



Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization:
Master of Science in Petroleum Engineering
Specialization - Reservoir Engineering

Spring semester, 2017

Open / ~~Restricted~~ access

Writer: Herman Muriel

.....
(Writer's signature)

Faculty supervisor: Merete Vadla Madland and Reidar Inge Korsnes

Thesis title:

**EVOLUTION OF WETTING INDEX OVER TIME IN MIXED WET KANSAS CHALK
USING TRIAXIAL CELLS**

Credits (ECTS): 30

Key words:

Chalk, Wettability Alteration, Reactive Brine, Chromatography, Dissolution, Precipitation, Ion Exchange, geochemistry, specific surface area.

Pages: 110

Stavanger, 15/06/2017
Date/year

ABSTRACT

Magnesium chloride effects have been widely studied in short and long-term core flooding experiments through outcrop chalk cores. Three main changes are induced by this reactive brine: ion exchange, dissolution of calcite and precipitation of new magnesium bearing minerals. Can these combined mechanisms increase the water wetness of chalk reservoirs?

This experimental work evaluates the potential of simplified brine $MgCl_2$ to modify the initial wetting state of outcrop Kansas chalk cores. Wettability measurements were based on Chromatographic Wettability Test developed by Strand et al. (2006) and carried out at room temperature. The flood of magnesium chloride was performed at Ekofisk reservoir temperature with a flooding rate of 1 PV/day. Wetting state was evaluated every 10 days flooding cycle. Reactive brine flooding was performed using a hydraulic operated triaxial cell with testing conditions of 15 [Bars] confining pressure and 7 [Bars] pore pressure.

The results show that magnesium chloride potential to modify the wetting state of mixed wet Kansas chalk cores is minimum, even though, the chromatographic wettability tests suggest the opposite. Chromatographic wettability test is able to quantify the initial wetting state but not to measure the changes in evolution of the wetting state by flooding a reactive brine through the calcite surface. Insight of aging and sulphate content are presented for outcrop Kansas chalk. The observed effluent concentration suggests a reduction in Mg^{2+} , while the Ca^{2+} concentration is increased. This, together with density measurements, indicate the precipitation of magnesium bearing minerals causing the dissolution of calcite surface, observing a general increase in the core density to a more magnesite state. Density was found to be higher in the core's inlet. Furthermore, specific surface area measurements were carried out. An apparent link between specific surface area and the chromatographic wettability test area measured was implied. Magnesium chloride could potentially increase the specific surface area of the core, while sodium chloride could reduce it (Unpublished work by Wang et al. (2017)). Same trends were found in the chromatographic separation test results.

TABLE OF CONTENT

ABSTRACT	i
LIST OF FIGURES	v
LIST OF TABLES	vii
ACKNOWLEDGEMENTS	viii
CHAPTER 1	1
INTRODUCTION	1
1.1 Background	1
1.2 Why Wettability Alteration?.....	3
1.3 Objective	4
1.4 Outline of the Thesis	5
CHAPTER 2	7
LITERATURE REVIEW.....	7
2.1 Wettability Alteration Measurements	8
2.1.1 Quantitative Wettability Measurements	8
2.1.2 Qualitative Wettability Measurements	8
2.1.3 Chromatographic Wettability Test.....	9
2.1.4 Chromatographic Wettability Test and Specific Surface Area (SSA).....	10
2.2 Carbonate Reservoir Geology	11
2.3 Wettability of Carbonates	13
2.3.1 Factors Influencing Initial Wetting State of Carbonates	13
2.3.1.1 Mineral Composition of the Rock.....	14
2.3.1.2 Crude oil Components	14
2.3.1.3 Formation Water	16
2.3.1.4 Aging.....	17
2.3.1.5 Reservoir Conditions.....	18
2.3.1.6 Core Cleaning	18
2.4 Wettability Alteration in Carbonates by Smart Water	19
2.4.1 Smart Water Mechanism	21
CHAPTER 3	23
METHODS AND EXPERIMENTAL PROCEDURES	23
3.1 Materials	23
3.1.1 Rock Samples	23
3.1.2 Oil	24

3.1.3 Brine Composition	24
3.2 Preparation of Cores, Oil and Injected Brines.....	25
3.2.1 Preparation of Oil.....	25
3.2.2 Preparation of Brines.....	26
3.2.2.1 Wettability Test Brines.....	26
3.2.2.2 Flooding Brines.....	27
3.2.3 Preparation of Cores Samples.....	29
3.2.3.1 Core Drilling.....	29
3.2.3.2 Core Shaping.....	29
3.2.3.3 Saturating the Core and Porosity Calculation.....	32
3.2.4 Preparation of Mixed Wet Cores.....	34
3.3 Tests Equipment.....	36
3.3.1 Hassler Type Core Holder	36
3.3.2 Hydraulically Triaxial Cell.....	37
3.3.3 Dionex IC S-5000+ Ion Chromatography System.....	42
3.3.3.1 Deionized Water Requirements for IC	43
3.4 Experimental Procedures Applied in Triaxial Cells.....	44
3.4.1 Mounting the Core.	44
3.4.2 Increasing Confining Pressure	46
3.4.3 Increasing Pore Pressure.....	46
3.4.4 Increasing Temperature.....	47
3.4.5 Decreasing Temperature.....	48
3.4.6 Dismantling the Triaxial Cell.....	48
3.5 Tests Carried Out in Triaxial Cells	49
3.5.1 Water Wet Cores: Establishing the water wet reference area.....	49
3.5.2 Water Wet Cores: Addressing changes in specific surface area (Core K4).....	50
3.5.3 Mixed Wet Cores: Modifying the wetting state.....	51
3.6 IC Analysis and Further Testing.....	52
3.6.1 IC Analysis	52
3.6.2 Specific Surface Area Measurements.....	55
3.6.3 Chalk Mineral Density Measurements	57
CHAPTER 4	58
EXPERIMENTAL RESULTS AND COMMENTS	58
4.1 Water Wet Cores: Establishing Water Wet Reference Area.....	58
4.1.1 Hassler's Cell: Reproducibility in different cores.....	59
4.1.2 Hassler's Cell: Flow Rate Effect.....	59
4.1.3 Triaxial Cell: Flow Rate Effect.....	60

4.1.4 Triaxial Cell: Reproducibility in the same Core	61
4.1.5 Triaxial Cell: Reproducibility in different cores.....	62
4.1.6 Triaxial Cell: Effect of the sealing material.....	63
4.1.7 Triaxial Cell: Effect of increasing temperature.....	65
4.2 Water Wet Cores: Addressing the effect of flooding non-reactive and reactive brines.	66
4.3 Mixed Wet Cores: Initial Wetting State and Changes in Wettability Index.....	68
4.3.1 Hassler’s Cell: Initial Wetting State.....	68
4.3.2 Triaxial Cell: Initial Wetting State and Wetting Index Evolution.....	69
4.3.2.1 Triaxial Cell: Rubber Sleeve.....	69
4.3.2.2 Triaxial Cell: Shrinking Sleeve and Reproducibility	71
CHAPTER 5	76
DISCUSSION	76
5.1 Establishing Initial Wetting State: Insight of Aging and Core Restoration	76
5.1.1 Initial Wetting State of mixed wet Kansas chalk cores.....	76
5.1.2 Sulphate Content in Kansas Chalk.....	79
5.2 Effect of Flooding Magnesium Chloride and Sodium Chloride through Kansas Chalk Cores at 130°C.....	81
5.2.1 Can Magnesium Chloride (MgCl ₂) modify the wetting state?.....	81
5.2.2 Changes in Mineralogy	84
5.2.3 Changes in Specific Surface Area, SEM and EDS analysis	86
CHAPTER 6	91
CONCLUDING REMARKS AND FUTURE WORKS	91
6.1 Concluding Remarks.....	91
6.2 Future Works.....	93
REFERENCES.....	94

LIST OF FIGURES

Figure 1: Geographic distribution of carbonate reservoirs (Carbonate Reservoirs, Schlumberger 2007).	2
Figure 2: Capillary pressure and Relative Permeability for water-wet and mixed-wet conditions (Fundamentals of Wettability; Oilfield Review 2007).	3
Figure 3: Wetting States present in the porous medium (Fundamentals of Wettability; Oilfield Review 2007). 7	
Figure 4: Chromatographic separation of SO_4^{2-} and SCN^- for a preferential oil-wet core. Completely water-wet conditions are assumed using heptane as oil or at 100 % water saturated condition (Strand, 2005).	11
Figure 5: Correlation between Wettability Index and Aging Temperature (Zhang and Austad 2005).....	15
Figure 6: Spontaneous imbibition of brines into chalk cores saturated with different crude oil with different AN (Standnes and Austad 2000).	16
Figure 7: SEM micrograph shows common occurrence of magnesite crystals with rhombic habit (arrows) in the Mons chalk core tested at 130 °C. (Medetbekova 2015).....	21
Figure 8: Proposed mechanism when Mg^{2+} , Ca^{2+} and SO_4^{2-} are active at higher temperatures. Modified from (Zhang et al. 2007a).....	22
Figure 9: From left to right: 1) Centrifuge. 2) Inside of the centrifuge. 3) Centrifuge's Speeds. 4) Titration equipment.....	26
Figure 10: Left: Brine on top of a magnetic Stirrer. Right: Filtration Apparatus.	28
Figure 11: pH Mettler Toledo.	28
Figure 12: Coring Machine to drill out the outcrop Kansas Chalk.....	29
Figure 13: Lathe machine used to shape the oversized cores.....	30
Figure 14: Diamond cut-off used to cut the cores to the required length.....	30
Figure 15: Calliper used to measure the length and diameter of the final cores.....	31
Figure 16: Analytical balance weighting the dry weight of the core.....	32
Figure 17: Left: Vacuum Pump. Middle: Lid sealing the vacuum chamber. Right: Vacuum chamber setup ready to vacuum the core.	33
Figure 18: Left: Saturated core. Middle: Weight of the saturated core. Right: Saturated core placed inside of cylindrical container.	34
Figure 19: Oven used for wettability alteration.....	35
Figure 20: Left: Hassler's Cell Core Flooding Setup. Middle: Aging Cell. Right: Oven used for aging.	36
Figure 21: Left: Actual Hassler type core holder at the lab. Right: Sketch of Hassler type core holder.	37
Figure 22: Sketch of the Hassler's Cell Setup (Halvorsen, 2010).....	37
Figure 23: Left: Sketch of the triaxial cell used on the tests (Nermoen et al. 2015). Right: Actual Triaxial cell at the lab.....	38
Figure 24: Left: Heating Jacket. Middle: Heating jacket attached to the confining chamber in a triaxial cell. Right: Omron Control Box keeping the temperature constant at 130°C.....	39
Figure 25: Digital gauges monitoring the values.....	39
Figure 26: Left: Gilson pumps Serie 307. Right: Flooding cells for wettability test, one containing SW-0T and the other SW-1T.	40
Figure 27: Left: LabView Software. Right: LabView Interface.....	40
Figure 28: Left: Trilution LH Software. Right: Trilution Interface.....	41
Figure 29: Fractional Sampler Working.	41
Figure 30: Sketch of the experimental Triaxial Setup (Kjørsløvik and Østensen, 2014).....	42
Figure 31: Dionex IC S-5000+ Ion Chromatography System.....	42
Figure 32: Left: Deionized specifications obtained using Milli-Q. Right: Milli-Q filter.....	43
Figure 33: Left: Steel base core containing the first O ring, rubber seal, drainage plate and filter paper. Middle: Core mounted containing the previous elements in the inlet and outlet. Right: Core with the shirking sleeve and spiral on the top.....	45
Figure 34: Left: Heating gun melting the shrinking sleeve to the core. Middle: Confining oil inside of the confining chamber. Right: Final setup, showing the heating jacket, bolts and the triaxial cell.	46
Figure 35: Spring connected to the confining valve while increasing temperature in the triaxial cell.	48
Figure 36: Left: Liquid handler diluting the sample. Right: Trilution software showing the program used for dilution: The lines were cleaned twice and the samples were diluted 500 times.	53

Figure 37: Left: Elements used to prepare the sample for the IC. Middle: Syringe chromatographer filter. Right: IC samples prepared.....	53
Figure 38: Left: IC trays inside of Ion Chromatographer. Right: IC characteristic program.....	54
Figure 39: Peak Responses in the IC chromatography analysis outcome.....	55
Figure 40: Micrometrics TriStar II: Surface Area and Porosity.....	55
Figure 41: Left: Smashed sample. Middle: Empty weight of the sample tube. Right Weight of the sample tube containing smashed sample.....	56
Figure 42: Left: Degasser set at 60°C containing the three sample tubes. Middle: Instrument with the liquid N ₂ container in the bottom. Right: Samples attached to the instrument.....	57
Figure 43: AccuPyc II 1340 Gas Pycnometer.....	57
Figure 44: Chromatographic wettability test on three (K1, K5 and K6) completely water wet Kansas chalk cores.....	59
Figure 45: Chromatographic wettability test performed on water wet core K1 at different flow rate in the Hassler's Cell.....	60
Figure 46: Chromatographic wettability tests performed on water wet core K1 at different flow rate in the Triaxial Cell.....	61
Figure 47: Chromatographic wettability tests performed on water wet core K2 in the Triaxial Cell.....	62
Figure 48: Chromatographic wettability test on four (K1, K2, K3 and K4) completely water wet Kansas chalk cores.....	63
Figure 49: Chromatographic wettability tests performed on water wet core K2 in the Triaxial Cell. Effect of the sealing material: Shrinking Sleeve vs Rubber Sleeve.....	64
Figure 50: Chromatographic wettability tests performed on water wet core K4 in the Triaxial Cell. Effect of flooding distilled water for 2 days at 130[°C].....	65
Figure 51: Chromatographic wettability tests performed on water wet core K4 in the Triaxial Cell. Effect of flooding NaCl over a week and MgCl ₂ over 2 weeks at 130[°C].....	67
Figure 52: Chromatographic wettability test performed on mixed wet core K10 in the Hassler's Cell.....	68
Figure 53: Chromatographic wettability tests performed on mixed wet core K9 in the Triaxial Cell. Wetting Index Evolution after the 1 st MgCl ₂ cycle.....	70
Figure 54: Interaction between MgCl ₂ and Kansas chalk core K9 surface.....	71
Figure 55: Chromatographic wettability tests performed on mixed wet core K7 in the Triaxial Cell. Wetting Index Evolution after four MgCl ₂ cycles.....	72
Figure 56: Chromatographic wettability tests performed on mixed wet core K8 in the Triaxial Cell. Wetting Index Evolution after two MgCl ₂ cycles.....	73
Figure 57: Interaction between MgCl ₂ and Kansas chalk core K7 surface.....	73
Figure 58: Interaction between MgCl ₂ and Kansas chalk core K8 surface.....	74
Figure 59: Wetting Index vs Days aged at room temperature for mixed wet cores tested. All cores were initially aged at 90°C for 21 days.....	77
Figure 60: Wetting Index vs Residual Oil Saturation for mixed wet cores tested.....	78
Figure 61: Effluent sulphate content of core K11 flooded with distilled water at room temperature.....	80
Figure 62: Mixed wet cores K7 and K8 preserved in distilled water after being removed from the triaxial cell.....	82
Figure 63: Interaction between flooding brines (NaCl and MgCl ₂) and Kansas chalk core K4 surface.....	84
Figure 64: Core K4 Inlet removed from the rest of the core for density and specific surface area analysis.....	85
Figure 65: Left: Typical Coccolith structure present in outcrop Kansas chalk core's outlet K4 [1µm] scale. Right: SEM analysis after NaCl and MgCl ₂ flooding cycles in Core's outlet K4 [10 µm] scale.....	88
Figure 66: SEM analysis in largest pores present in Core's outlet K4 [2 µm] scale.....	88
Figure 68: EDS analys of largest pore present in core's outlet K4.....	89

LIST OF TABLES

Table 1: Chromatographic Wettability Index test related to the Wetting State.....	10
Table 2: Major Carbonate Reservoir Characteristics (Ahr 2011).....	12
Table 3: Physical properties of Kansas Chalk (Megawati 2015).....	23
Table 4: Ionic Composition of Synthetic Seawater for Chromatographic wettability test.....	24
Table 5: Ionic Composition of Magnesium Chloride.	24
Table 6: Ionic Composition of Sodium Chloride.	25
Table 7: Physical Properties of cores used to establish the water wet reference area.....	32
Table 8: Physical Properties of mixed wet cores used to evaluate Wettability Index evolution.	32
Table 9: Deionized water requirements for IC.	43
Table 10: Main differences between Hassler's Cell and Triaxial Cell core flooding setups.	58
Table 11: Summary of results obtained in water wet cores used to establish the water wet reference area.	66
Table 12: Summary of results obtained in tests performed on water wet core K4.	67
Table 13: Summary of results obtained in mixed wet cores used to establish the initial wetting state of mixed wet Kansas cores and evaluate the potential of MgCl ₂ as a wettability modifier agent.....	74
Table 14: Mixed Wet Cores observed and measured parameters.....	77
Table 15: Physical properties of core K11 used to determine the presence of sulphate in outcrop Kansas core.	80
Table 16: physical properties of core K4 before and after testing.....	85
Table 17: Physical properties of inlet and rest of the core K4.	85
Table 18: Specific surface area measurements obtained in core K4.....	86

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor Dr. Merete Vadla Madland for giving me the opportunity of being part of this interesting project. Thanks for the constant encouragement to keep improving myself and get the best of my work.

I would specially like to thank to Dr. Reidar Inge Korsnes for sharing his knowledge during this six months' journey. Thanks for showing me how much fun researching can be and how awesome working in the lab is. This experience was educative and uttermost formative which helped me realize what I would like to do on my future endeavours.

Thanks to Dr. Anders Nermoen for sharing his scientific expertise and providing with significant and constructive suggestion during the development of my thesis.

Thanks to Jaspreet Singh Sachdeva for all the advises given and conversations had while working in the lab.

Thanks to Norway and specially the University of Stavanger for welcoming these last two years. They will always have a place in my heart.

CHAPTER 1

INTRODUCTION

With oil prices currently settling around 50 Usd/Bbl, petroleum industry is passing through a tough time that makes most of the IOR techniques economically unfeasible except perhaps waterflooding. But, crisis provide the perfect time for innovation and improvements of the technology already existent. Waterflooding has been implemented for more than 70 years for two main purposes:

- i. Pressure Support: inject water into the aquifer to keep the reservoir pressure above bubble pressure (Under saturated Conditions).
- ii. Oil displacement.

Injected water for the above aims has not similar chemical composition as the formation water present in the reservoir, therefore, the existent equilibrium between Crude-Brine-Rock will be disturbed. The increase in recovery is due to the oil displaced by water injected taking advantages of the viscous forces. The equilibrium reached in the reservoir due to the interaction of the Crude-Brine-Rock determines the wetting state of the rock. The wettability of the rock/fluid system is important because it is a major factor controlling the location, flow, and distribution of fluids in a reservoir (Anderson 1986).

This chapter provides a brief introduction to the dissertation carried out, starting with stating the problem, pointing out the main targets of this research and toward the end, an outline of this thesis is mentioned.

1.1 Background

It is estimated that roughly more than 60% of the oil reserves and 40% of the gas reserves worldwide are found in carbonate reservoirs (World Energy Outlook 2006). For instance, Middle East has 62% of the world's proved conventional oil reserves (BP Statistical Review 2007), approximately 70% of these reserves are held in carbonate reservoirs (Schlumberger Market Analysis, 2007). Middle East reservoirs additionally hold 40% of the world's proved gas reserves (BP Statistical Review 2007), 90% of these reserves are located in carbonate reservoirs (Schlumberger Market Analysis, 2007). The main carbonate reservoirs in the world can be appreciated in **Figure 1**.

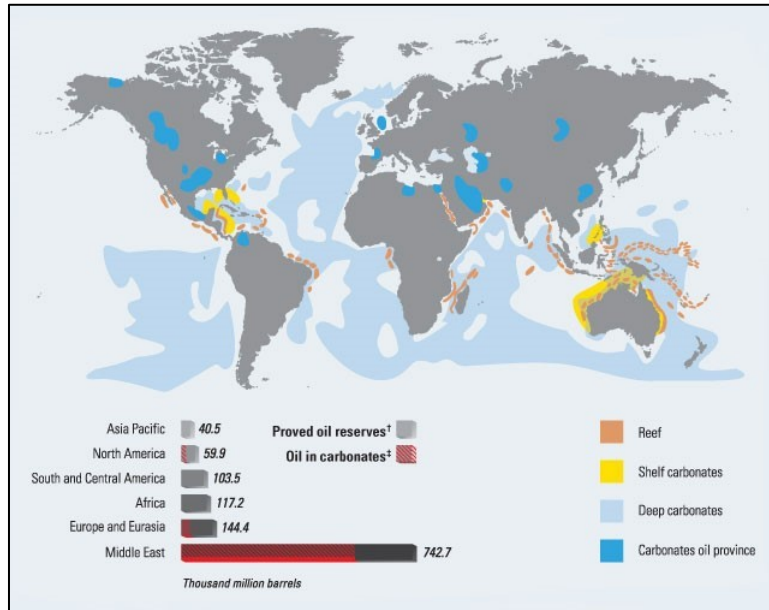


Figure 1: Geographic distribution of carbonate reservoirs (Carbonate Reservoirs, Schlumberger 2007).

Unfortunately, carbonate rocks usually present a very complex texture and pore network due to natural depositional and diagenetic history. Thus, heterogeneities may be found at all scales, pores, grains, and textures. All these heterogeneities in conjunction with the usual initial wetting state of the carbonates reservoirs pose big challenges in reservoir characterization, production and future management, generating recovery factor which rarely exceed 35%. For instance, the Ghaba North field in Oman is a fractured, oil-wet carbonate that has reached only 2% recovery after more than 20 years of production (Al-Hadhrami and Blunt, 2001).

True is, roughly 90% of the carbonate reservoirs are neutral to oil wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972), which means Spontaneous Imbibition of water will not take place. The fact that spontaneous imbibition does not occur is mainly due to the capillary pressure state of the mixed wet and oil wet reservoirs. For instance, in **Figure 2**, the main differences between water wet and mixed wet states are appreciated. The capillary pressure is positive for water wet reservoirs and non-positive for mixed and oil wet reservoirs. Capillary pressure is defined as follows:

$$P_C = P_{\text{non-wetting phase}} - P_{\text{wetting phase}} \quad \text{Eq. 1.}$$

Therefore, for mixed wet and oil wet reservoirs, the water pressure tops the oil pressure, hampering the spontaneous imbibition of the water.

