	Finished
27		1.1.C SW1/2T	Unknown		24	300.0	Anion SW-T 16 min	TestProcess	Finished
28		1.1.C SW1/2T	Unknown		25	300.0	Anion SW-T 16 min	TestProcess	Finished
29		1.1.C SW1/2T	Unknown		26	300.0	Anion SW-T 16 min	TestProcess	Finished
30		1.1.C SW1/2T	Unknown		27	300.0	Anion SW-T 16 min	TestProcess	Finished

Figure 11.3. An example of the list of sample data, containing their names and positions in the sampler.

- **Preparing the system before measurement**

All the steps in this section have to be done separately for Anions and Cations.

Air has to be vented from the lines of the pumps prior to starting the measurement. It is done by 1/2 turning priming knob of pumps, as shown in Figure 11.4.

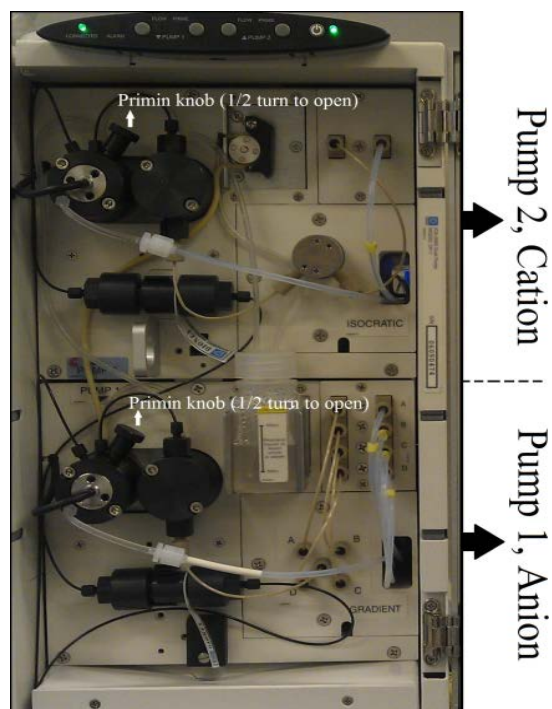


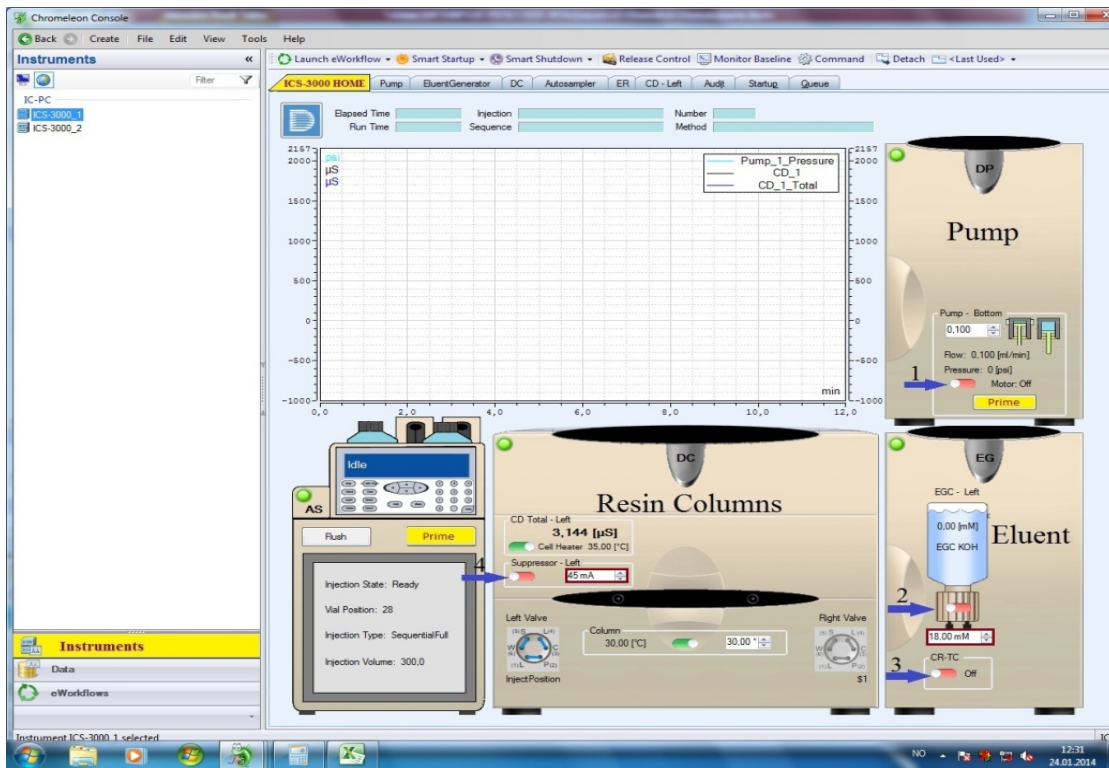
Figure 11.4. Venting the air from pumps.