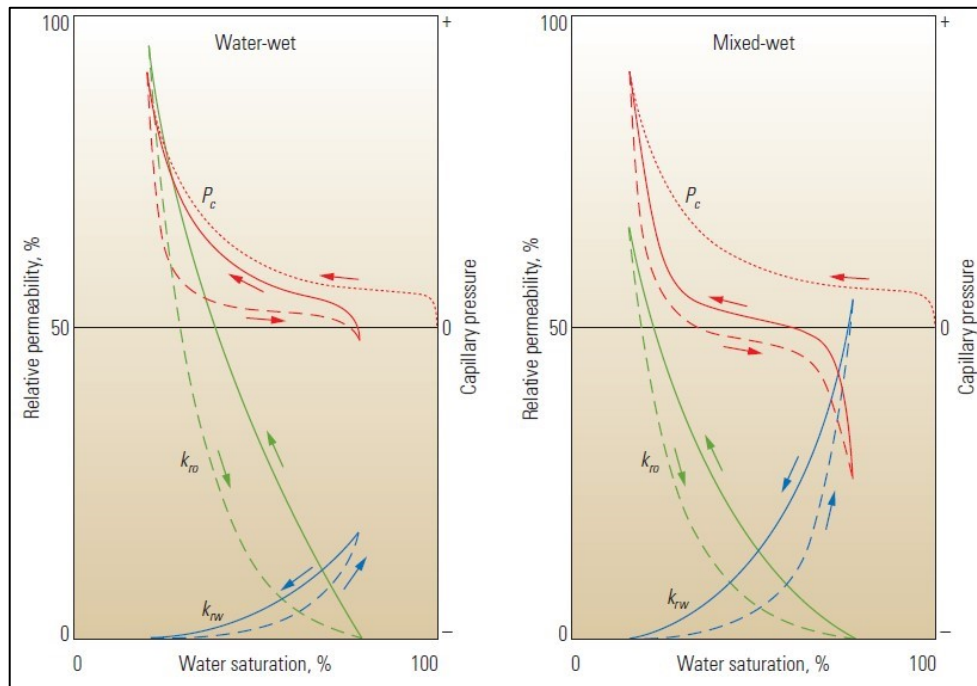


Figure 2: Capillary pressure and Relative Permeability for water-wet and mixed-wet conditions (Fundamentals of Wettability; Oilfield Review 2007).

Hence, modifying the wetting state from an oil or mixed to a water wetting state would generate changes in the capillary pressure, relative permeability curves, and fluid distribution in the pore space that will lead to an increase in the hydrocarbon recovery from carbonate rocks (Tabary et al., 2009).

1.2 Why Wettability Alteration?

Besides of the oil barrel price, hydrocarbon recovery factor is perhaps the most important parameter to determine the economic and commercial feasibility of hydrocarbon reservoirs. Wagner et al (1959) showed that altering the wetting state to a more water wet system increased the oil recovery. But what makes wettability so important when you are trying to predict and optimize reservoirs production? Wettability plays an important role in the first two stages of reservoir production. During primary recovery, Bobek et al (1958) showed that water drive process tends to be more efficient in water wet reservoirs. Similarly, while performing secondary recovery by waterflooding, the performance is proportionally linked to the initial wetting state of the reservoir. For instance, Bobek et al (1958) found on core flooding experiments that oil recoveries from water wet rock to be higher than those from oil wet rock by 15% of the original oil in place.

Several studies to link wettability to oil recovery where carried out by Jadhunandan and Morrow

(1991) found the ultimate oil recovery reaches its maximum near the neutral wetting state and not at strongly water wet state as it was thought before. These results confirmed experiments carried out almost 20 years before by Salathiel (1973) which showed that reservoirs with mixed wettability can exhibit higher oil recovery during waterflooding than water wet reservoir.

Understanding what is happening in the reservoir when rock experiences changes in the wetting state is crucial to succeed in wettability alteration. Therefore, shifting the initial wetting state from strongly oil wet to strongly water wet induces several changes on capillary and gravitational forces that may enhance oil recovery.

- i. **Shifting from strongly oil-wet to neutral wet state:** capillary forces that trap the oil in porous medium are reduced and then vanished. The gravitational forces may start playing a role on recovery at this stage. But wettability alteration may not have a direct impact on oil recovery at this stage, it reduces negative capillary forces, which, in turn, enhance the oil recovery by gravity forces (Mohammed and Babadagli, 2015).
- ii. **Alteration of wettability from neutral-wet state toward strongly water-wet state:** capillary imbibition is induced. Both gravity and capillary forces are expected to contribute in oil recovery in this stage (Mohammed and Babadagli, 2015).

Thus, slight changes in the wetting state from oil wet state to a more water wet state could potentially improve the production of a reservoir which lead to increase the oil recovery. It is worth mentioning that the term wettability alteration is commonly referred as wettability restoration because the initial wetting state of the reservoir is believed to be initially water wet before oil was trapped inside of it.

1.3 Objective

The main focus of this research project is to evaluate the potential to modify the wetting state of a mixed wet outcrop kansas chalk cores to a more water wet wetting state while flooding a reactive brine at Ekofisk field temperature (130°C).

Ekofisk and Valhall are ones of the most important chalks reservoirs in the Norwegian Continental Shelf, injection of seawater is carried out in both reservoirs. When seawater is injected in the reservoirs, the equilibrium between Crude-Brine-Rock will be modified which will influence the wetting state but also the mechanical strength of the rock will be altered. Seawater contains chalk

surface reactive ions such as Ca^{2+} , Mg^{2+} and SO_4^{2-} , which can behave as potential determining ions to modify the surface charge of Calcite (CaCO_3) (Pierre et al., 1990; Zhang and Austad, 2006).

Therefore, to accomplish this target, the reactive brine chosen for this study was Magnesium Chloride (MgCl_2), where both ion Mg^{2+} (Reactive ion) and Cl^- (Inert ion) are present in the seawater. Several works have widely documented the effect of flooding magnesium chloride to outcrop chalk cores. The flood of magnesium chloride (MgCl_2) induces three main changes inside the chalk framework: ion exchange represented between Mg^{2+} contained in the flooding brine with calcium in the chalk surface, initially reported by Korsnes et al., 2006a; Korsnes et al., 2006b; Zhang et al., 2007. This retention of magnesium causes precipitation of new minerals, specially magnesite (Madland et al. 2011), although huntite was also reported, and finally dissolution of calcite triggered by formation of secondary minerals ((Madland et al. 2009, 2011; Megawati et al. 2011, 2012),. affecting the mechanical strength of the chalk rock (Madland et al. 2011). Can all these phenomena induced by flooding magnesium chloride modify the wetting state of chalks rocks?

The flooding experiments were carried out using hydraulically operated triaxial cells at 7 [Bars] Pore Pressure and 15 [Bars] Confining pressure. The changes in the wetting state were evaluated using the chromatographic wettability test developed by Strand et al. (2006) and carried out at ambient temperature.

1.4 Outline of the Thesis

This dissertation provides a journey beginning from fundamentals of wettability, going through a deep literature review about Wettability Alteration in Carbonate Reservoirs and how to establish initial wettability of outcrop cores till the results obtained of flooding a reactive brine at high temperature.

Chapter 2 mainly focus on a literature review about research works that have been done in wettability alteration by Smart Water in carbonate reservoirs. It also highlights the fundamentals of wettability and critical parameters that must be taken into account in wettability alteration studies. Furthermore, it is important to notice that trying to simulate the initial wetting state of a reservoir while working with outcrop cores is perhaps one of the most challenging task performed, therefore, the chapter also a little background how to establish the initial wetting state.

Chapter 3 takes the reader through a detailed tour regarding all the procedures implemented while performing all wettability test during this dissertation; besides, all the materials used like brines, oil

and outcrops chinks are also included. Moreover, the chemical analysis of all the samples taken during every core flooding experiment are also explained.

Chapter 4 points out the results from the wettability tests performed on outcrop Kansas chalk. These results include both water wet and mixed wet cores tested. Results from mixed wet cores include the evolution of the wettability index over time while flooding magnesium chloride at high temperature.

Chapter 5 assesses and discusses the results presented in chapter 4 while providing some conclusions and comments about the phenomena observed. Finally, chapter 6 summarizes the work performed and offers final concluding remarks and recommendations for future work on the field.

CHAPTER 2

LITERATURE REVIEW

Wettability or wetting state is defined as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids" (Craig 1971). In the reservoir, the ternary system is represented by the rock, the formation brine and the crude. Three wetting states have been identified in the literature. For instance, Anderson (1986) identified the wetting states illustrated in **Figure 3**.

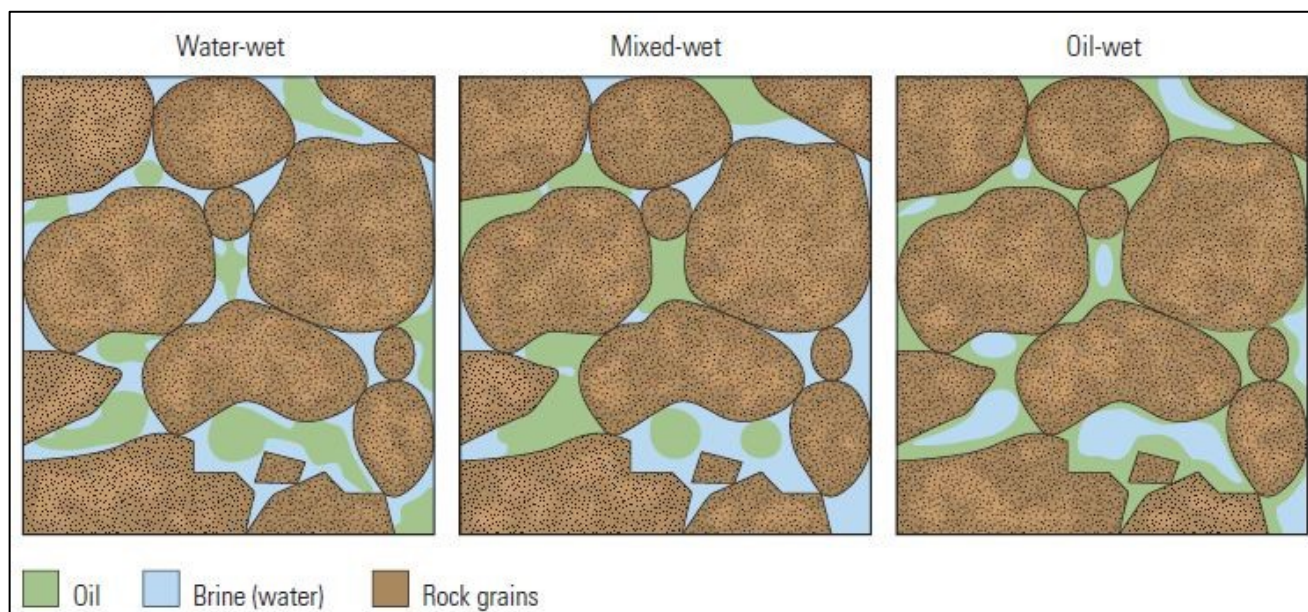


Figure 3: Wetting States present in the porous medium (Fundamentals of Wettability; Oilfield Review 2007).

In **Figure 3**, the water wetting state found in the left figure, clearly shows how the water covers the rock's surface and the oil is in the centre of the pores. For the mixed wet case in the middle figure, both oil and water cover the rock's surface, because oil has displaced the water in some rock's surface and remaining in the centre of some of the pores. And for the oil wetting state in the right figure, the oil has completely displaced the water from the rock's surface and the water locates in the centre of the pores.

The wettability of the rock-fluid system is important because it is a major factor controlling the location, flow, and distribution of fluids in the reservoir (Anderson 1986). These come to play an important role in Naturally Fractured Carbonate Reservoirs (NFCR) and subsequently in wettability

alteration processes in these kind of reservoirs (Mohammed and Babadagli 2015). As it was stated before, most part of these reservoirs are neutral to oil wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972). In these kind of reservoirs, while performing waterflooding, the water will follow the easiest path, this is through the fracture. Early water breakthrough is expected and low oil recovery is achieved. The waterflooding in NFCR is quite inefficient leaving all the oil behind in the matrix. Water will not imbibe into the matrix because capillary pressures are quite low or negative depending if it neutral or oil wet (Austad et al 1998). Therefore, to maximize oil recovery, wettability alteration is required (Jerauld and Rathmell 1994). Wettability alteration allows to improve spontaneous imbibition of water into matrix block, this has been considered as the main mechanism for oil production in NFCR (Austad et al., 2005).

2.1 Wettability Alteration Measurements

Being able to quantify the initial wetting state of the reservoir, and the changes of this state while wettability alteration is performed are fundamental to ensure the success of the waterflooding or in this case, Smart Water Flooding.

Several techniques or procedures have developed through the years to measure wettability. Anderson (1986) proposed:

2.1.1 Quantitative Wettability Measurements

- i. Contact Angle.
- ii. Amott Harvey Method.
- iii. USBM Wettability Index.
- iv. Combines Amott/USBM method.
- v. Zeta Potential Measurements.

2.1.2 Qualitative Wettability Measurements

- i. Spontaneous Imbibition Method.
- ii. Microscope Examination.
- iii. Flotation Method.
- iv. Glass Slide Method.
- v. Relative permeability Methods.

- vi. Permeability/Saturation Relationships.
- vii. Capillary Pressure Curves.
- viii. Capillarimetric Method.
- ix. Displacement Capillary Pressure.
- x. Reservoir Logs.

However, the initial wetting state and wettability alteration quantifications performed during the development of this dissertation were based on Chromatographic Wettability Test proposed by Strand et al. (2006).

2.1.3 Chromatographic Wettability Test

Strand et al (2006) developed the Chromatographic wettability test procedure initially for chalks reservoirs, but it has also been proved to work for limestones (Fathi et al. 2010). This core flooding experiment is often carried out using Hassler's Core Holder, but in this case, triaxial cells were the main setup used to perform this research. The principle of this test resides on the affinity of sulphate ion (SO_4^{2-}) to the water wet areas of the carbonate surface; therefore, the sulphate concentration is delayed in the effluent during core flooding experiments. On the other hand, the thiocyanide or tracer (SCN^-) possesses no affinity to the carbonate surface and flood through the core without any adsorption, causing no delay in the effluent during the flooding experiment. This phenomenon is appreciated in a chromatographic separation between adsorbing sulphate ion and non-adsorbing tracer ion, thiocyanide in this case.

The area between the effluent curves for tracer and Sulphate must be directly proportional to the water wet surface area in the porous medium, because both water-soluble components, SCN^- and SO_4^{2-} , must contact the same water-wet area (Strand et al 2006).

The wettability index for this chromatographic test is defined as follows:

$$\text{Wettability Index (WI)} = \frac{A_{\text{Wet}}}{A_{\text{Water wet}}} \quad \text{Eq. 2.}$$

Where, **A_{wet}** is the area between the thiocyanide and sulphate obtained in the chromatographic wettability test for a given core and **A_{water wet}** is the area obtained between the thiocyanide and sulphate for a completely water system.

The quantitative and qualitative interpretation of the wettability index can be appreciated in **Table 1**.

Table 1: Chromatographic Wettability Index test related to the Wetting State.

Wettability Index	Wetting State
0	Completely Oil Wet System
$0 < WI < 0.5$	Mixed Wet: Preferentially Oil Wet
0.5	Neutral Wettability
$0.5 < WI < 1$	Mixed Wet: Preferentially Water Wet
1	Completely Water Wet System

The chromatographic wettability test is very suitable for the total wetting range but it takes a greater importance at neutral wetting conditions. This test is not time consuming and can be run at residual oil saturation (Strand et al 2006). It is important to run this test at S_{or} , Strand et al (2006) found that an increase in S_{or} from 0 to 0.22 causes a decrease in the area of 6-7% due to a decrease in the access to water wet surface area.

A typical plot of the chromatographic wettability test can be appreciated in **Figure 4**. It is worth mentioning that in the chromatographic wettability test developed by Strand et al (2006), the water wet reference area was calculated in a core assumed to be strongly water wet (saturated with heptane).

2.1.4 Chromatographic Wettability Test and Specific Surface Area (SSA)

Specific surface area is defined as the total surface area divided by the mass of a material (this case the core) per unit of mass. The most common units are $[m^2/Kg]$ or $[m^2/g]$. This property is greatly important for adsorption processes, heterogeneous catalysis and reactions on surfaces. Adsorption of sulphate and not adsorption of thiocyanide (Tracer) allows to quantify the specific water wet surface area due to the water-soluble nature of these anions contacting this area.

The specific surface area (SSA) can be measured using adsorption BET isotherm (Brunauer et al. 1938). However, the measurement is dependent on the species adsorbed. SSA can be affected by precipitation of new minerals on the surface material. Precipitation of new minerals could potentially increase the water wet area on calcite ($CaCO_3$), nevertheless, this has not been proved yet.

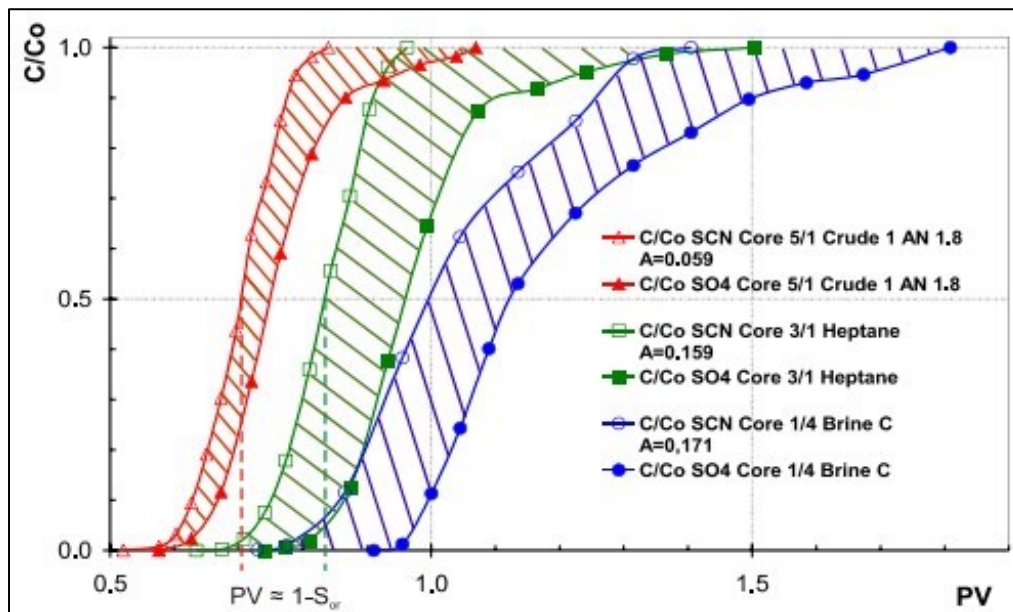


Figure 4: Chromatographic separation of SO_4^{2-} and SCN^- for a preferential oil-wet core. Completely water-wet conditions are assumed using heptane as oil or at 100 % water saturated condition (Strand, 2005).

2.2 Carbonate Reservoir Geology

Carbonates are sedimentary rocks mostly deposited in marine environments. As it was stated before, these reservoirs contain around 60% of oil reserves and 40% of gas reserves in the world. Carbonates are largely made up of skeletal remains and other biological constituents that include faecal pellets, lime mud (skeletal), and microbial mediated cements and lime muds (Ham and Pray 1962). These porous and permeable rocks are mainly composed by calcium carbonate (CaCO_3). Carbonate minerals are highly reactive (Choquette and Pray, 1970; Moore, 2001). This reactivity is very important to fully understand the diagenesis and reservoir quality of carbonates reservoirs (Ehrenberg and Nadeau 2005). The main difference between carbonate and siliciclastic reservoirs is the extreme geologic and petrophysical heterogeneity that carbonates reservoirs exhibit (Lucia 2003). These heterogeneities are mainly dictated by diverse geological processes happened during the burial history of the reservoir (Harbaugh 1967, Ehrenberg and Nadeau 2005, Ahr 2011, Burchette 2012). In fact, the heterogeneities can be appreciated in several scales (reservoir, core, pore, etc.). The most highly varying properties are porosity, permeability and flow mechanisms (Jardine and Wilshart 1982). Therefore, understanding the nature of these heterogeneities allows to characterize carbonate reservoirs and lead to reliably predict the reservoir performance when waterflooding is implemented (Lucia 2003).

Ahr (2011) defined carbonates as anionic complexes of $(\text{CO}_3)^{2-}$ and divalent metallic cations such as Ca, Mg, Fe, Mn, Zn, Ba, Sr and Cu, along with a few less common others. The bond between the

metallic cation and the carbonate group is not as strong as the internal bond in the CO₃ structure (Ahr 2011); this comes to play an important role while looking for wettability alteration in carbonate reservoirs. For instance, while flooding a reactive brine chemicals reaction such as ion exchange take place.

The most common carbonate minerals are Calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). These two minerals subsequently form limestones and dolostone. These carbonate rocks make up about 90% of all naturally carbonates reservoirs (Reeder, 1983). Dolomite rock or dolostones is formed during diagenesis in a process called dolomitization, where calcite is gradually replaced (Weyl 1960, Morrow 1982, Morrow 2001). Diagenesis, defined as the physical and chemical changes occurring during the conversion of sediments to sedimentary rock, is extremely important in carbonates rock; for instance, in **Table 2**, the amount of primary porosity for carbonate rocks is around 40-70%, primary porosity refers to the initial porosity when the rock is formed. But after all diagenetic changes, porosity is severely reducing around values between 5 to 15%.

Table 2: Major Carbonate Reservoir Characteristics (Ahr 2011).

Reservoir Characteristic	Carbonates
Amount of primary porosity	40-70%
Amount of ultimate porosity	Small fraction of original porosity, around 5-15%
Influence of Diagenesis	Major – Can create, obliterate, o totally modify porosity.
Influence of fracturing	Major importance in reservoir properties if present.
Porosity-Permeability relationships	Highly varied; may be independent of particle texture.