Switch 1 (marked by blue arrow) and prime button (yellow marked) in the pump section have to be turned on and pressed, respectively (Figure 11.5).

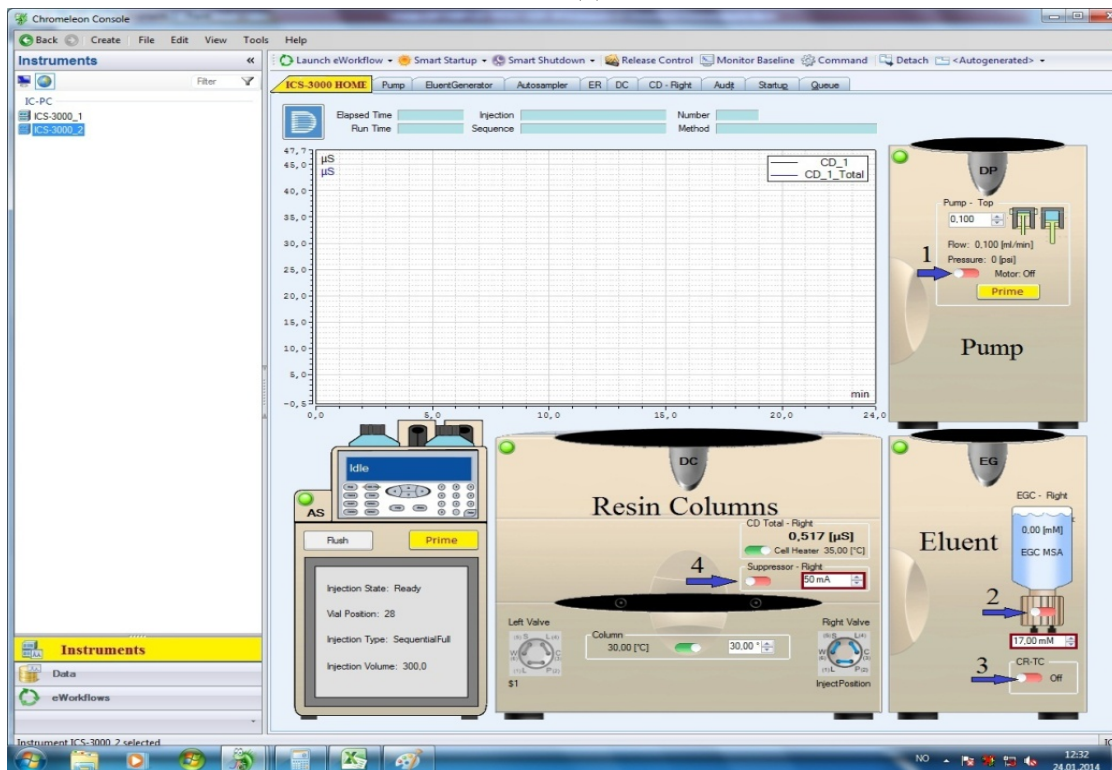
Eluent concentration (mM) and suppressor current (mA) (marked by red rectangles) have to be specified. For analysis of Anion these values are 18 mM and 45 mA and for Cations are 17 mM and 50 mA .

Then, switches 2, 3 and 4 (marked by blue arrows) have to be turned on in the Eluent and Resin Column. After that it is necessary to wait until the value of CD total (μs) is stabilized. The stabilized value has to be checked with the previous values and recorded in the related note book.

Before starting the program, the prime button in the sampler section of software has to be pressed (marked by yellow color in Figure 11.5).



(a)



(b)

Figure 11.5. Preparing the instruments in the program of the IC software for a) Anion and b) Cation.

The made data file which has been saved in the related folders added in the Queue list (Figure 11.6) then the program is started.

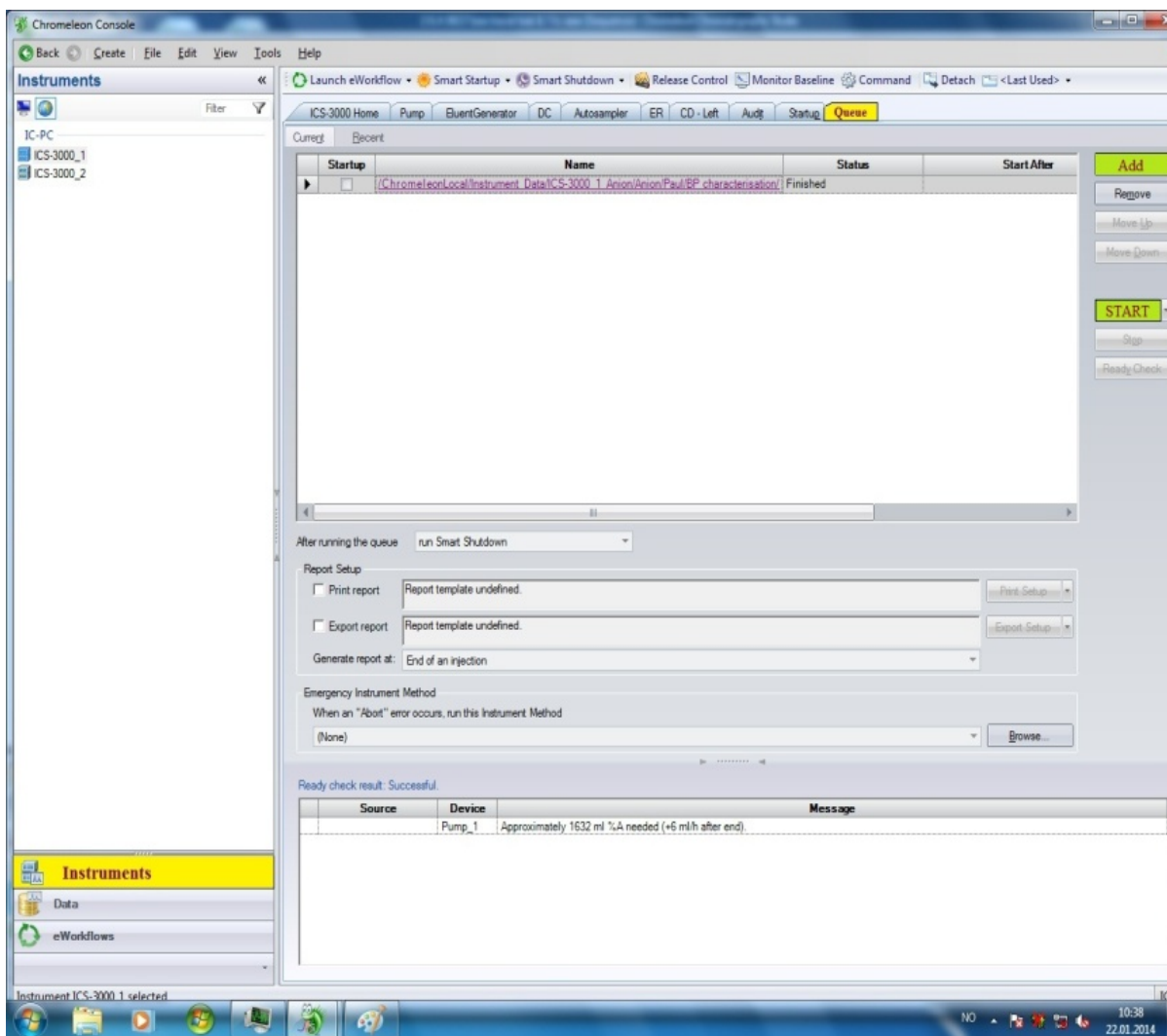


Figure 11.6. Adding and starting the measurement in IC system.

- **Analyzing the results**

Different ions show their conductivity peak in different intervals of retention time in the resin column (Figure 11.7). For example as shown in Figure 11.7, the peak of sodium ion appears at about 4.50-6.20 min. First, the base lines for all the ions of the entire samples have to be corrected. Then the resulted areas ($\mu\text{s} \cdot \text{min}$) of a specific ion in all the samples have to be transferred to concentration, based on the average area of the reference samples (which is normally diluted sea water).