However, this does not always happen. For instance, two insignia field from the Norwegian continental shelf, Valhall and Ekofisk possess rather high porosities. Ekofisk between 30 to 40% and Valhall in the range of 40%. Chalks are a very special biogenic limestone, formed from debris of microscopic calcite plates called coccolith (Hardman 1982). Chalks are mainly composed by calcite (CaCO₃), but clay minerals, authigenic and glauconite can also be found. Chalks reservoirs was the main focus of this study. However, due to scarcity of authentic cores from the reservoirs, outcrop chalks were used to perform this study. Specifically, Kansas Chalk was used, which is 97.20% pure calcite. See **Table 3**. Thus, other minerals could have affected the results presented in this work.

Moreover, carbonate reservoirs are often fractured. Nelson (2001) defined fractured reservoirs as “reservoirs in which natural fracture have, or are predicted to have, a significant effect on fluid flow either in the form of increased reservoir permeability and/or reserves or increased permeability

anisotropy". Fractured reservoirs are highly challenging to develop and therefore to produce; specially, poor sweeping of the reservoir while performing waterflooding are expected due to early breakthrough of the water. The water tends to follow the easiest path through the rock: this is through the fracture. This together with usual wetting state of carbonate reservoirs (roughly 90% of the carbonate reservoirs are neutral to oil wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972)) lead to low oil recoveries. On the opposite site, fracture can affect positively the reservoir, improving permeability and easing the fluid of flows through the fracture.

2.3 Wettability of Carbonates

Through a serie of publication in 1986 and 1987 Anderson thoroughly explained how the wetting state or wettability controls several reservoir characteristics like capillary pressure, fluid relative permeability curves, electrical properties, Archie saturation exponent, fluid distributions and flows in the reservoir. Most of carbonates reservoirs are either neutral or oil wet. In 1972, Treiber and Owens carried out wettability tests based o contact angle measurements in 55 oil producing carbonate reservoirs. They found that 66% of these reservoirs were oil wet, 7% were considered as intermediate wet and 27% were water wet. These results were totally confirmed by the core analysis of 161 carbonate reservoirs (limestone, dolomitic limestone, calcite dolomite, and dolomite) performed by Chilingar and Yen 1983. Based one more time in contact angle measurements, they found that 15% were considered strongly water wet, 65% oil wet, 12% intermediate wettability and 8% water wet. The cores analysed by Chillingar and Yen came from different regions around the world including United States, China, Mexico, Canada and India.

2.3.1 Factors Influencing Initial Wetting State of Carbonates

The wetting state is the result of the chemical interaction between the reservoir rock, the formation water and crude oil invading the reservoir. This chemical equilibrium was achieved by an interaction of the three components over millions of years. Thus, it is important to describe how carbonate mineral composition, crude oil components and formation water influence the initial wetting state of the reservoir.

Buckley et al. (1998) proposed the following mechanisms of interaction between crude oil, rock and rock:

- i. Polar Interactions that predominate between oil and rock in the absence of a water film.

- ii. Surface precipitation, dependent mainly on crude oil solvent properties with respect to the asphaltenes.
- iii. Acid/base interactions that control surface charge at oil/water and rock/water interfaces.
- iv. Ion binding or specific interactions between charged sites and higher valency ions.

2.3.1.1 Mineral Composition of the Rock

Rock chemistry is mainly influenced by the mineral composition of itself. Therefore, carbonate rock chemistry varies from sandstone rock chemistry. The mineral composition of each rock dictates the way polar compound interact with rock surface and adsorption of them to it, leading to changes in the initial wetting state of the rock (Denekas et al 1959, Buckley and Liu 1998).

Carbonate reservoirs have been found to possess a positive charged surface at normally pH reservoir conditions ($\text{pH} < 8$) (Stumm et al. 1992). Pierre et al. (1990), also pointed out that carbonate surface rock is usually charged at basic conditions ($\text{pH} < 9.5$). The contraire case is found on sandstones where the surface is usually negative charged above of 2 and therefore becomes more oil-wet after being exposed to the basic components (Menezes et al., 1989).

Ahr (2011) defined carbonates as anionic complexes of $(\text{CO}_3)^{2-}$ and divalent metallic cations such as Ca, Mg, Fe, Mn, Zn, Ba, Sr and Cu, along with a few less common others. The presence of these divalent metallic cations makes the carbonate surface positive. Thus, this facilitates the adsorption of the negatively charged carboxylates, RCOO^- present in the crude oil (Fathi et al. 2011).

Finally, Strand et al. (2007) studied the effect of silica content in chalks. The study found that silica could increase the water wet condition of chalks. Silica, usually found in sandstones, negatively charged can act as an inhibitor, preventing the oil from contacting the carbonate surface.

2.3.1.2 Crude oil Components

Once the crude oil invades the reservoirs, the chemical equilibrium initially established between the formation water and the reservoir rock is altered. A new chemical equilibrium is now developing. But how and what are the most important parameters of the oil that could affect the wetting state of the reservoir?

In carbonate reservoirs, the crude oil composition is perhaps the most critical parameter that can dictate the wetting state of carbonates (Buckley 1996). Lowe et al. (1973) found that carboxylic acid

groups (R-COOH) can adsorb on the positively charged carbonate surface in alkaline conditions (R-COO⁻). This carboxylic group is often found in the heavier fraction of the oil, asphaltenes and resins (Morrow et al. 1986, Anderson 1986a, Morrow 1990, Dubey and Waxman 1991, Radke et al. 1992); making these fractions extremely important dictating the wetting state (Buckley 1995, Buckley et al 1998, Buckley 2001). These fractions are rich in NSO (Nitrogen, sulphur, oxygen) compounds. Skauge et al. (1999) showed that acid and base number are proportional to asphaltene concentration. Subsequently, Zhang and Austad (2005) found that increasing acid number (AN) decreases the water wetness in chalks. Similarly, the same effect has been observed in limestone (Ravari et al. 2011).

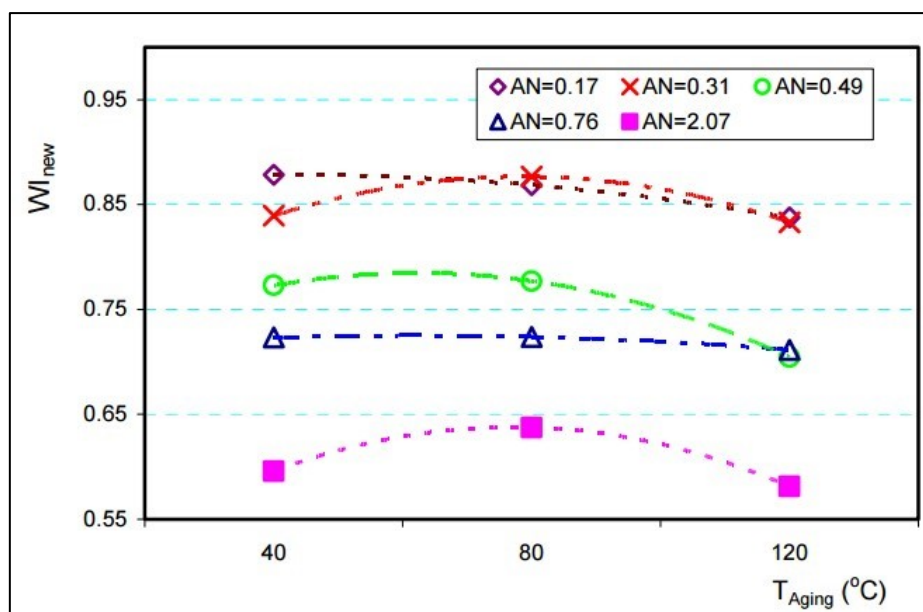


Figure 5: Correlation between Wettability Index and Aging Temperature (Zhang and Austad 2005).

Thus, the lowest Wettability Index is achieved when the acid number is higher. Zhang and Austad (2005) concluded that the wettability of a carbonate oil reservoirs is mainly dictated by the acid number of the crude oil. Therefore, the water wetness of the chalks decreases as the acid number increases. They also concluded that the aging temperature probably plays a minor role regarding chalk wettability. See **Figure 5**.

Standnes and Austad (2000) found that the highest oil recovery by imbibition was achieved when the acid number was lowest. They also concluded that high AN seems to cause a stronger alteration of the mineral surface towards more oil wet. Therefore, it is reasonable to conclude that the WI decreases (Oil Wet) with increasing the acid number and therefore, low oil recovery is also expected. See **Figure 6**.

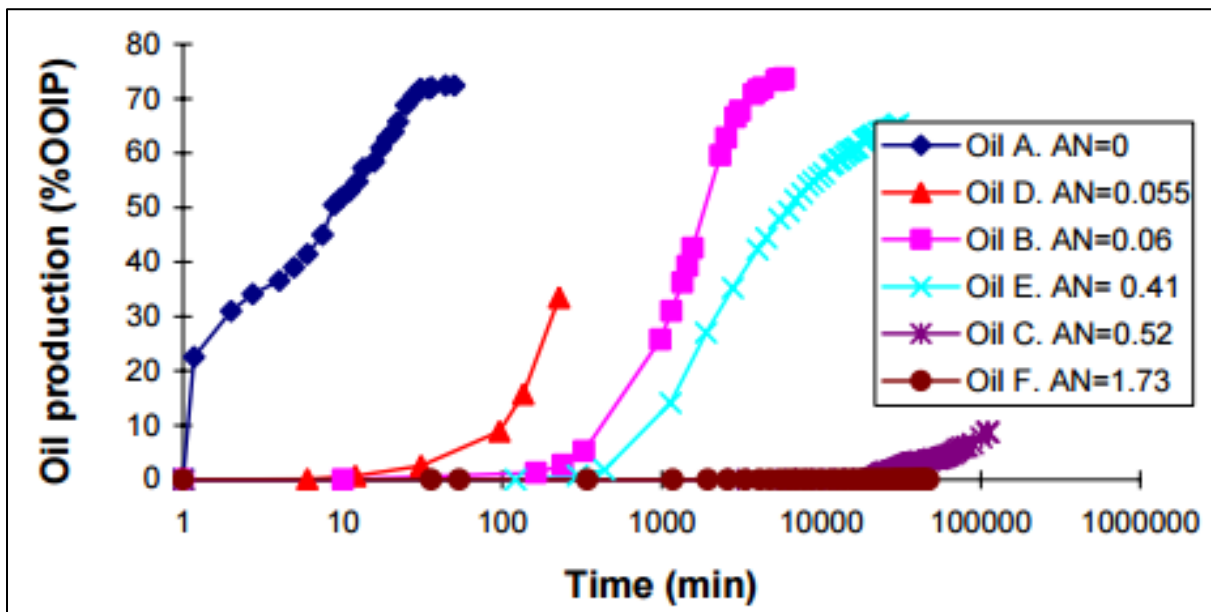


Figure 6: Spontaneous imbibition of brines into chalk cores saturated with different crude oil with different AN (Standnes and Austad 2000).

2.3.1.3 Formation Water

Formation water is related to the water found in the reservoir in the moment of depositions. For instance, carbonate reservoirs are mainly found in marine environments, thus, it is valid to assume this water will rich in ions like Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} . In fact, a high concentration of calcium provokes a positively charged surface (CaCO_3). Formation water is one of three main elements interacting in the reservoir which ultimately dictates the wetting state. However, injected water often differs in chemical composition from the formation water; a new chemical equilibrium is now set in motion.

Punternvold et al. (2007) found that sulphate ion increases the water wetting state in carbonates. Sulphate can either be present in formation water or the rock surface. This was later confirmed by Austad et al. (2009).

Wettability is strongly affected by the salinity and pH of the brine because they affect the surface charge on the rock surface and fluid interfaces. (Stumm and Morgan 1970, Leja 1982). Anderson (1986) established the most important brine properties that could affect the wetting state are chemical composition, salinity and pH. For instance, carbonate reservoirs have been found to possess a positive charged surface at normally pH reservoir conditions ($\text{pH} < 8$) (Stumm et al. 1992). Pierre et al. (1990), also pointed out that carbonate surface rock is positively charged at basic conditions ($\text{pH} < 9.5$).

During a series of imbibition experiments carried out by Puntervold et al (2007) in Stevns Klint outcrop chalk material, cores with initial water saturation provided a higher recovery and a higher water wet surface area.

2.3.1.4 Aging

Due to the scarcity and difficulty to obtain cores preserved at reservoir conditions, outcrop cores are used to mimic reservoir rocks as core materials in flooding experiments. However, restoring the wetting state of outcrop cores has not been standardized. Wetting state is direct result of the interaction between formation water, crude oil and reservoir rock; thus, trying to simulate millions of years have been a special challenging task. The fact that there is not a standardized procedure to restore wettability, poses even more challenges. Understanding the dynamics of wettability restoration in the laboratory will enhance the ability to mimic reservoir conditions before carrying out core tests and help to ensure that experimental data are representative of the reservoir (Al-Mahorooqi et al 2005).

During a series of experiments carried out by Graue et al. (1999) while measuring the wetting state based on Amott test, the Amott Index decreased with aging in chalk cores. Graue et al. (2002) also found that aging process accelerate while flooding oil through the core during the aging process. Al-Mahrooqi et al. (2005) found that Wettability alteration begins at the start of aging and occurs more rapidly at higher temperatures. On the opposite side, Hopkins et al. (2016) realised that adsorption of polar components occurs immediately as the core enter in contact with oil.

The aging process highly varies; however, the aging process is extremely important in wettability restoration because allows the adsorption of polar components presented in the crude oil in the rock surface (Piñerez 2017). What remains unclear which parameter is the most critical: PV of oil injected, aging's time, aging's temperature, aging pressure. For instance, Rühl et al. (1963) and Kowalewi et al. (2002) have reported changes in the wetting state as early as 10 days of ageing. on the other hand, Wendel et al. (1985) carried out series of experiments aging the cores for 1000 hours (40 days) at reservoir temperature. This aging period was chosen for two reasons: several experiments have shown that up to 1000 hours is required to reach wetting equilibrium (Cuiec 1975, Cuiec 1977, Mungan 1966, Ehrlich et al. 1974, Lorenz et al. 1974). Mungan (1972) was able to restore the wettability after aging for 6 days, while the wettability of the, rock/ oil/brine system used by Schmid (1964) and Riihl et al. (1963) was restored after only 3 days. Salathiel (1973) was able to restore wettability after 3 days.

The cores prepared during the development of this experimental work were aged for 21 days at 90°C.

2.3.1.5 Reservoir Conditions

The interaction between formation water, crude oil, and reservoir rock dictates the initial wetting state of the reservoir. This chemical equilibrium is the product of millions of years and takes place at reservoir conditions. What are the effects of reservoir's pressure and temperature in the initial wetting state of the reservoir?

Anderson (1986) stated that the solubility of polar components present in the oil increases with increasing pressure and temperature. However, temperature tends to play a much more important role. Wang and Gupta (1995) found that the wettability measurements using modified pendant drop method were not affected by pressure. Buckley (1995) realised that as pressure decreases towards the saturation pressure of oil, the solubility of asphaltenes in the crude oil decreases and precipitation and therefore adsorption onto the rock are expected.

Temperature has been found to be critical parameter dictating the wetting state in carbonate reservoirs. Carbonates reservoirs at high temperatures behave more water wet (Rao 1996). This can be explained because of decarboxylation process taking place in high temperature carbonate reservoirs. The AN, perhaps, the most critical parameter dictating the wetting state in carbonate reservoirs is temperature dependent, the acid number decreases with increasing temperature. Calcium carbonate (CaCO_3) behaves as a catalyst in a decarboxylation process (decomposing the carboxylic group), lowering the AN (Zhang and Austad 2005).

2.3.1.6 Core Cleaning

Cleaning procedures applied in outcrop cores could affect the wetting state measurements. Anderson (1986) suggested that there are two main reasons to clean the core:

1. To remove all liquids from core so that, porosity, permeability and fluid saturations can be measured.
2. To obtain a strongly water wet core, considered the first step in restoring the wettability of a contaminated core.

There are different kind of solvents that can potentially be used to clean cores. For instance, flooding organic solvents helps to remove any organic compound without altering the rock wettability

(Anderson 1986). Depending on the solvent used to clean the core, the initial wetting state can or cannot be affected (Grist et al. 1975). Several studies have been carried out about cleaning procedures in order to obtain a strongly water wet core, however the chosen cleaning procedure is highly dependent on what kind of rock aims to be cleaned. For instance, Strand et al. (2008) and later on confirmed by Shariatpanahi et al. (2012) found that Seawater flooded at high temperature is an efficient solvent to clean limestones cores.

Punternold et al. (2007) found that small amount of sulphate ion in non-flushed core had a major impact on the initial wetting state of the chalk core. The author also found that during spontaneous imbibition tests, a reduction in the water wetness of the cores was observed after 4 PV of distilled water were flooded through the core. A decrease in water wetness was observed using the chromatographic wettability test. Punternold et al. (2007) concluded that outcrop chalk cores must be flushed before being tested with at least 4 PV of distilled water or brine without sulphate to remove negatively charged potential determining ion of sulphate, which was proved to have a direct impact on the wetting conditions of chalks.

2.4 Wettability Alteration in Carbonates by Smart Water

Carbonate reservoirs are mostly neutral to oil wet (Chilingar and Yen, 1983; Cuiec, 1984; Treiber et al., 1972), thus, modifying the wetting state from an oil or mixed to a water wetting state would generate a change in the capillary pressure, relative permeability curves, and fluid distribution in the pore space that will lead to an increase in the hydrocarbon recovery from carbonate rocks (Tabary et al., 2009). But how to achieve these changes in the wetting state that positively affect the reservoir?

In general, to produce oil from oil wet reservoirs, Mohammed and Babadagli (2015) proposed the following methodology:

- i. Establish the mechanisms that shifted the wettability to oil-wet.
- ii. Determine the reservoir and fluid characteristics (current status of wettability, size of the reservoir, vertical continuity, fluid densities and viscosities, etc.).
- iii. Study the interplay between different forces under reservoir conditions (capillary, gravity, and viscous force).
- iv. Determine which properties to be changed (viscosity, density, wettability, etc.).
- v. Screen wettability alteration methods based on the reservoir rock type (sandstone, limestone, chalks, etc.) and the mechanism that had changed the reservoir wettability.

- vi. Optimize the parameters of wettability alteration.

Norwegian continental shelf possesses important carbonate reservoirs. For instance, Ekofisk and Valhall are main carbonate reservoirs located in the NCS. Seawater is currently being injected for a long time in both reservoirs. Ekofisk has been under seawater injection for more than 3 decades with great success (Austad 2005). But why Seawater has been highly effective increasing the oil recovery in Ekofisk Field?

Seawater has been proved right to act as a wettability modifier in carbonate reservoirs, increasing the water wetness of the reservoir rock (Zhang et al. (2007) Puntervold and Austad (2008), Puntervold et al. (2009), Ravari et al. (2011)). The increase in oil recovery is attributed to wettability alteration on the matrix.

Pierre et al. (1990) initially established that seawater contains reactive ions Ca^{2+} , Mg^{2+} and SO_4^{2-} towards the chalk surface and therefore act as potential determining ion changing the surface charge of the rock (CaCO_3). Zeta potential measurements carried out by Zhang and Austad (2006) confirmed that Ca^{2+} , Mg^{2+} and SO_4^{2-} act as potential determining ions.

Several experimental studies have been carried out to test and quantify the effect of potential determining ions on carbonates, especially on chalk reservoirs.

Magnesium ion (Mg^{2+}) is a reactive ion to the chalk surface. However, the reactivity of the magnesium is temperature dependent. Magnesium has a strong hydration energy, which makes it less reactive at low temperature (Austad 2013). At 100 °C and 130 °C, Mg^{2+} can substitute Ca^{2+} at high temperature (Korsnes et al. 2006, Zhang et al., 2007). This effect could lead to changes in the mechanical strength of chalks.

Analysis of the concentration of Mg^{2+} in the effluent confirmed a 1:1 substitution, by revealing correspondingly reduced concentrations (Korsnes et al., 2006a; Korsnes et al., 2006b; Zhang et al., 2007). At 70 °C there were no detectable changes in the concentration, suggesting a threshold temperature for the observed substitution. Several studies carried out later confirmed the precipitation of magnesite onto the chalk surface (Medetbekova 2015, Pedersen et al. 2015, Minde et al. 2017). See **Figure 7**. This process is illustrated by the following equilibrium substitution equation:



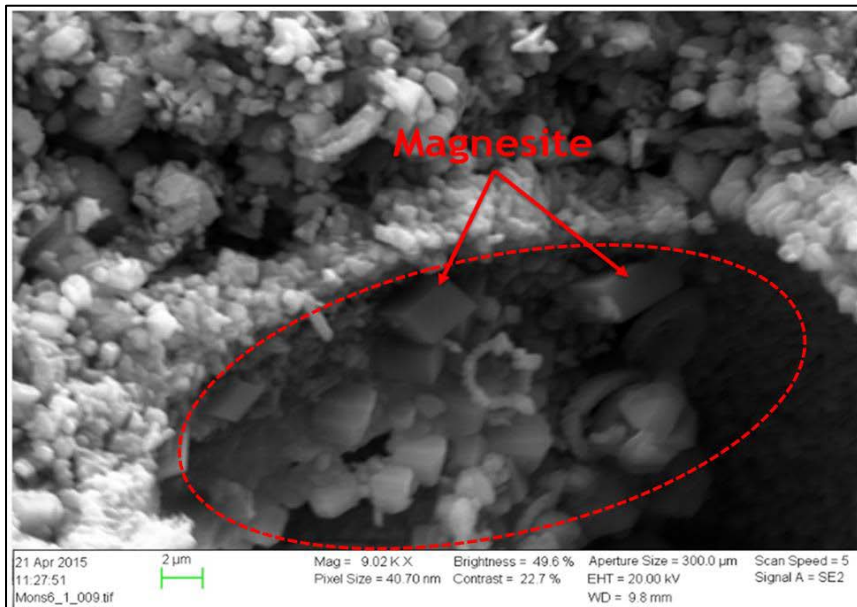


Figure 7: SEM micrograph shows common occurrence of magnesite crystals with rhombic habit (arrows) in the Mons chalk core tested at 130 °C. (Medetbekova 2015).

2.4.1 Smart Water Mechanism

Zhang et al. (2007) experimentally verified that Mg^{2+} is also a strong potential determining ion towards chalk surface, and suggested the potential of this ion to increase the positive charge density of chalk surface. Smart water mechanism can be appreciated in **Figure 8**:

- **Smart Water Mechanism:** At high temperature, Magnesium ion (Mg^{2+}) substitutes calcium ion (Ca^{2+}) from the chalk surface, and the degree of substitution increases with increasing temperature (Zhang et al. 2007). Zhang et al. (2007) also suggested the possibility to displace Ca^{2+} linked to carboxylic groups on the chalk surface.

This substitution reaction has been observed in several geomechanics studies (Korsnes et al., 2006a; Korsnes et al., 2006b), affecting the mechanical strength of chalks (Madland et al. 2011). This phenomenon has been called water weakening of chalk. Hiorth et al. 2010 suggested that the dissolution effect of the oil wet surface increases the oil recovery.

More recent studies have shown precipitation of magnesite onto the chalk surface (Medetbekova 2015, Jettestuen 2015, Minde et al. 2017).

Therefore, by understanding the chemical mechanism for wettability alteration, it is possible to optimize the ion composition in the injected water to maximize the oil recovery. From an economical

point of view, it is important to inject the optimized fluid from the start of the waterflooding (Austad 2013).

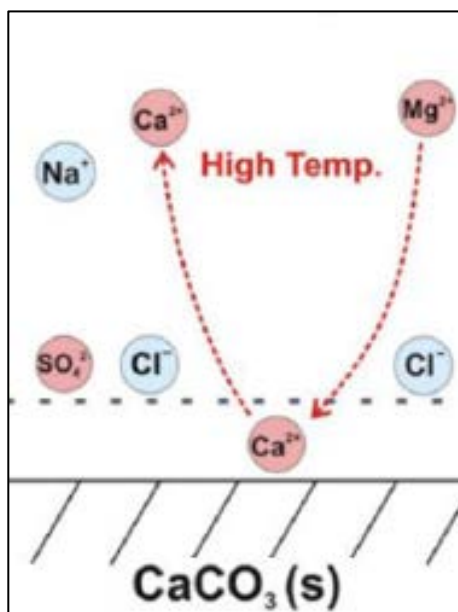


Figure 8: Proposed mechanism when Mg^{2+} , Ca^{2+} and SO_4^{2-} are active at higher temperatures. Modified from (Zhang et al. 2007a).

Magnesium ion is strongly hydrated. Thus, magnesium activity is minimum at low temperature. However, magnesium activity increases with increasing temperature due to dehydration of water molecules surrounding the ion. Magnesium (Mg^{2+}) is able to substitute calcium ion (Ca^{2+}) at high temperature (Zhang et al. 2007). This ion exchange leads to two simultaneous reactions inside the chalk matrix. One, dissolution of calcite. Calcium is removed from the chalk surface due to precipitation of new magnesium bearing minerals in the calcite surface (Madland et al. 2009, 2011; Megawati et al. 2011, 2012), the differences in atomic weight between magnesium and calcium trigger changes in the mechanical strength of chalk that lead to compaction and subsidence of the caprock. So, there has been suggestion that the combinations of these phenomena could be able to alterate the wetting state of the rock to a more water wetness state, by removing the oil wetted calcite, leading to increase in oil recovery (Hiorth et al. 2010). But is this really happening? Is the dissolution of calcite and precipitation of new magnesium bearing minerals able to trigger wettability alteration in mixed wet chalk rocks?

CHAPTER 3

METHODS AND EXPERIMENTAL PROCEDURES

This chapter foregrounds the experimental procedures performed during every experiment carried out throughout the development of this dissertation since the preparation of the core until the sample analysis using the Ion Chromatography (IC) and specific surface area measurements procedure.

Two setups were used to perform the wettability tests. These are the Hassler Type Core Holder and Hydraulically Triaxial Cells; while the wettability tests were executed using the chromatographic wettability test methodology proposed by Strand et al (2006).

3.1 Materials

3.1.1 Rock Samples

Kansas outcrop chalk were used during all the experiments carried out in this dissertation. Analysis of Kansas chalk indicates between 95 to 97%, which resembles clean North Sea chalk lacking significant chert and clay minerals (Tang and Firoozabadi 2001). Therefore, Kansas chalk exhibits very close properties with some of the North Sea reservoir chalks regarding capillary pressure, porosity, permeability and relative permeability.

A summary of the outcrop Kansas chalk properties is presented in **Table 3**.

Table 3: Physical properties of Kansas Chalk (Megawati 2015).

CHALK TYPE	AGE	POROSITY [φ] (%)	PERMEABILITY [K] (mD)	CARBONATE CONTENT (%)	SPECIFIC SURFACE AREA [SSA] (m²/g)
Kansas (KA)	Late Cretaceous	37-40	1-2	97.20	2.95

3.1.2 Oil

The crude oil used to prepare the mixed wet cores was based on a North Sea crude oil. This crude oil was obtained by diluting the biodegraded Heidrun Crude oil with acid number (AN) = 2.82 and base number (BN) = 1.13 mg of KOH/g with n-heptane in a volume ratio of 60/40. The acid number measured of the diluted oil was 2.12 mg of KOH/g.

3.1.3 Brine Composition

The wettability measurements were performed based on the test procedure developed by Strand et al. (2006). Thus, the brines used are SW-0T (without sulphate and tracer) and SW-1T (with Sulphate and tracer). The compositions of the brines are shown in **Table 1**.

Table 4: Ionic Composition of Synthetic Seawater for Chromatographic wettability test.

	SW-0T	SW-1T
	Mole/l	Mole/l
HCO₃⁻	0.002	0.002
Cl⁻	0.583	0.492
SO₄²⁻	0.000	0.024
SCN⁻	0.000	0.024
Mg²⁺	0.045	0.045
Ca²⁺	0.013	0.013
Na⁺	0.460	0.393
Li⁺	0.000	0.024
K⁺	0.010	0.034
Ba²⁺	0.000	0.000
Sr²⁺	0.000	0.000
Density (g/cm³)	1.022	1.022
Total Dissolved Solids (g/l)	33.38	33.38

Furthermore, Magnesium Chloride (MgCl₂) was used to evaluate the potential of determining ion Mg²⁺ to change the wetting state on mixed wet cores while flooding at 130 °C.

This brine was prepared in such a way that the Ionic Strength was kept constant and equal to the synthetic seawater ionic strength injected in North Sea chalk reservoirs. See **Table 5**.

Table 5: Ionic Composition of Magnesium Chloride.

Magnesium Chloride (MgCl₂)	
Ion	Concentration mol/l
Mg ²⁺	0.219
Cl ⁻	0.438
Ionic Strength	0.657

Moreover, Magnesium Chloride (MgCl₂) and Sodium Chloride (NaCl) were used to evaluate the possibility of increasing the specific surface area in a water wet Kansas core. Sodium Chloride was also prepared keeping the ionic strength equal to the ion strength of seawater. See **Table 6**.

Table 6: Ionic Composition of Sodium Chloride.

Sodium Chloride (NaCl)	
Ion	Concentration mol/l
Na ⁺	0.657
Cl ⁻	0.657
Ionic Strength	0.657

It is worth mentioning that Ionic strength is a function of the concentration of all ions present in the solution and is defined as follows:

$$I = \frac{1}{2} * \sum_{i=1}^n C_i * Z_i^2 \quad \text{Eq. 4.}$$

where C_i is the molar concentration of ion i (M, mol/l), and Z_i is the charge number of that ion. One half is because cations and anions were considered.

3.2 Preparation of Cores, Oil and Injected Brines

3.2.1 Preparation of Oil

The diluted oil was based on the biodegraded Heidrun Crude oil provided by Statoil. In order to prepare the oil in the ratio of 60/40 (crude oil/n-heptane), the following procedure was implemented:

1. Take a 1 L cylinder graduated and firstly pour 600 ml of crude oil followed by 400 ml of n-heptane.
2. Transfer the mixture to a 1 L plastic bottle with a stirrer inside of it.
3. Place the bottle for 20 minutes on the magnetic stirrer.
4. Later, transfer the 0.5 L of the stirred oil to another plastic bottle.
5. Place both plastic bottles containing 500 ml each in the centrifuge. Make sure, the bottles are placed in opposite sides (See **Figure 9**).
6. Set the centrifuge's speed at 90%. This is achieved by slowly increasing the speed from 5 till 45 during a 3-4 minutes' window. The increasing must be slowly in order to avoid overloading (See **Figure 9**).

7. After having centrifuged the oil, filter the oil through a 5 μm filter paper. Collect the oil in a glass bottle.

The dilution of the oil is made by two main purposes. First, to economize the North Sea reservoir oil provided by the company and second but most important to try to mimic the crude oil present in the North Sea reservoir. When the oil is kept at ambient condition, the gas initially dissolved in the oil at reservoir condition is released, causing the viscosity to increment. By diluting the original oil with n-heptane, the viscosity can be reduced and reach a value close to the one at reservoir condition.

This oil was used to prepare the mixed wet cores and subsequently during aging process of them.

After preparing the diluted oil, the acid number was measured using the acid-base titration procedure. The acid number measured was 2.12 mg of KOH/g. The acid-base titration procedure allows to find the concentration of an acid or base by neutralizing the acid or base with an acid or base of known composition. In particular, the titration procedure developed by Fan, T., & Buckley, J. S. (2007) was implemented.



Figure 9: From left to right: 1) Centrifuge. 2) Inside of the centrifuge. 3) Centrifuge's Speeds. 4) Titration equipment.

3.2.2 Preparation of Brines

3.2.2.1 Wettability Test Brines

All brines containing sulphate and carbonate salts could precipitate during mixing, even though the ion concentrations are below precipitation points.

To avoid precipitation during the mixing process, the following procedure was implemented:

1. Pour 400 ml of distilled water (DW) inside of a volumetric conical flask with a stirrer inside.
2. Place the volumetric flask on a magnetic stirrer with a funnel on the top of it.
3. Start with adding all the chloride salts (NaCl, LiCl, KCl, $\text{MgCl}_2 \times 6\text{H}_2\text{O}$, $\text{CaCl}_2 \times 2\text{H}_2\text{O}$). While adding all the salts, pour water through the funnel to remove any salt presented either on the funnel's surface or in the container where the salts were weighted.
4. Proceed by adding all the sulphates (Na_2SO_4)
5. Subsequently, add all the carbonates (NaHCO_3).
6. Finally, add the tracer (KSCN).
7. Take the volumetric flask out of the magnetic stirrer and remove the stirrer of the conical flask using a magnet; add distilled water until the 1 L mark. Put the stirrer back into the volumetric flask.
8. Place the volumetric flask back on the magnetic stirrer.
9. Stir the brine for 2 hours.
10. Filter the brine solution through a 0.65 μm filter paper using a glass filtration apparatus (See **Figure 10**).
11. Store the filtered brine in a glass flask with screw cap.

3.2.2.2 Flooding Brines

Magnesium Chloride (MgCl_2), Sodium Chloride (NaCl) were prepared following the next steps:

1. Pour 400 ml of distilled water (DW) inside of a volumetric conical flask with a stirrer inside.
2. Place the volumetric flask on a magnetic stirrer with a funnel on the top of it.
3. Add 44.52 g of $\text{MgCl}_2 \times 6\text{H}_2\text{O}$ (MW=203.30) to obtain a 0.219 M MgCl_2 brine or 38.4 g of NaCl (MW=58.44) to obtain 0.657 M NaCl brine. These molarities concentrations provide an ionic strength of 0.657.
4. Take the conical flask out of the magnetic stirrer and remove the stirrer of the conical flask using a magnet; add distilled water until the 1 L mark. Put the stirrer back into the volumetric flask.
5. Place the volumetric flask back on the magnetic stirrer.
6. Stir the brine for 2 hours.
7. Filter the brine solution through a 0.65 μm filter paper using a glass filtration apparatus (See **Figure 10**).

8. Store the filtered brine in a glass flask with screw cap.

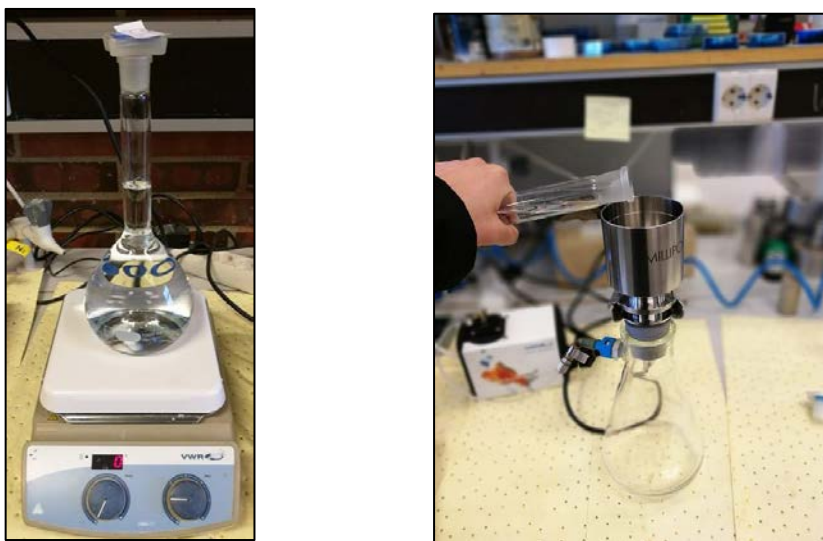


Figure 10: Left: Brine on top of a magnetic Stirrer. Right: Filtration Apparatus.

The pH of all the brines prepared were measured using pH Mettler Toledo (See **Figure 11**) just right after filtration.



Figure 11: pH Mettler Toledo.

All the brines were prepared the same day they were used for testing to avoid changes in pH over time due to excessive storage days. A sample of each brine tested was saved as an original in order to ease the analysis while using the Dionex IC S-5000+ Ion Chromatography System.

Also, 1.1 M NaCl brine was prepared to saturate the water wet cores to be used for wettability alteration.

3.2.3 Preparation of Cores Samples

Every core used in the experiments carried out during the lab work were prepared following the next methodology.

3.2.3.1 Core Drilling

A large Kansas outcrop chalk was drilled out using a Coring machine. The coring machine possesses an oversized diameter and circulate water for cooling. The oversized unshaped cores are put into a drying oven overnight set at a temperature higher than 100°C to ensure that all water present is totally removed. The drilling direction were marked on the oversized cores. It is worth mentioning that all the oversized cores were drilled out in the same direction and from the same block to ensure that most of the properties of the cores to be obtained were as similar as possible. Coring machine can be appreciated in **Figure 12**.



Figure 12: Coring Machine to drill out the outcrop Kansas Chalk.

3.2.3.2 Core Shaping

The oversized unshaped cores are placed in a lathe machine (See **Figure 13**) and subsequently shaped to a 38.1 mm diameter. A core plug used for mechanical testing usually have a diameter between 1' - 2 1/2'' (Fjaer 2008). An 1 1/2'' or 38.1 mm diameter is a common diameter used for uniaxial or triaxial test (Fjaer 2008). Also, triaxial cells are designed to hold plugs of 38.1 mm. Even though

no mechanical test was performed during this dissertation, the use of triaxial cells to evaluate wettability required the use of this special diameter.



Figure 13: Lathe machine used to shape the oversized cores.

After having the cores shaped with the desired diameter, the next step was to cut the cores to the desired length. The International Society for Rock Mechanics recommends that samples intended for standard rock mechanical tests should be right, circular cylinders with a length (L) to diameter (D) ratio between 2 and 3 (Fjaer 2008).

Cores were cut using a diamond cut-off wheels (Struers Discotom 500) (See **Figure 14**). The target of cutting the shaped cores besides having the desired length was to get smooth surfaces at the inlet and outlet of the cores plugs.



Figure 14: Diamond cut-off used to cut the cores to the required length.

After cutting the cores plugs to the desired length, end pieces adjacent to the inlet and outlet were kept in order to be further analysed. Having the end pieces allows to study the chemical changes in the surface of the core after testing, especially after wettability alteration processes. These analyses are achieved by Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) or X-ray powder diffraction (XRD).

The final diameter and length were measured as an arithmetic average of three measurements around the core of each parameter. These measurements were performed using a Digital Vernier Calliper (See **Figure 15**).



Figure 15: Calliper used to measure the length and diameter of the final cores.

The bulk volume (V_B) of the core can now be calculated using the averaged values previously measured and assuming the volume of a cylinder.

$$V_B = \frac{\pi * D^2 * L}{4} \quad \text{Eq. 5.}$$

where D is diameter and L is the length of the core.

The final core plugs are placed one more time into a drying oven overnight set at a temperature higher than the boiling point of the water. A summary of all the cores used during this experimental work can be found on **Table 7** and **Table 8**.

Table 7: Physical Properties of cores used to establish the water wet reference area.

Core	K1	K2	K3	K4	K5	K6
Core Length [mm]	71.89	72.87	69.96	68.61	68.82	67.88
Core Diameter [mm]	38.06	38.12	38.12	38.12	38.07	38.09
Dry Mass [g]	138.83	141.26	136.17	136.82	134.19	134.37
Pore Volume (PV) [ml]	30.64	31.04	29.5	27.54	28.84	27.63
Porosity (Φ) [%]	37.47	37.32	36.95	35.17	36.82	35.72

Table 8: Physical Properties of mixed wet cores used to evaluate Wettability Index evolution.

Core	K7	K8	K9	K10
Core Length [mm]	71.72	72.45	73.16	74.43
Core Diameter [mm]	38.12	38.11	38.14	38.13
Dry Mass [g]	137.86	139.23	140.75	148.38
Pore Volume (PV) [ml]	30.21	31.16	31.43	30.16
Porosity (Φ) [%]	36.91	37.70	37.60	35.49

3.2.3.3 Saturating the Core and Porosity Calculation

After the cores were dried overnight, the weight of each of them was measured using an analytical balance. This weight was considered as the dry weight (W_{DRY}) of the core (See **Figure 16**). The core is now ready for saturation.

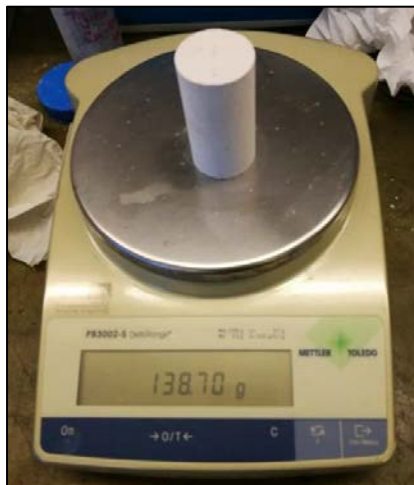


Figure 16: Analytical balance weighting the dry weight of the core.

The cores were saturated following the next steps (See **Figure 17** and **Figure 18**):

1. After measuring the dry weight of the core. Place the core inside of a small cylindrical plastic container. Make sure the container is appropriate for the size of the core.
2. Place the container in the middle of the vacuum chamber. Place the O-ring in the top of the vacuum chamber and then seal the chamber with the lid. Align the plastic container with the ventilation valve located in the lid of the vacuum chamber.
3. Close the ventilation valve. Open the valve connecting the vacuum chamber to the vacuum pump. Set the speed gear of the vacuum pump to II. Start the vacuuming process.
4. Change the from speed gear II till 0 during a 45 minutes' span. Each switch is done after the pressure reach a specific inflection pressure point.
5. The vacuuming process finishes when the pressure inside of the chamber is 4 – 5 Pa lower than the atmospheric pressure. Turn off the vacuum pump.
6. Clean the saturation line with distilled water. Saturate the saturation line with distilled water and connect it to the ventilation valve. Slowly open the valve and let the water fill up the plastic container. Assure that the level of the distilled water completely covers the core.
7. Leave the core with the saturation fluid inside of the chamber for at least 45 minutes to assure that the saturation process is fully completed.

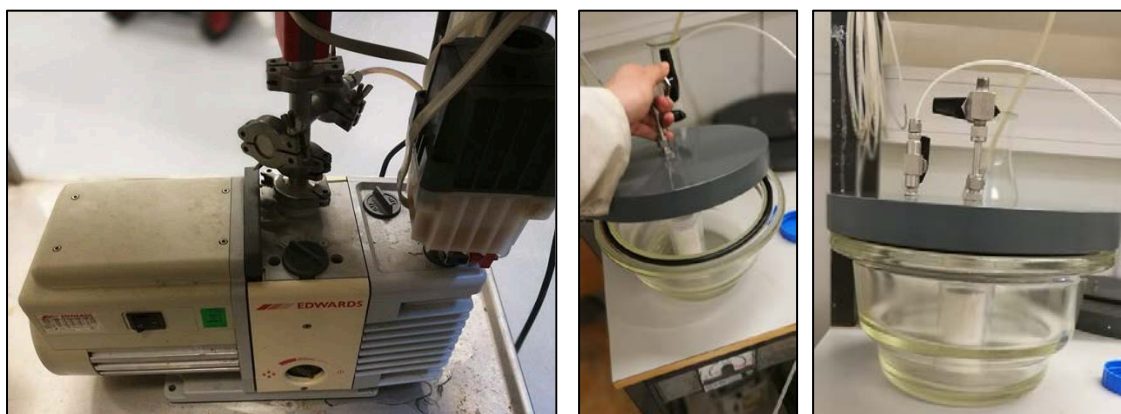


Figure 17: Left: Vacuum Pump. Middle: Lid sealing the vacuum chamber. Right: Vacuum chamber setup ready to vacuum the core.



Figure 18: Left: Saturated core. Middle: Weight of the saturated core. Right: Saturated core placed inside of cylindrical container.

Porosities calculations of the cores are based on weight analysis. After the core is fully saturated, the weight of the saturated (W_{SAT}) core can be measured. The pore volume (V_P) can be now calculated using the following equation:

$$V_P = \frac{W_{SAT} - W_{DRY}}{\rho_{DW}} \quad \text{Eq. 6.}$$

Where ρ_{DW} is the density of the distilled water (1 g/cm^3).

by definition, porosity is:

$$\phi = \frac{V_P}{V_B} \quad \text{Eq. 7.}$$

The saturation procedure explained above was exactly the same procedure while saturating the core with a different brine. Before preparing the mixed wet cores, the cores were previously saturated with 1.1 M NaCl.

3.2.4 Preparation of Mixed Wet Cores

In order to obtain homogeneous wetting conditions, the mixed wet cored tested during the development of this dissertation were prepared following the same procedure. It is worth noting that several methods of preparing mixed wet cores have been reported in the different experimental studies.

1. Saturate the water wet core with 1.1 M NaCl brine.
2. Place the saturated core inside of a Hassler Type Core Holder.
3. Set the temperature of the universal oven (Beschickung – loading Modell 100 – 800) at 50°C (See **Figure 19**).



Figure 19: Oven used for wettability alteration.