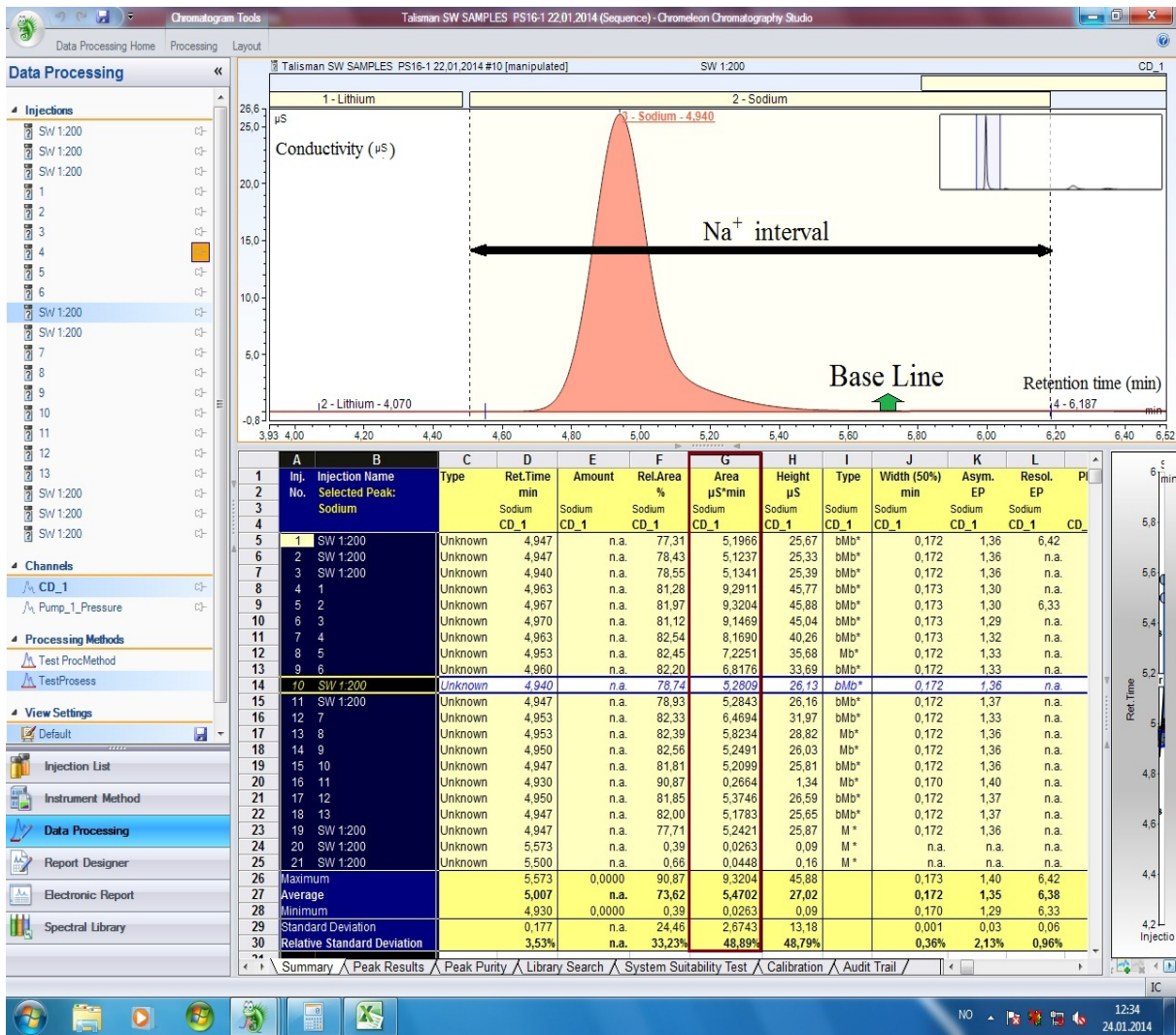


Figure 11.7. Analyzing the obtained results after IC measurements.

11.2 Input data of PHREEQC simulator

- Concentration of sulfate (SO_4^{2-}) in limestone core at atmospheric pressure in different reaction temperatures (20°C to 130°C)

Table 11.1. Simulation brine properties ($\text{SW0NaCl} \times 4\text{SO}_4^{2-}$) at atmospheric pressure

water	pH	pe	redox	density	units	Na	Cl	K	Ca	Mg	S(6)
1kg	7	4	pe	1	mole/L	0.194	0.125	0.01	0.012	0.044	0.096

Table 11.2. Limestone (pure calcite) at atmospheric pressure

Unit	Calcite	Anhydrite
mole	9.9	0.1

- Concentration of sulfate (SO_4^{2-}) in dolomitic core at atmospheric pressure in different reaction temperatures (20°C to 130°C)

Table 11.3. Simulation brine properties ($\text{SW} \text{d}_{20}$) at atmospheric pressure

water	pH	pe	redox	density	units	Na	Cl	K	Ca	Mg	S(6)
1kg	7	4	pe	1	mole/L	0.022	0.026	0.0005	0.00065	0.0022	0.0012

Table 11.4. Limestone (dolomitic) at atmospheric pressure

Unit	Calcite	Anhydrite	dolomite
mole	6.5	0.2	3.3

- Concentration of sulfate (SO_4^{2-}) in limestone core at reservoir pressure in different reaction temperatures (20°C to 130°C)

Table 11.5. Simulation brine properties ($\text{SW0NaCl} \times 4\text{SO}_4^{2-}$) at reservoir pressure

water	pH	pe	redox	density	units	Na	Cl	K	Ca	Mg	S(6)
1kg	7	4	pe	1	mole/L	0.194	0.125	0.01	0.012	0.044	0.096

Table 11.6. Limestone (pure calcite) at reservoir pressure

Unit	calcite	Anhydrite
mole	9.9	0.1

- Concentration of sulfate (SO_4^{2-}) in dolomitic core at reservoir pressure in different reaction temperatures (20°C to 130°C)

Table 11.7. Simulation brine properties ($\text{SW} \text{d}_{20}$) at reservoir pressure

water	pH	pe	redox	density	units	Na	Cl	K	Ca	Mg	S(6)
1kg	7	4	pe	1	mole/L	0.022	0.026	0.0005	0.00065	0.0022	0.0012