4. Place the Hassler Type Core Holder (See **Figure 20**) containing the core into the oven. Connect the core holder to the lines. The flooding lines were previously filled up with 1.1 M NaCl brine. Set the confining pressure to 16 [Bars]. The confining pressure is provided by Nitrogen.
5. Flood 2 PV a day of diluted oil in each direction of the core. Make sure the same volume of oil was flooded in each direction.
6. After flooding 4 PV for 2 days, the core is taken to initial water saturation; this allows to calculate initial water saturation of the core. Afterwards, the oil flooded core is placed into an aging cell.
7. Before putting the core into an aging cell (See **Figure 20**), place 2 marbles inside of the aging cell. Then, place the core into the aging cell. Verify that the inlet of the core is in contact with the marbles.
8. Add diluted oil inside of the aging cell until it covers all the core. Seal the aging cell and put it inside of a laboratory drying oven (Termaks 9000 Series) (See **Figure 20**) at a constant temperature of 90°C for 3 weeks.

The weight the aging cell containing the core was checked 3 times to ensure that evaporation was not taking place. First, before putting the aging cell into the oven. Second, 2 hours later after putting it in. The last weight measurement was taken 3 weeks after taking the aging cell out of the oven. The aging process subsequently continues at ambient temperature until the core is taken out from the aging cell for testing.



Figure 20: Left: Hassler's Cell Core Flooding Setup. Middle: Aging Cell. Right: Oven used for aging.

3.3 Tests Equipment

3.3.1 Hassler Type Core Holder

Hassler type core holders (See **Figure 21**) are defined as core holders that have radial pressure applied to the core sample (Core Lab). These core holders are commonly used for gas and liquid permeability and other core flooding experiments. The Hassler Core Holder has been widely used for chromatographic wettability test developed by Strand et al (2006).

A typical sketch of the hassler's Cell setup can be appreciated in **Figure 22**. The pore pressure is applied using a back-pressure regulator set at 7 [Bars]. The confining pressure is provided through water and set at 20 [Bars]. The sealing material surrounding the core is a rubber sleeve, ensuring the flow of the injected brines through the cross-sectional area of the core. The hassler's cell setup also requires the use of gauges to monitor pore pressure, differential pressure and temperature; also, the use of steel cylinders containing the wettability brines, Gilson pump, software controlling all the operational parameters are necessary and a fraction sampler collector to take samples during the wettability tests. However, this setup was not the main setup where the experiments were carried out. The triaxial setup will be explained in detail in the upcoming sections.



Figure 21: Left: Actual Hassler type core holder at the lab. Right: Sketch of Hassler type core holder.

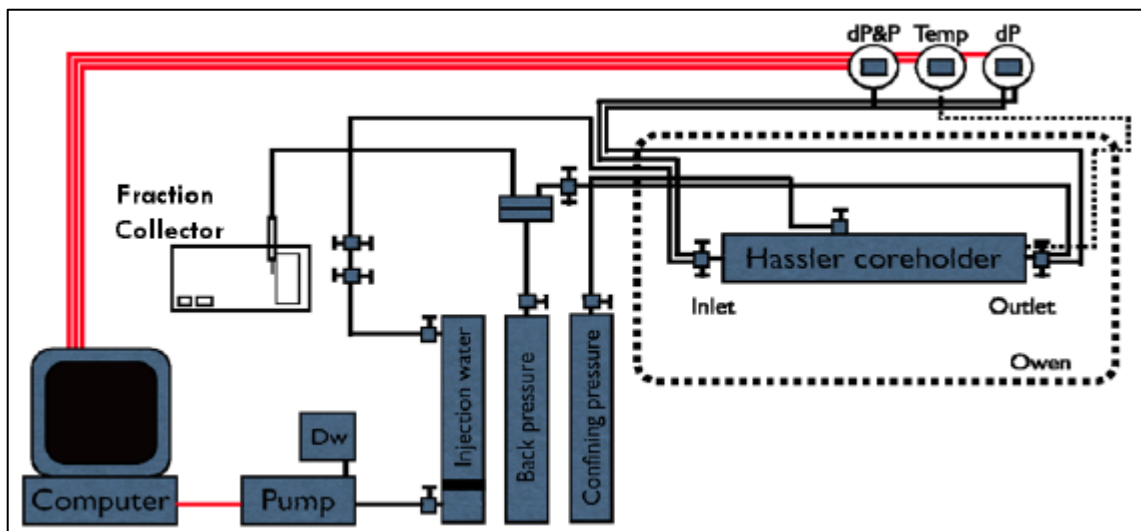


Figure 22: Sketch of the Hassler's Cell Setup (Halvorsen, 2010).

3.3.2 Triaxial Cell

Triaxial cell (See **Figure 23**) allows to simulate reservoir stress state conditions and performs geomechanics tests to measure the mechanical properties of rocks, this case, reservoir rocks. The triaxial cells allows to do the mechanical tests while flooding or not through the core. It also allows to perform the tests at different temperatures. The pore pressure is also provided using a back-pressure regulator and set at 7 [Bars]. The confining pressure is provided using synthetic silica oil and set at 15 [Bars]. In general, the cores used for mechanical tests are sealed using a shrinking sleeve melted to it. Shrinking sleeve is used for mechanical tests because besides of partly sealing the core, allows to measure the radial deformation of the core when this is put under deformation tests. However, for wettability tests performed on triaxial cells, shrinking sleeve can be substituted by rubber (Sealing material used in Hassler's Core holder).

In general, the triaxial has three main chambers: Confining Chamber, Upper Chamber and Lower Chamber. The upper and lower chamber are extremely important while performing mechanical tests, they allow to apply pressure in the axial direction while lowering the piston to contact the top of the core and subsequently unloading the core (moving the piston up).

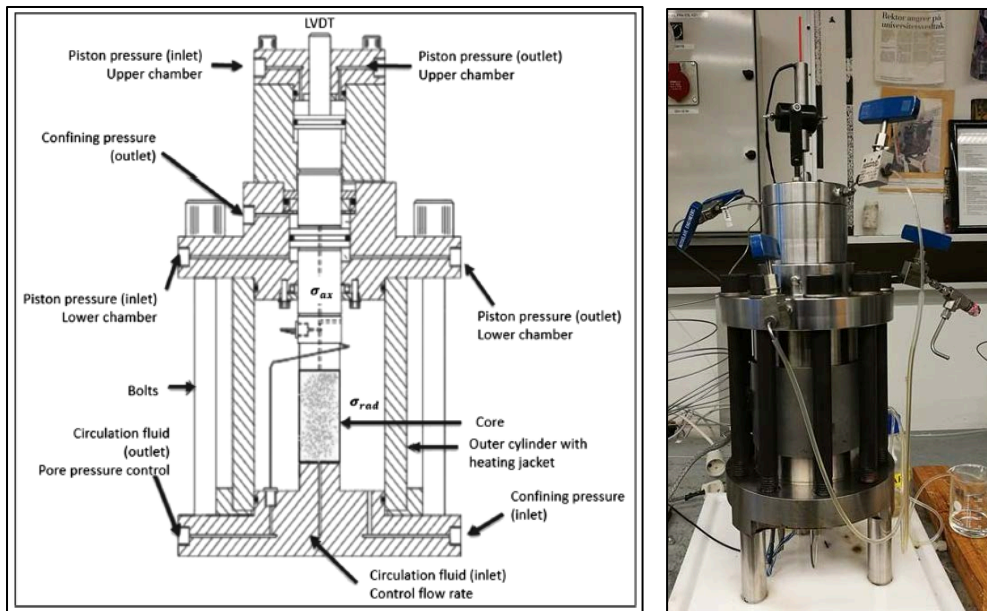


Figure 23: Left: Sketch of the triaxial cell used on the tests (Nermoen et al. 2015). Right: Actual Triaxial cell at the lab.

In order to perform the experimental tests in the triaxial cells, we also require the following components:

- **Heating Jacket:** the heating jacket is connected to the confining chamber, allowing to raise the temperature of the whole setup (Core Included) to the desired temperature (130°C). Once the temperature is approaching the target temperature, small fluctuations of temperature are expected in the range of 0.1 °C upper or below the 130° because of fluctuation in the ambient temperature. PID values help to keep the temperature stable and equal to 130°C. See **Figure 24**.



Figure 24: Left: Heating Jacket. Middle: Heating jacket attached to the confining chamber in a triaxial cell. Right: Omron Control Box keeping the temperature constant at 130°C.

- **Gauges:** digital gauges allow to mainly monitor variations in confining pressure, pore pressure, differential pressure and sometimes temperature. The values measured for these gauges are sent to the computer software that control the experiment. See **Figure 25**.



Figure 25: Digital gauges monitoring the values.

- **Pump and Flooding Cells:** the flood of all fluids is controlled by Gilson Pumps Serie 307. They can pump as low as 0.001 ml/min and as high as 10 ml/min. There are three pumps: one controlling the movement of the piston (this was not used), second pump controlling the confining pressure, pumping confining oil into the confining chamber and the third one controlling the flood of brines through the cores. This last one pumps distilled water to the top of the flooding cells. The flooding cells are hard steel cylinders with a piston cell inside which divide the cylinder in two sections. One containing distilled water and the other containing the brine that need to be flooded through the core.

The distilled water flood into the top of the cylinder displacing the piston cell, expelling the brine through the lower part of the cylinder directly to the core. See **Figure 26**.

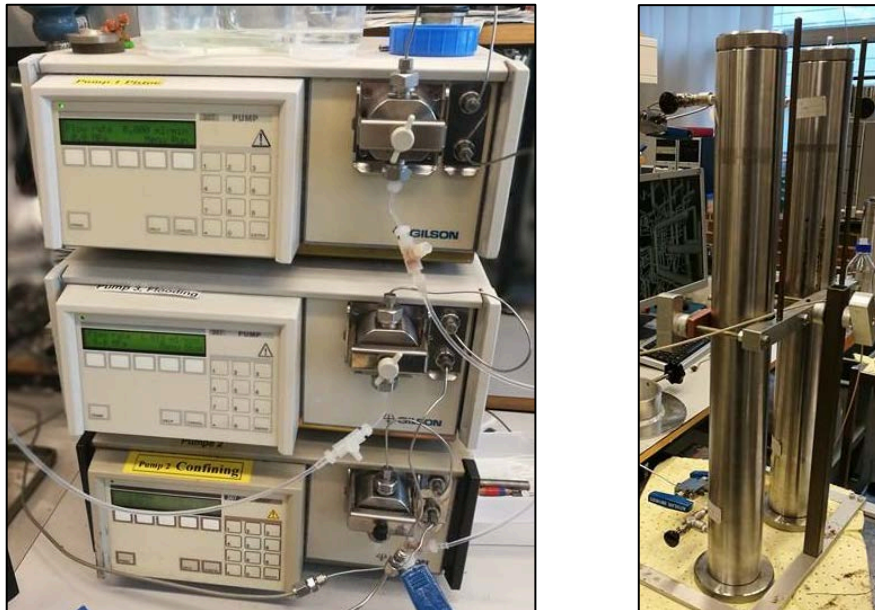


Figure 26: Left: Gilson pumps Serie 307. Right: Flooding cells for wettability test, one containing SW-0T and the other SW-1T.

➤ **Computer Software and Fractional Sampler:**

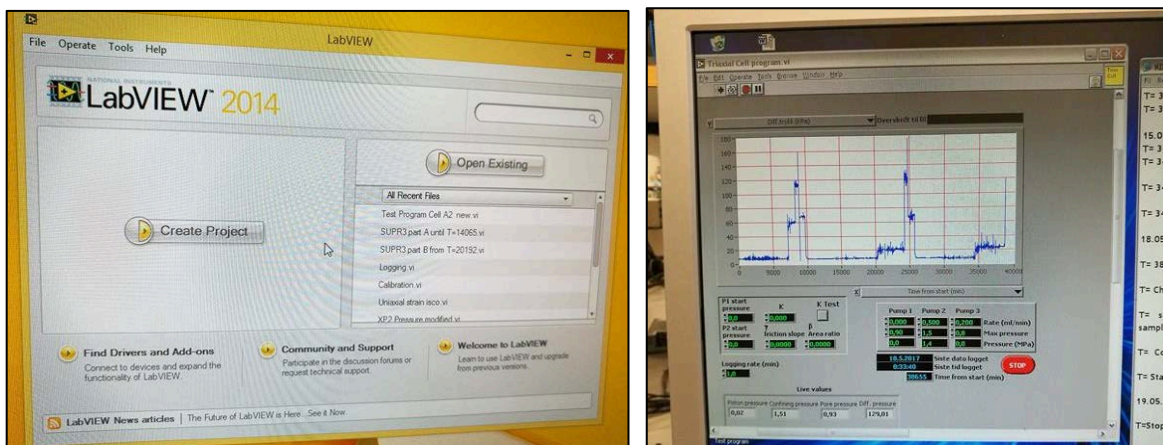


Figure 27: Left: LabVIEW Software. Right: LabVIEW Interface.

All the wettability tests performed on triaxial cells were controlled through the software called LabVIEW (Laboratory Virtual Instrument Engineering Workbench). This software is extremely useful allowing to control the flood of fluids of all three Gilson pumps, control and monitor the triaxial cell, obtaining responses on different operational parameters in real time. It also allows to process and

manipulate the data through plots in real time and at the same time generate a log file that can be processed using a spreadsheet software like Microsoft Excel. See **Figure 27**.

While performing the chromatographic wettability test, it is necessary to take samples to check how the concentration of the tracer and sulphate change with time. A fractional sampler connected to the effluent outlet was used to take a maximum of 44 samples during the chromatographic test (See **Figure 29**); the fractional sampler (Gilson GX-271 liquid handler) is controlled by Trilution LH Software (See **Figure 28**). The fractional sampler and the Trilution program were also used to dilute 500 time the samples taken from the chromatographic test before being analysed by Dionex IC-5000+ Ion Chromatography System.

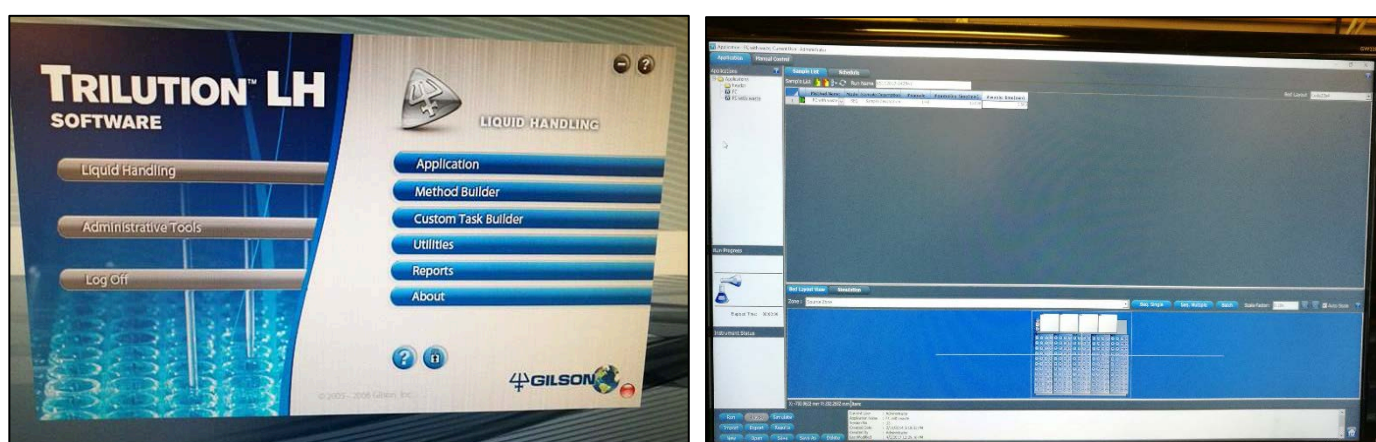


Figure 28: Left: Trilution LH Software. Right: Trilution Interface.



Figure 29: Fractional Sampler Working.

A general sketch, showing the triaxial and some of the components used during the experiments can be appreciated in **Figure 30**.

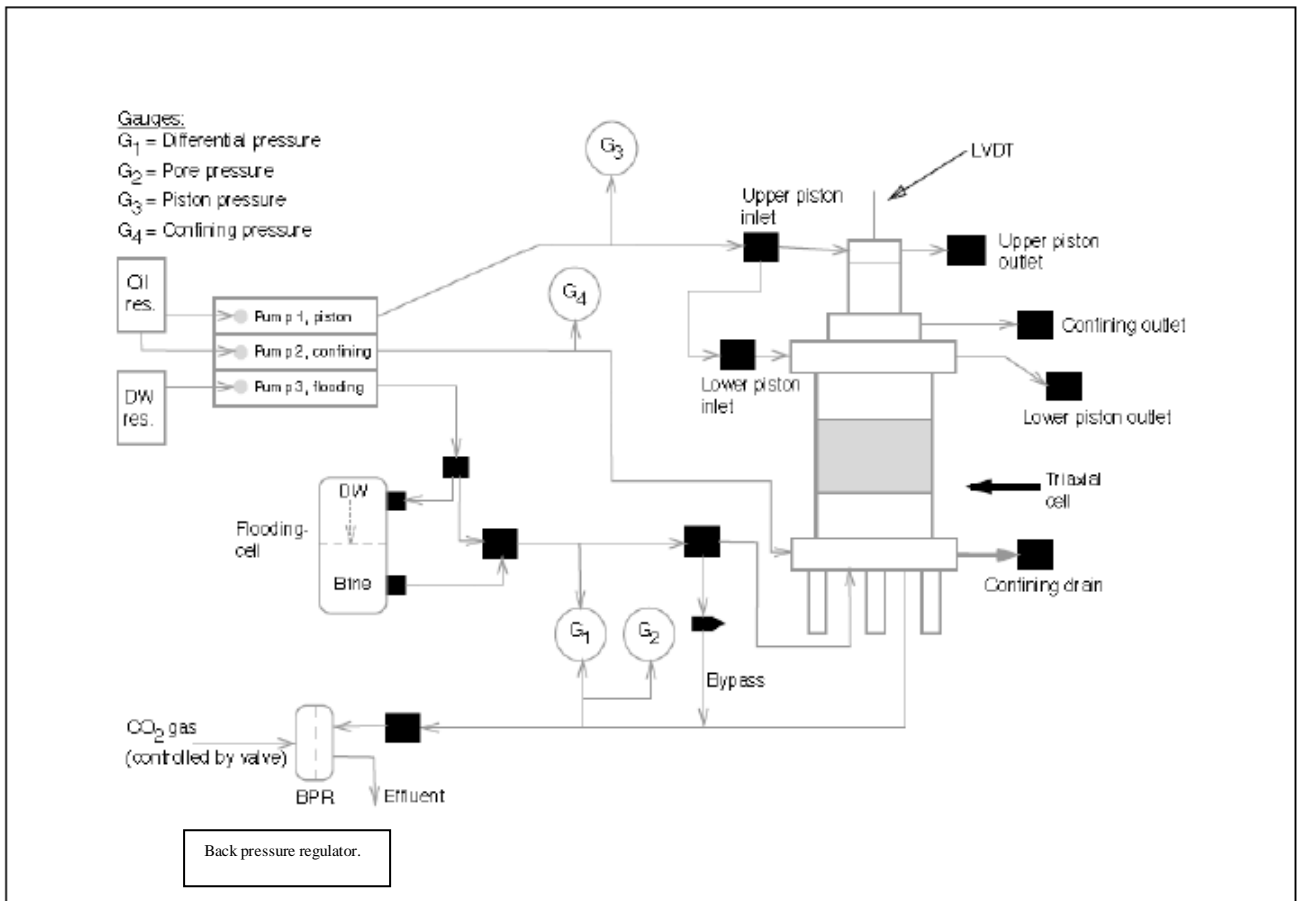


Figure 30: Sketch of the experimental Triaxial Setup (Kjørsløvik and Østensen, 2014).

3.3.3 Dionex IC S-5000+ Ion Chromatography System

The chemical analysis of all the samples taken during all the wettability tests carried out were performed using the Dionex IC-5000+ Ion Chromatography System. See **Figure 31**. The ion chromatography process allows the separation and quantification of ions concentration based on their affinity to the ion exchanger.



Figure 31: Dionex IC S-5000+ Ion Chromatography System.

3.3.3.1 Deionized Water Requirements for IC

In particular, to ensure the good performance of the chromatographer, the deionized water used for eluent generation or when manually preparing eluent and regenerant has to meet the specifications listed in **Table 9**.

Table 9: Deionized water requirements for IC.

CONTAMINANT	SPECIFICATION
Ions-Resistivity	> 18.0 (megohm-cm)
Organics-TOC	< 10 ppb
Pyrogens	< 0.03 (Eu/ml)
Particulates > 0.2 μ m	< 1 (units/ml)
Colloids-Silica	< 10 ppb
Bacteria	< 1 (cfu/ml)

A Milli-Q was used to filter the distilled water and to obtain deionized water with the specifications required. See **Figure 32**.



Figure 32: Left: Deionized specifications obtained using Milli-Q. Right: Milli-Q filter.

3.4 Experimental Procedures Applied in Triaxial Cells

The main core flooding setup used to carry out the dissertation was the Triaxial Cell. During all the tests performed during the investigation, the main stages performed in the triaxial cells can be summarized as follows:

3.4.1 Mounting the Core.

1. Before starting to mount the core, make sure that all the lines are completely filled and without air present in the system. Also, all the flooding brines except distilled water, must be contained inside of steel cylinders. The presence of air in the system can affect the performance of the setup.
2. Flood the initial brine until the inlet of the core. This is achieved when a constant flow is observed in the top of the steel core located in the base of the triaxial cell.
3. Grease is used to facilitate the sealing of the core to be mounted. Therefore, the grease is applied in the two O rings, the two small rubber seals, the steel core base and steel spiral placed in the top of the core.
4. Place one of the O ring and one of the rubber seal on the steel base core. Afterwards, add a filter paper with a diameter equal to 38.1 mm in the top of the steel base core and later a drainage plate with the same diameter on top of the filter paper.
5. Place the saturated core (either a water wet or a mixed wet) on the top of the drainage plate. The drainage plate is used to ensure the uniformity in the fluid distribution through the cross-sectional area of the core. Make sure the rubber is sealing the inlet of the core.
6. Add the second rubber on the outlet of the core. Later, place the second drainage plate and the second filter paper on the top of the core.
7. Add the shrinking sleeve; the shrinking sleeve must be long enough that allows to cover from the steel base core to the spiral.
8. Place the spiral on the top of the core. Double check the shrinking sleeve has an appropriate length. Connect the spiral to outlet line. See **Figure 33**.