Table 11.8. Limestone (dolomitic) at reservoir pressure

Unit	calcite	Anhydrite	dolomite
mole	6.5	0.2	3.3

11.3 Materials and Instruments Pictures



Figure 11.8. Limestone Core



Figure 11.9. Chalk Core



Figure 11.10. IEC Model 2K-Centrifuge

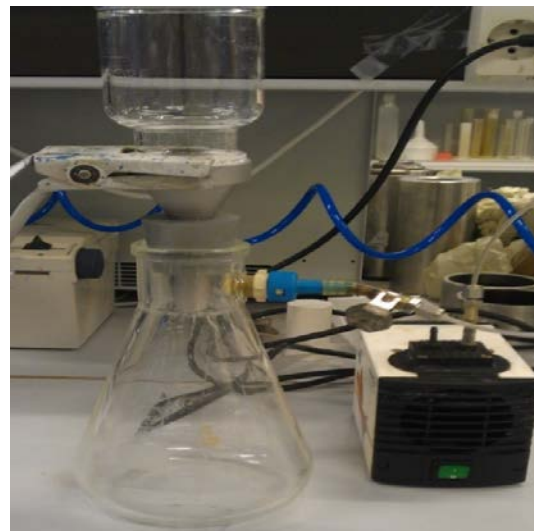


Figure 11.11. Filtration Process



Figure 11.12. A Mettler Toledo DL55 Autotitrator

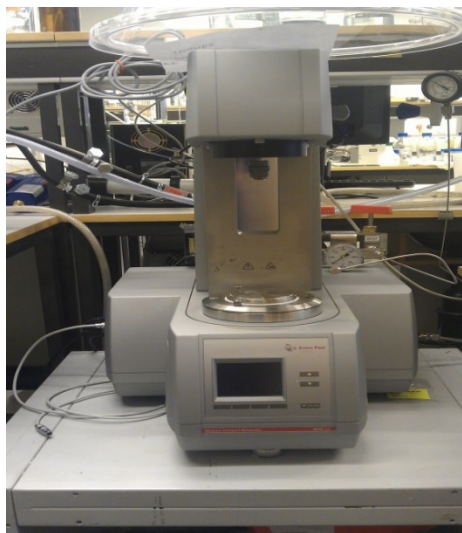


Figure 11.13. Modular Compact Rheometer MCR 302



Figure 11.14. METTLER TOLEDO pH meter



Figure 11.15. DMA 4500 Anton Paar Density Meter



Figure 11.16. ZEISS SUPRA 35VP, SEM & EDAX system



Figure 11.17. Core Cleaning Setup



Figure 11.18. Ion Chromatography System



Figure 11.19. Water Saturation Setup



Figure 11.20. Desiccator



Figure 11.21. Imbibition Amott cell



Figure 11.22. Drainage Amott cell

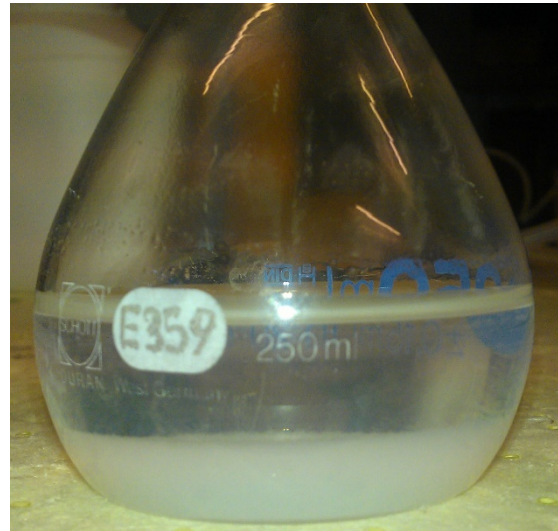


Figure 11.23. Phosphate Precipitation