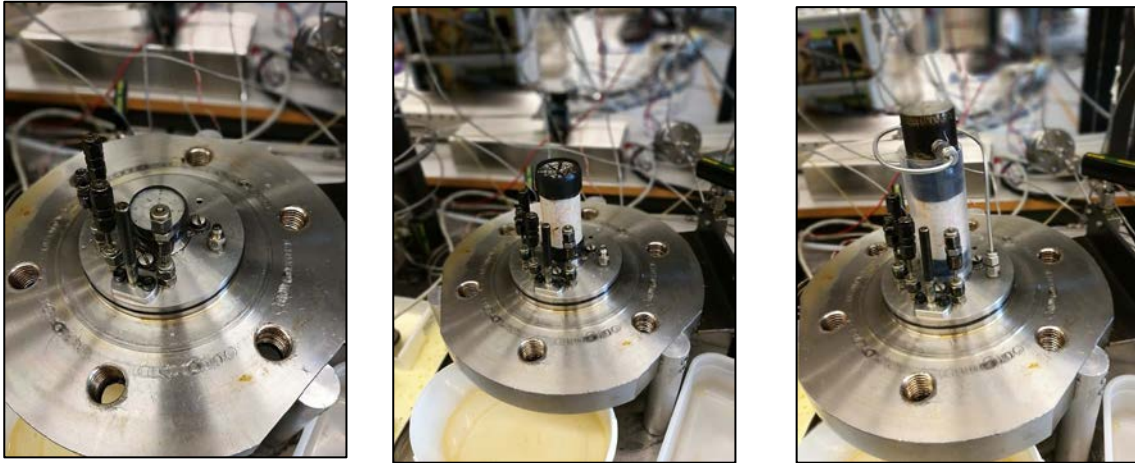


Figure 33: Left: Steel base core containing the first O ring, rubber seal, drainage plate and filter paper. Middle: Core mounted containing the previous elements in the inlet and outlet. Right: Core with the shirking sleeve and spiral on the top.

9. Using a heating gun to melt the shrinking sleeve to the core. The melted shrinking sleeve must cover the core, the two O rings, the two small rubber seals, the steel base core and the spiral. This is achieved by pressing the spiral on the top of the core and at the same time using the heating gun to melt the shrinking sleeve. Start from the bottom and slowly move to the top. Ensure there is minimum or no air at all left between the shrinking sleeve and the core.
10. Place the steel jacket that makes up the confining chamber of the setup. Use force to press down the steel jacket to the base of the triaxial cell.
11. Add confining oil to the confining chamber. Make sure the drainage valve is completely closed.
12. Place the top triaxial cell (Upper and lower chamber). Excess of confining oil will be removed, ensuring the chamber is air freed.
13. Add the heating jacket to steel jacket. This heating jacket allows to increase temperature in the setup. Align the heating jacket with the six bolts entries of the triaxial.
14. Place the six bolts and tight them. Use a torque wrench gun to accelerate the process. See **Figure 34**.
15. Usually, during mechanical tests, a LVDT is placed on the top of triaxial cell to measure the deformation in the axial direction. However, no deformation was expected under the operational conditions which the wettability tests were carried out.

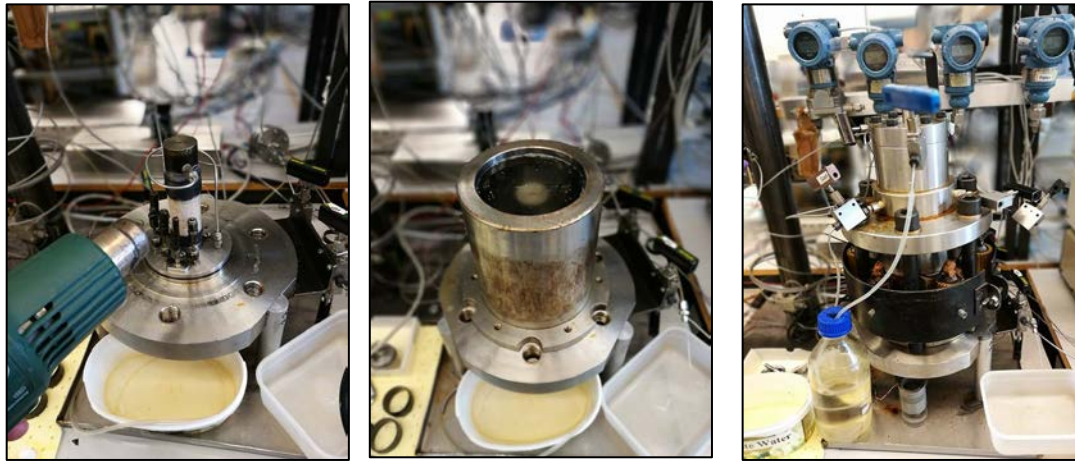


Figure 34: Left: Heating gun melting the shrinking sleeve to the core. Middle: Confining oil inside of the confining chamber. Right: Final setup, showing the heating jacket, bolts and the triaxial cell.

3.4.2 Increasing Confining Pressure

1. Open confining valve. Start pumping confining oil to the confining chamber. Use a high flow rate to remove the air from the confining chamber. This is achieved when confining oil start dripping from the confining valve outlet. Bypass must be closed
2. Set the flow rate at 2 ml/min. Close the confining valve.
3. Now, the confining pressure slowly increases. Set the pressure limit at 5 [Bars]. Once the maximum pressure is reached. The confining pump will automatically stop pumping. With bypass closed and without any flow through the core, wait until the differential pressure reaches a plateau indicating a constant value of the same.

3.4.3 Increasing Pore Pressure

1. With differential pressure constant and confining pressure set at 5 [Bars], pore pressure is now ready to be increased.
2. Set the back-pressure regulator at 7 [Bars]. Open bypass. This allows a faster increase of the pore pressure in the core.
3. Start pumping brine through the bypass. Pore pressure and confining pressure are increased simultaneously. Pores pressure until 7 [Bars] and confining pressure until 12 [Bars]. control both flow rate in such a way that there is 5 [Bars] of difference between confining and pore pressure at any moment. Confining pressure must always be higher than pore pressure to avoid confining oil leaking into the core.
4. Once the confining pressure reached to 12 [Bars] and pore pressure to [7 Bars], confining pressure is one more time increases until 15 [Bars]. The wettability tests carried out in the

triaxial cells were performed at 7 [Bars] pore pressure and 15 [Bars] confining pressure. Confining Pump rate is set to 0.5 ml/min to control small changes in confining pressure through the development of the test.

With the operational conditions now achieved, the flood of brines through the core can now be performed. This will be explained later.

3.4.4 Increasing Temperature

The flood of Magnesium Chloride and Sodium Chloride were performed at 130°C. However, before increasing the temperature, the core was saturated with this brine by flooding 4 PV through the core. Puntervold et al. (2007) recommended to flood 4 PV of distilled water through the core to clean it. The same principle was applied while saturating the core. The increasing temperature was performed in the following way:

1. After flood 4 PV of the brine through the core. Decrease the flow rate to 1 PV/day.
2. Connect the heating jacket to the controller box. Set the PID values and temperature desired.
3. Once the whole setup is being heated up, the confining pressure will increase due to expansion of steel and confining. Therefore, a device is required to control the changes in confining pressure.
4. Set the confining pump rate to 0 ml/min to avoid the pump of cold oil into the chamber. Connect the spring to the confining valve. See **Figure 35**.
5. With the spring connected and completely closed to the confined valve, open fully the confining valve. Regulate the increase of confining pressure with the spring. Try to keep the confining pressure between 15 and 16 [Bars].
6. Once the temperature reaches 130°C, close the confining valve, remove the spring and connect the confining outlet line.
7. Set the confining pump rate at 0.5 ml/min.

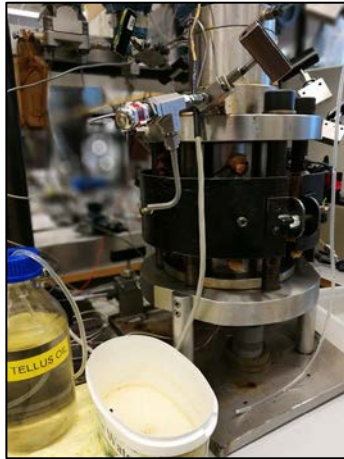


Figure 35: Spring connected to the confining valve while increasing temperature in the triaxial cell.

3.4.5 Decreasing Temperature

All the wettability tests were carried out at room temperature. Therefore, after the flooding either magnesium Chloride or Sodium Chloride at 130°C, the temperature was decreased till room temperature to perform the wettability test. And later on, the temperature was increased to continue the flooding of the reactive or non-reactive brine.

Decreasing temperature is a rather simple process. The principle resides in the compensation of the oil which was removed from the confining chamber while increasing temperature. Once the decreasing temperature process starts, the steel and the confining oil will contract leading to the confining pressure to decrease. Therefore, the confining oil pump rate is set at 2 ml/min, allowing to keep the confining pressure at values around 15 [Bars].

3.4.6 Dismantling the Triaxial Cell.

Before dismantling the triaxial setup, the cores are usually cleaned by flooding at least 6 PV of distilled water. The cleaning of the core at the end of test allow to reuse the core one or several times more afterwards. Mixed wet cores also were flooded with distilled water; however other solvents are required to clean this kind of cores properly. After cleaning the core, in order to extract the core from the triaxial cell, the following procedure was implemented:

1. Stop the pumps. Decrease the pore pressure by setting the back-pressure regulator back to 0 [Bars]. Wait until pore pressure reaches 0 [Bars] by monitoring the pore pressure gauge.
2. Open Drainage Valve. Open confining valve. Monitor the confining pressure gauge until it

reaches 0 [Bars].

3. Connect the air entry to confining valve. Slightly open the air valve, allowing the air inside of the confining chamber. A raise in the confining pressure is expected in the confining pressure gauge until the confining oil is completely flushed out of the confining chamber.
4. Close the air valve and remove it from the confining valve.
5. Remove the six bolts. Dismantle the triaxial cell.
6. Extract the core out from the shrinking sleeve. Help yourself with a cutter. Save the core.

The wettability index evolution through time while flooding a reactive brine was entirely carried out in triaxial cells. However, some tests, one mixed wet core and three water wet cores test were carried out using Hassler's cell core flooding setup. This setup has been well documented in other investigations and will not be explained here.

Small variations in the triaxial cell setup were used. For instance, during some tests, instead of sealing the core with a shrinking sleeve, a long rubber sleeve was used. It is worth mentioning that the shrinking sleeve is used and recommended during the geomechanics tests performed in this sort of cell.

3.5 Tests Carried Out in Triaxial Cells

In general, the series of tests carried out using triaxial cells can be summarized in two big groups:

- I. **Water Wet Cores:** to establish the water wet reference area for the chromatographic wettability test. Also, a water wet core was used to evaluate the potential of MgCl_2 to modify the specific surface area.
- II. **Mixed Wet Cores:** To address the potential of MgCl_2 to modify the wetting state.

3.5.1 Water Wet Cores: Establishing the water wet reference area.

1. Saturate the core with SW-0T.
2. Install the saturated core into the triaxial. Establish 15 [Bars] confining pressure and 7 [Bars] pore pressure.
3. Connect the fractional sampler containing a maximum of 44 sampling glasses to the outlet.

The glasses were weighted before testing.

4. Flood 4 PV of SW-0T through the core. Increase the flow rate to 0.2 ml/min. Monitor the differential pressure until it becomes constant.
5. Once the differential pressure is relatively constant, switch from SW-0T to SW-1T. Monitor the differential pressure one more time until is constant again.
6. Remove all the caps and seal from the sampling glasses. Set up the sampling program using the Trilution Software. Establish the sampling time and wasting time. All the tests performed in triaxial cell were carried out using a flow rate of 0.2 ml/min. The sampling time was established at 10 minutes and the wasting time was initially established at 10 minutes in the beginning of the project but was later optimized until 2.5 minutes. The sampling process of 44 glasses, sampling for 10 minutes and wasting for 2.5 minutes takes around 9.2 hours. Perform the sampling process.
7. Gradually put back the caps of the glasses once the sampling process is performing to avoid evaporation in the samples taken.
8. Once the sampling process finishes, switch brines from SW-1T to distilled water. Start the cleaning of the core. Weight the 44 glasses containing the samples taken. Check the flow rate based on the weight difference of the empty glasses and the glasses with samples. Assume a density close or slightly higher than 1.
9. Switch from SW-1T to distilled water. After flooding 6 PV of distilled water. Dismantle the triaxial cell and extract the core.

3.5.2 Water Wet Cores: Addressing changes in specific surface area (Core K4).

1. Saturate the core with DW.
2. Install the saturated core into the triaxial. Establish 15 [Bars] confining pressure and 7 [Bars] pore pressure.
3. Connect the fractional sampler containing a maximum of 44 sampling glasses to the outlet.
4. Flood 4 PV of SW-0T through the core. Increase the flow rate to 0.2 ml/min. Monitor the differential pressure until it becomes constant. Once the differential pressure is relatively constant, switch from SW-0T to SW-1T. Monitor the differential pressure one more time until is constant again.
5. Perform the sampling process (**Initial** Wettability Test). Flood 6 PV of distilled water. Set the flow rate to 1 PV/day.
6. Increase the temperature till 130°C.

7. Flood distilled water at 130°C for 2 days.
8. Decrease temperature till room temperature.
9. Switch from distilled water to SW-0T. Flood at least 4 PV of SW-0T. Switch from SW-0T to SW-1T.
10. Perform the sampling process (**Second** Wettability test). Saturate the core with NaCl (0.657 M) by flooding at least 4 PV. Set the flow rate to 1 PV/day.
11. Increase the temperature till 130°C.
12. Flood Sodium Chloride for 7 days at high temperature. Take samples every other day.
13. Decrease temperature till room temperature.
14. Switch from NaCl to SW-0T. Flood at least 4 PV of SW-0T. Switch from SW-0T to SW-1T.
15. Perform the sampling process (**Third** Wettability test). Saturate the core with MgCl₂ (0.219 M) by flooding at least 4 PV. Set the flow rate to 1 PV/day.
16. Increase the temperature till 130°C.
17. Flood Magnesium Chloride for 7 days at high temperature. Takes samples every other day.
18. Decrease temperature till room temperature.
19. Switch from MgCl₂ to SW-0T. Flood at least 4 PV of SW-0T. Switch from SW-0T to SW-1T.
20. Perform the sampling process (**Fourth** Wettability test). Saturate the core with MgCl₂.
21. Flood Magnesium Chloride for another 7 days at high temperature. Takes samples every other day.
22. Decrease temperature till room temperature.
23. Switch from MgCl₂ to SW-0T. Flood at least 4 PV of SW-0T. Switch from SW-0T to SW-1T.
10. Perform the sampling process (**Fifth** Wettability test). Switch from SW-1T to distilled water. After flooding 6 PV of distilled water. Dismantle the triaxial cell and extract the core. Preserve the core for further testing.

3.5.3 Mixed Wet Cores: Modifying the wetting state

1. Remove the mixed wet core out from the aging cell.
2. Install the mixed wet into the triaxial. Establish 15 [Bars] confining pressure and 7 [Bars] pore pressure.
3. Connect the outlet to a burette.
4. Flood at least 4PV of SW-0T at 0.2 ml/min) through the core. to establish residual oil saturation (S_{or}).
5. Measure the volume of oil produced collected in the burette.

6. Switch from SW-0T to SW-1T. Perform the sampling process (**Initial** Wettability Test). Switch from SW-1T to MgCl₂. Flood at least 4 PV. Set the flow rate at 1 PV/day.
7. Increase the temperature till 130°C.
8. Flood MgCl₂ at 130°C for 10 days. Takes samples every other day.
9. Decrease temperature till room temperature.
10. Switch from MgCl₂ to SW-0T. Flood at least 4 PV of SW-0T. Switch from SW-0T to SW-1T.
11. Perform the sampling process (**Second** Wettability test). Saturate the core with MgCl₂ (0.219 M) by flooding at least 4 PV. Set the flow rate to 1 PV/day.
12. Increase the temperature till 130°C. Repeat 8, 9, 10 and 11.
13. After performing the last wettability test, switch from SW-1T to distilled water. Flood at least 6 PV of distilled water through the core.
14. Dismantle the triaxial cell and extract the core. Place the mixed wet core after testing inside of a cylindrical container full of distilled water. Preserve the core for further testing.

3.6 IC Analysis and Further Testing

3.6.1 IC Analysis

The samples taken during the wettability tests performed in triaxial cell setup or hassler's cell setup were analysed using the Ion Chromatography analysis. Also, the samples taken every other day during the flooding of the brines at high temperature were also analysed using IC analysis.

However, to perform the IC analysis, the samples must firstly go through a dilution process. The dilution of the process is required to ensure that Dionex IC S-5000+ Ion Chromatography System be able to successfully detect the peaks of each ion. If the samples are not diluted, the ions peaks obtained using the chromatographer would take the maximum value, not allowing to properly quantify the concentration of each of them

The dilution of the samples was performed using the Gilson GX-271 liquid handler controlled by the Trilution software. The samples were diluted 500 times (See **Figure 36**). Once, the samples are diluted, the samples are now ready to be prepared for the IC chromatographer. To prepare the samples for the IC chromatographer, the following methodology was applied:

1. Take a 5-ml syringe. Extract around 2 ml of deionized water. Saturate the syringe with deionized water. Expelled the deionized water out from the syringe.

2. Take the diluted sample and shake it with a seal cap in top. Extract around 1 ml of the diluted sample. Remove the diluted sample out from the syringe. Extract the rest of the diluted sample.
3. Connect a syringe filter to the syringe. Saturate the filter with the diluted sample by expelling the sample through the filter until 1.5 ml are left in the syringe.
4. Pour the remaining 1.5 ml into the IC glass.
5. Repeat 1, 2, 3, and 4 for the rest of the diluted samples. See **Figure 37**.



Figure 36: Left: Liquid handler diluting the sample. Right: Trilution software showing the program used for dilution: The lines were cleaned twice and the samples were diluted 500 times.



Figure 37: Left: Elements used to prepare the sample for the IC. Middle: Syringe chromatographer filter. Right: IC samples prepared.

Afterwards, when the samples are prepared. The trays containing the IC glasses are placed inside of the Dionex IC S-5000+ Ion Chromatography System. While preparing the samples, the original brines are also prepared in order to have reference values when analysing the peaks obtained in the

chromatographer. For instance, while analysing the wettability test samples, it is necessary to prepare the brines SW-0T and SW-1T. While analysing the samples taken in the effluent every other day, we need to prepare the original brines NaCl (0.657 M), MgCl₂ (0.219 M), Synthetic Seawater and Magnesium-calcium chloride MgCaCl₂ standard, where concentrations of ions in the standard are 0.219 mol/l Mg²⁺ and 0.013 mol/l Ca²⁺. See **Figure 38**.

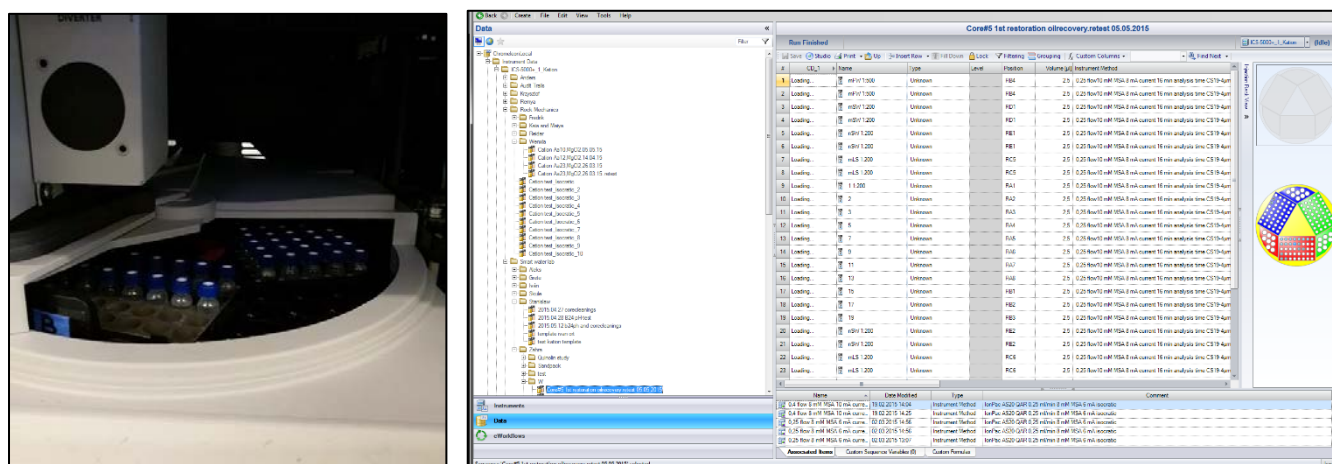


Figure 38: Left: IC trays inside of Ion Chromatographer. Right: IC characteristic program.

The Dionex IC S-5000+ Ion Chromatography System is controlled through a software (See **Figure 38**). Software used to analyse cation and anions differs and is depending on which ions have been targeted. For example, while analysing the samples taken during the chromatographic test the following programs were used:

1. **Cations:** 0.25 flow 6.5mM MSA 5 mA current 20 min CS19-4µm 2mm Cations - Isocratic - New cleaning procedure -Loop overflow 10X
2. **Anions:** 0.25 flow 20 mM KOH 13 mA current, 20 min, Isocratic Anion_washing before and after -New cleaning procedure - Loop overflow 10X

Anions program must be 20 minutes because of the presence of thiocyanide. Thiocyanide in optimal operational conditions is detected in the range of 16 minutes.

However, while analysing the effluent samples and thiocyanide is not present, anion program is modified to save up some time while the cation program remains identical.

1. **Anion:** 0.25 flow 20 mM KOH 13 mA current, 12 min, Isocratic Anion_washing before and after -New cleaning procedure - Loop overflow 10X

Once the chromatography analysis is finished (See **Figure 39**). A series of peaks are obtained. The peaks are proportionally related to the concentration of ions presented in the samples. To establish this relation, the peaks of the standards are used along with the original concentration of each ion present in the brine. For instance, the original concentration of Thiocyanide and sulphate is SW-1T are both 0.024 mol/l. The peaks are adjusted for every sample and subsequently manipulated in Microsoft Excel Spreadsheets to obtain characteristics plots like in **Figure 4**.

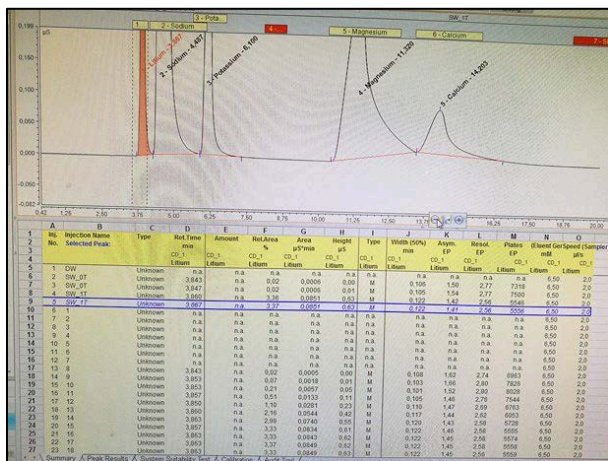


Figure 39: Peak Responses in the IC chromatography analysis outcome.

3.6.2 Specific Surface Area Measurements



Figure 40: Micrometrics TriStar II: Surface Area and Porosity.

Specific surface area measurements were carried out based on BET theory. The Micrometrics Tristar II instrument for specific surface area and porosity measurements was used. See **Figure 40**. The following methodology was used to estimate the specific surface area:

1. The sample must be completely dried. Once, the sample is dried, break it and smash it. Reduce it to small pieces and powder. See **Figure 41**.
2. Weigh the sample tube. Record this value as empty tube weight. Add around 2 grams of samples into the tube. Record this weight as the weight of the sample tube filled with the sample rock. Repeat this step for the other 2 samples. The TriStar II can measure up to 3 samples per test. Always use gloves during the entire process. See **Figure 41**.
3. Connect the sample tubes to the vacuum (Degasser) and be sure the O-ring reaches the neck of the sample tube. Set the temperature of the degasser at 60°C. open the vacuum valve very slowly to prevent suction of sample to the filters. See **Figure 42**.
4. Degas the samples for 5 hours or when vacuum pressure reach stability around 20-30 mTorr. In the meantime, prepare the program controlling the TriStar II.
5. When the degas process is finished, easily open the gas valve to release the vacuum and slightly pressurize the sample.
6. Weight the sample again. Input the new slightly less weight into the program altogether with the previous empty weight recorded.
7. Cover the sample tube with white isothermal jacket and put a clean and dry filler into the sample tube to decrease the free space and speed up the analysis time. See **Figure 42**.
8. Connect each sample tube to the instrument, maximum 3 samples at a time. See **Figure 42**.
9. Fill the liquid N₂ container to specified height. Use special gloves and eyes protection. Place the liquid N₂ cell below the sample tubes. See **Figure 42**.
10. Start analysis. The results will be displayed after 9 hours.

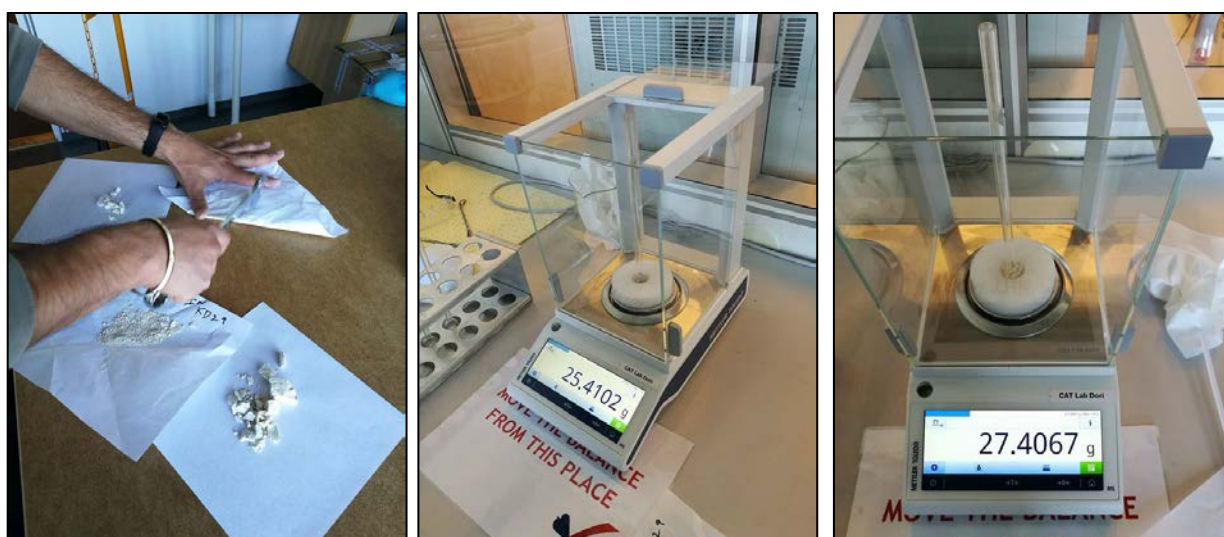


Figure 41: Left: Smashed sample. Middle: Empty weight of the sample tube. Right Weight of the sample tube containing smashed sample.



Figure 42: Left: Degasser set at 60°C containing the three sample tubes. Middle: Instrument with the liquid N₂ container in the bottom. Right: Samples attached to the instrument.

3.6.3 Chalk Mineral Density Measurements



Figure 43: AccuPyc II 1340 Gas Pycnometer.

AccuPyc II 1340 Gas Pycnometer was used to measure the volume of chalk core. See **Figure 43**. A water wet core previously flooded with NaCl and MgCl₂ was used. The inlet of the core was previously cut. Therefore, two volumes were measured. One from the inlet and the other from the rest of the core. The inlet and the rest of the core were previously weighted. With the volumes obtained, the averaged densities were estimated. This gas pycnometer uses helium as a gas reference to estimate volume. The instrument's principle resides in the relation between pressure and volume. Two known volumes chambers were used depending on the size of the sample to be measure. The two chambers used were 35 and 100 cm³.

CHAPTER 4

EXPERIMENTAL RESULTS AND COMMENTS

The main experimental results obtained in different tests carried out on water wet and mixed wet Kansas chalk cores are presented in this chapter.

4.1 Water Wet Cores: Establishing Water Wet Reference Area

To quantify the wetting state using the Chromatographic wettability test, the first step is to establish the water wet reference area of outcrop Kansas chalk. Several experiments were carried out to achieve this goal. The water wet cores properties used to establish the water wet reference area can be found in **Table 7**. This wettability test has been widely covered using the Hassler's Cell core flooding setup: thus, some tests were carried out in this setup to help us to compare and understand the results obtained in the main setup: Triaxial Cell. The main differences between both setups are appreciated in **Table 10**.

Table 10: Main differences between Hassler's Cell and Triaxial Cell core flooding setups.

SETUP	SEALING MATERIAL	FLOODING DIRECTION THROUGH THE CORE	CONFINING PRESSURE [BARS]	FLOODING RATE [ML/MIN]
Hassler's Cell	Rubber Sleeve	Horizontal	20	0.1
Triaxial Cell	Shrinking Sleeve	Vertical (against Gravity)	15	0.2

The average percent deviation among areas data were calculated to measure the dispersion between the areas obtained and the average between them. The following correlation was used:

$$\text{Deviation} = \frac{\sum_{i=1}^n (x_i - \frac{\sum_{i=1}^n x_i}{n})}{\sum_{i=1}^n \frac{x_i}{n}} * 100 \quad \text{Eq. 8.}$$

where n is the total number of data analysed and x_i is each area obtained in the tests.

4.1.1 Hassler's Cell: Reproducibility in different cores

The chromatographic separation between thiocyanide and sulphate can be appreciated in **Figure 44**. Notice the characteristic S shape (1 Jump) in the curves. The breakthrough of both thiocyanide and sulphate is achieved after 1 PV of flooding SW-1T. Around 1.5 PV all three thiocyanide curves have reached more than 95% of the original concentration. All three water wet cores tested in the Hassler cell were flooded with the wettability test brines at 0.1 ml/min. Cores K5 and K6 exhibit good reproducibility obtaining respective area of 0.220 and 0.227 which represent an average deviation less than 2% between them. However, core K1 shows a lower area with a value of 0.184, which represent a deviation of 8.9% and 10.5% to cores K5 and K6 respectively. The average deviation in areas obtained from the three core is 8.4%.

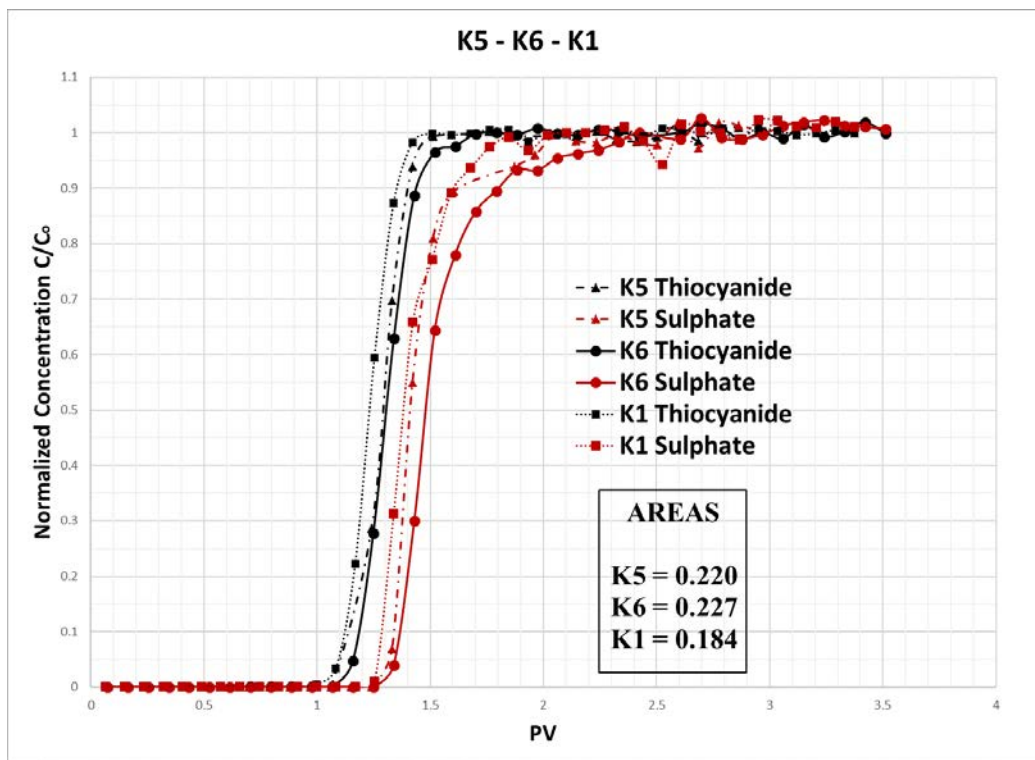


Figure 44: Chromatographic wettability test on three (K1, K5 and K6) completely water wet Kansas chalk cores.

4.1.2 Hassler's Cell: Flow Rate Effect

All the chromatographic tests performed on triaxial cell were carried at 0.2 ml/min flow rate, on the other hand, most of the tests carried out in the Hassler's Cell were performed at 0.1 ml/min. Thus, it was of particular interest to evaluate the effect of the flooding rate in the area obtained during the chromatographic test. Core K1 was placed in the Hassler's Cell and was tested at two different flow rates: 0.1 and 0.2 ml/min. The results obtained are exhibited in **Figure 45**. Both areas are extremely

close. Areas of 0.184 and 0.185 were obtained at 0.1 and 0.2 ml/min flow rate respectively. Notice again that the breakthrough of thiocyanide is achieved after 1 PV and 100% of the original concentration is obtained by 1.5 PV. Thus, these early results suggest that there are no significant differences between areas obtained in water wet cores flooding at 0.1 or 0.2 ml/min. The average deviation between these two areas is less than 0.5%.

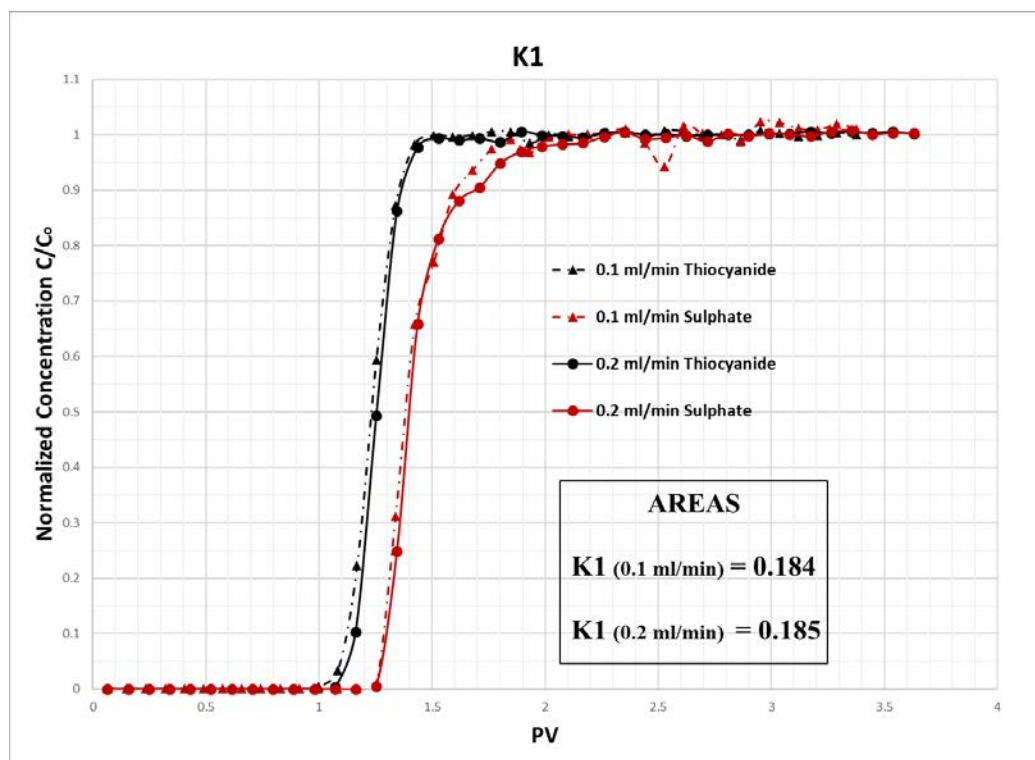


Figure 45: Chromatographic wettability test performed on water wet core K1 at different flow rate in the Hassler's Cell.

4.1.3 Triaxial Cell: Flow Rate Effect

Having established the minimum effect of flow rates 0.1 ml/min and 0.2 ml/min on the results in the Hassler's cell core holder. It was decided to perform the chromatographic tests on triaxial cells using a flow rate of 0.2 ml/min to save up time. However, in the early beginning of the experimental work, the core K1 was mistakenly flooded with a rate higher than 0.2 ml/min. It was flooded at 0.4 ml/min. The results are presented on **Figure 46**. The area obtained with a higher flow rate is lower with a value of 0.151 while the area obtained with a 0.2 ml/min flow rate was 0.220. The deviation of the results is around 18.5%. There are some remarkable differences that can be noted in this plot while comparing with the Hassler's Cell results. Firstly, the early breakthrough of both thiocyanide and sulphate before 0.5 PV; the earliest breakthrough is achieved at the highest flow rate. However, what is really interesting the characteristic shape is completely different to shape obtained in tests

performed using the Hassler's Cell setup. 2 jumps were observed instead of 1. Further experiments were carried out using triaxial cells to understand the differences in the plots obtained in both setups.

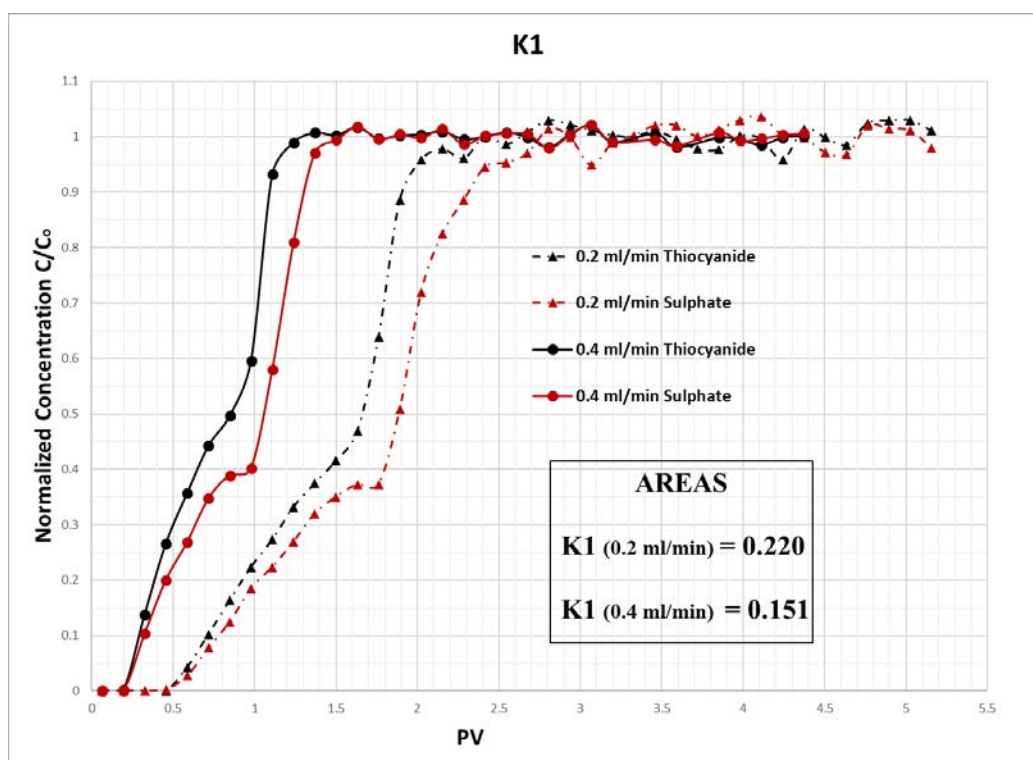


Figure 46: Chromatographic wettability tests performed on water wet core K1 at different flow rate in the Triaxial Cell.

4.1.4 Triaxial Cell: Reproducibility in the same Core

Trying to establish the reproducibility of the chromatographic wettability test on Kansas core, core K2 was tested twice under the same condition. See **Figure 47**. The sealing material surrounding the core was shrinking sleeve. The same shape, 2 jumps, was obtained. Notice the breakthrough of both ions in both tests occurring between 0.5 and 1 PV. Areas obtained were 0.220 in the initial test and 0.200 in the retests. The deviation between these values is around 4.7%.

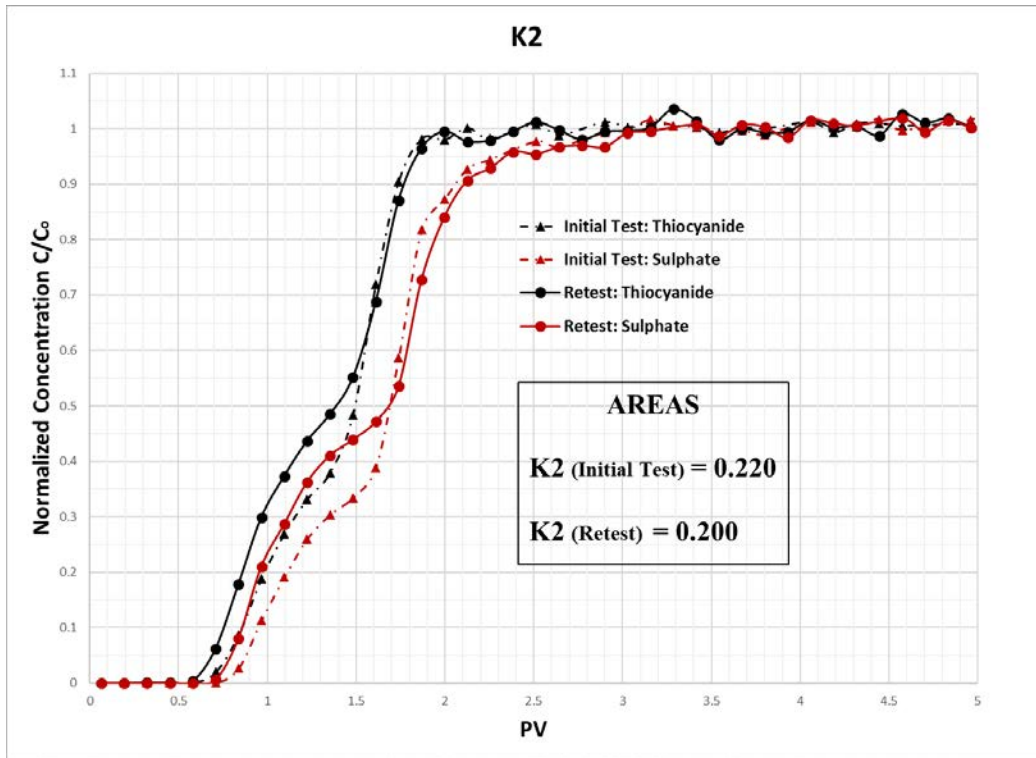


Figure 47: Chromatographic wettability tests performed on water wet core K2 in the Triaxial Cell.

4.1.5 Triaxial Cell: Reproducibility in different cores

After establishing that the same core can provide two different areas after being tested with a deviation less than 5%. Further tests were carried out to establish the average water wet reference area. The results are shown in **Figure 48**. 5 experiments tested in 4 different cores provided areas varying between 0.220 (highest) and 0.200 (lowest). The average deviation among these data is around 1.9% which shows good reproducibility of the results. In general, the breakthrough for thiocyanide and sulphate are obtained between 0.5 PV and 1 PV. However, the normalized concentration of thiocyanide reaches a maximum value around 2 PV differing from Hassler's Cell which is achieved around 1.5 PV. Sulphate breakthrough of course occurs later than the thiocyanide one and reaches a maximum after 2.5 PV. But why is the reason of this behaviour? Why is there an early breakthrough? And why does it take more time to reach the original concentration? **Sections 4.1.6 and 4.1.7** give insights about possible answers to different behaviours.

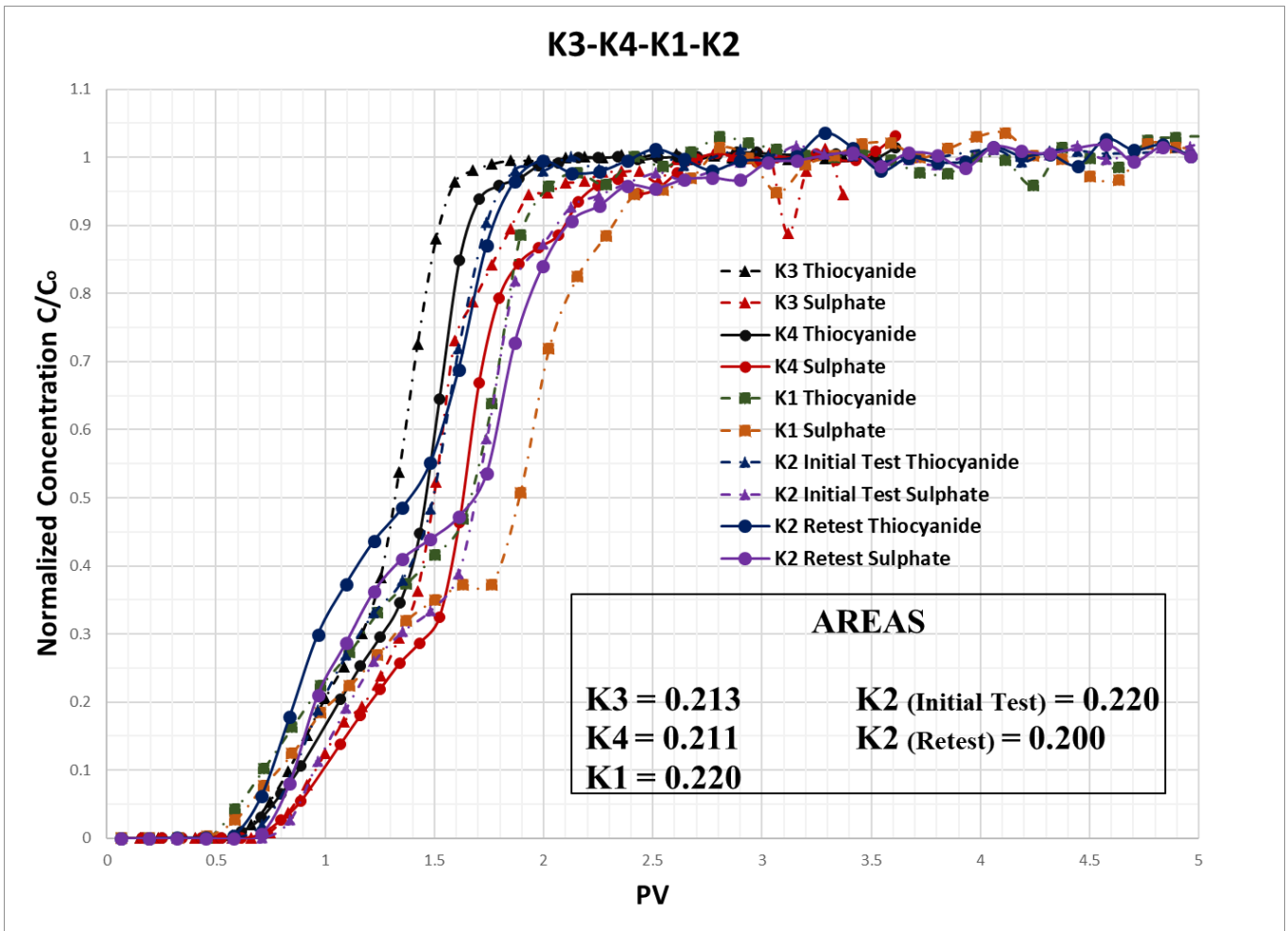


Figure 48: Chromatographic wettability test on four (K1, K2, K3 and K4) completely water wet Kansas chalk cores.

4.1.6 Triaxial Cell: Effect of the sealing material

In **Figure 49**, results of three tests performed on the same core are displayed. Notice the characteristics 2 jumps shape obtained while using the shrinking sleeve as a sealing material. Areas obtained using the shrinking sleeve are 0.220 for the initial test and 0.200 for the retest. Early breakthrough is obtained for both cases in both ions between 0.5 PV and 1 PV. The original concentration is achieved after 2 PV, indicating that more than 1 PV is required to reach a normalized concentration of 100%. On the other hand, while using a rubber sleeve as a sealing material on the same core, the breakthrough of both ions is retarded and obtained in the range between 1 to 1.5 PV exactly in the same range that was obtained in the hassler’s cell setup. Thiocyanide reaches a normalized concentration of 1 by 1.5 PV (quality criteria proposed by Strand et al. (2006)). Sulphate ion reaches more than 95% of original concentration by 2 PV. These early results suggest that even though breakthrough is achieved later than while using shrinking sleeve,

reaching a normalized concentration of 100% takes less than 1 PV. The shape of 1 jump indicates a rapid increase of concentration after breakthrough. The deviation among the three areas obtained in the same core is less than 4.5%. The results suggest that changes in the sealing material dictate the behaviour and performance of the chromatographic wettability test. The rubber sleeve has been widely used in core flooding experiments due to its excellent sealing properties to the cores, ensuring the flow perpendicular to the cross-sectional area. However, rubber sleeve cannot be used while performing geomechanics tests due to its thickness which will affect measurements of the radial deformation using an extensometer. The early breakthrough in shrinking sleeve tests is associated to inefficient sealing properties of the shrinking sleeve, allowing the flow not just to the cross-sectional area but also through the lateral walls of the core, area located between the core and the melted shrinking sleeve. The shrinking sleeve is widely used in geomechanics tests, because beside of providing protection to the core from confining oil, the shrinking sleeve is much thinner and will thereby not affect radial measurements that much. Thus, how to use a shrinking sleeve and provide good sealing properties to the core?

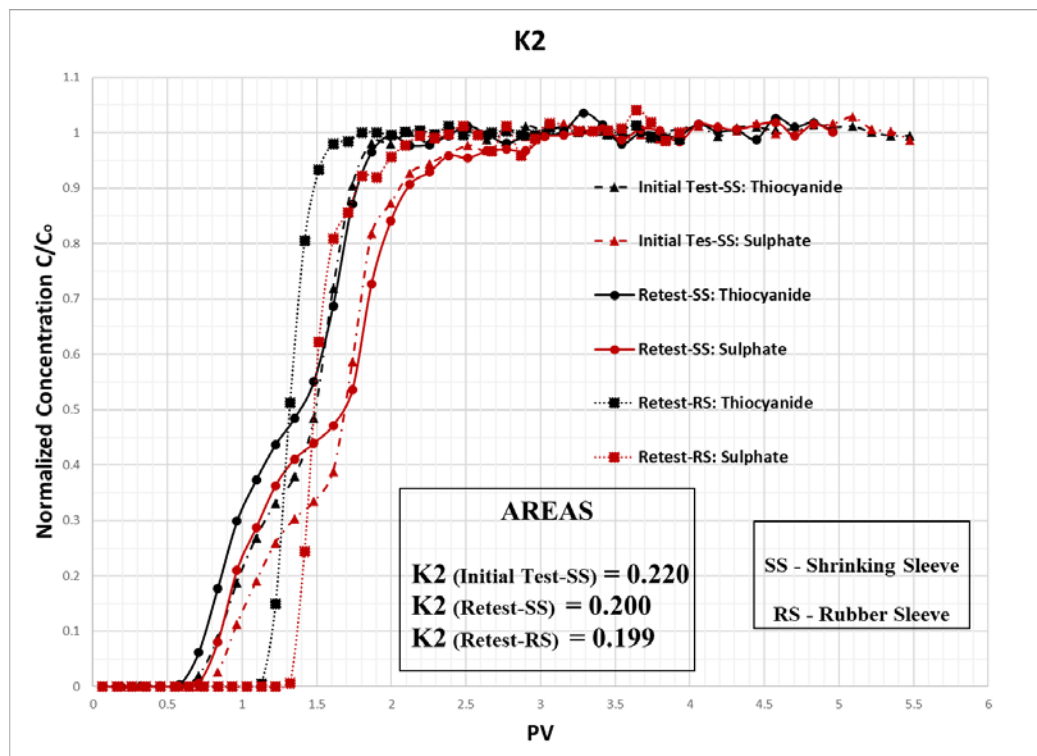


Figure 49: Chromatographic wettability tests performed on water wet core K2 in the Triaxial Cell. Effect of the sealing material: Shrinking Sleeve vs Rubber Sleeve.

4.1.7 Triaxial Cell: Effect of increasing temperature.

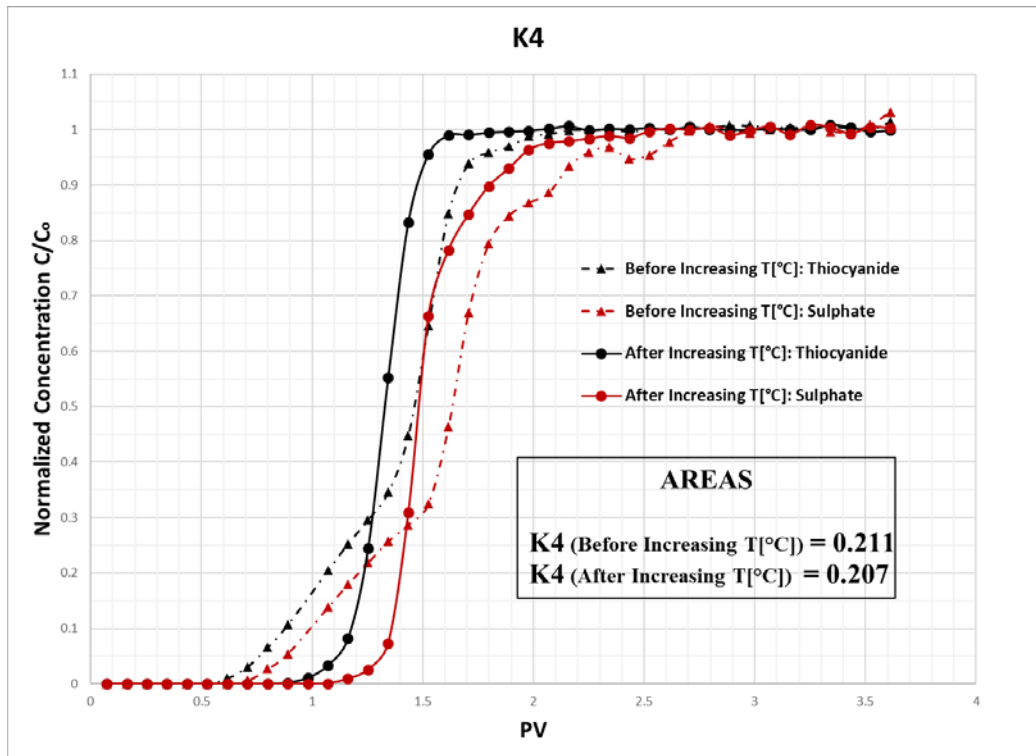


Figure 50: Chromatographic wettability tests performed on water wet core K4 in the Triaxial Cell. Effect of flooding distilled water for 2 days at 130[°C].

Water wet core K4 sealed by a shrinking sleeve, was initially tested providing an area of 0.211. The characteristic shape is noticed to have 2 jumps with early breakthrough and reaching 100% of original concentration after 2 PV for both ion. However, after flooding the core for 2 days with distilled water at 130°C, the shape of the curve drastically changed; reflecting similarities to the one obtained in hassler’s cell setup or in the triaxial cell setup using a rubber sleeve. The area obtained was 0.207. However, the breakthrough of thiocyanide is still earlier than in the previous two configurations but later than the obtained while using shrinking sleeve without increasing temperature. The increase in temperature produces a positive effect, improving the sealing properties of the shrinking sleeve to the core. The increase of temperature till 130°C increases the adherence of the melted shrinking sleeve to core, minimizing the flood previously obtained in the lateral walls of the core and ensuring the flow of brine through the cross-sectional area. The deviation of two areas, before and after increasing temperature till 130 °C is less than 1% suggesting no changes by flooding distilled water at 130°C.

A brief summary of all the tested performed to establish the water wet reference area for the chromatographic wettability test are shown in **Table 1**.

Table 11: Summary of results obtained in water wet cores used to establish the water wet reference area.

CORE	SETUP	SEALING	SHAPE	AREA THIOCYANIDE - SULPHATE
K1 0.2 ml/min	Triaxial Cell	Shrinking Sleeve	2 Jumps	0.220
K1 0.4 ml/min				0.151
K2 Initial Test				0.220
K2 Retest				0.200
K2 Retest		Rubber Sleeve	1 Jump	0.199
K3		Shrinking Sleeve	2 Jumps	0.213
K4 Before Increasing T[°C]				0.211
K4 After Increasing T[°C]				0.207
K1 0.1 ml/min	Hassler Cell	Rubber Sleeve	1 Jump	0.184
K1 0.2 ml/min				0.185
K5				0.220
K6				0.227

The water wet reference area was calculated taking the arithmetic mean of all the areas obtained except the one obtained in core K2 at 0.4 ml/min (red labelled). Arithmetic mean is defined as follows:

$$\bar{X} = \frac{1}{n} \sum_{i=1}^n x_i \quad \text{Eq. 9.}$$

where n is the total number of data and x_i are the set of data.

The water wet average reference area obtained during this experimental work was **0.207**. It is worth noting that the area obtained in core K4 after flooding distilled water for two days at 130°C was also considered because the flood of distilled water did not produce any effect in the area obtained (deviation less than 1%).

4.2 Water Wet Cores: Addressing the effect of flooding non-reactive and reactive brines.

Core K4 (See **Figure 50**) after being flooded with distilled water for two days, was subsequently flooded with sodium chloride for one week and magnesium chloride for two weeks at 130°C; performing a wettability test every weekly flooding cycle. The target was to see the effect of flooding a non-reactive brine (NaCl) and a reactive brine (MgCl₂) through a water wet core. The effect was

evaluated focusing on changes in the water wet area obtained in chromatographic wettability test and density of the core tested after testing. The two early results obtained in this core were presented section 4.1.7 and Figure 50. In Figure 51, the effect of flooding NaCl and MgCl₂ at high temperature on the water wet area can be appreciated.

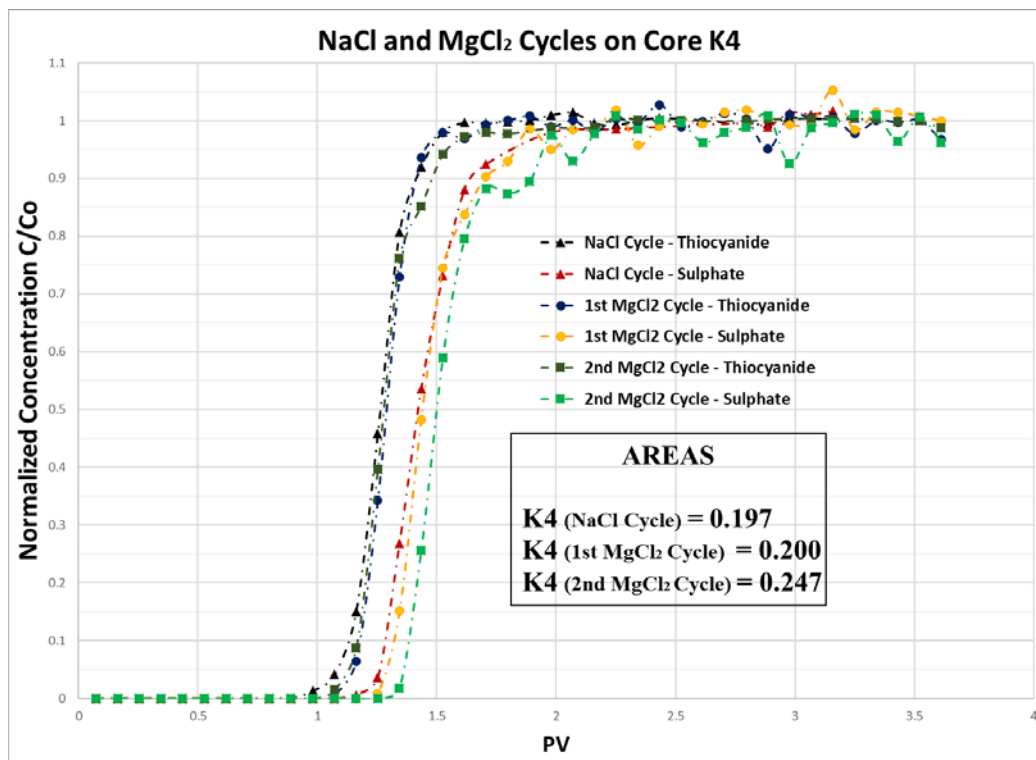


Figure 51: Chromatographic wettability tests performed on water wet core K4 in the Triaxial Cell. Effect of flooding NaCl over a week and MgCl₂ over 2 weeks at 130[°C].

A summary of all the results obtained of different tests performed on water wet core K4 ia shown in Table 12.

Table 12: Summary of results obtained in tests performed on water wet core K4.

CORE	SETUP	SEALING	SHAPE	AREA THIOCYANIDE - SULPHATE
K4 Before Increasing T[°C]	Triaxial Cell	Shrinking Sleeve	2 Jumps	0.211
K4 After Increasing T[°C]			1 Jump	0.207
K4 after NaCl Cycle				0.197
K4 After 1 st MgCl ₂ Cycle				0.200
K4 After 2 nd MgCl ₂ Cycle				0.247

The water wet area obtained after flooding NaCl was slightly reduced to 0.197. The deviation compared to area after flooding distilled water at high temperature is less than 0.8%. NaCl is a non-reactive brine toward the chalk surface, thus, no biggest changes are expected after flooding this

brine through a chalk core. After the first week of flooding $MgCl_2$, the area slightly increased to 0.200 compared to the one gotten after flooding $NaCl$. The deviation between these areas is less than 0.8%. However, $MgCl_2$ is a brine composed of reactive ion Mg^{2+} towards the chalk surface and inert ion Cl^- . A reaction between the core surface and the brine are expected. After flooding $MgCl_2$ for another week, the water wet area drastically increased to a value of 0.247, suggesting the possibility of an increment of the specific surface area due to precipitation of minerals rich in magnesium. Core K4 was further tested to evaluate the changes in mineral density. See **Figure 63** and **sections 5.2.2** and **5.2.3**.

4.3 Mixed Wet Cores: Initial Wetting State and Changes in Wettability Index.

Once established the water wet reference area, wetting states changes by aging while flooding magnesium chloride at $130^\circ C$ can now be evaluated. A total of 4 cores were tested. 1 core was initially tested in the Hassler's cell setup. However, this core was just tested for the initial wetting state. Furthermore, 3 cores were tested in triaxial cells, one of them using a rubber sleeve as a sealing material. The physical properties of all 4 cores are listed **Table 8**.

4.3.1 Hassler's Cell: Initial Wetting State

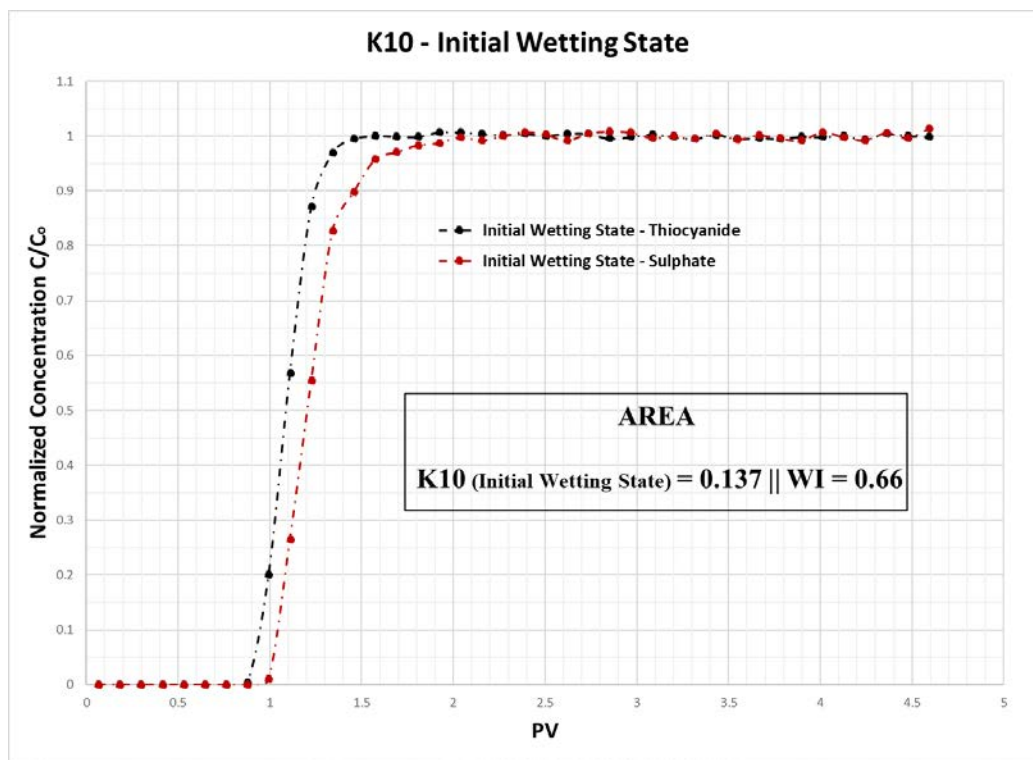


Figure 52: Chromatographic wettability test performed on mixed wet core K10 in the Hassler's Cell.

Core K10 was tested in the Hassler's cell. The chromatographic wettability test was performed using a flow rate of 0.1 ml/min. The wetting area was measured to be 0.137, corresponding to a wettability index of 0.66. See **Figure 52**. The volume of displaced oil by SW-0T obtained was measured. The residual oil saturation (S_{or}) after flooding was 36.79%, oil produced was measured to be 10.90 ml. The initial water saturation (S_{wi}) of core K10 was 27.07%.

4.3.2 Triaxial Cell: Initial Wetting State and Wetting Index Evolution

Three mixed wet cores were used to evaluate the potential of magnesium chloride ($MgCl_2$) to modify the wetting state of mixed wet outcrop Kansas chalk. One of them was tested using rubber sleeve as a sealing material and two of them using shrinking sleeve as a sealing material. All chromatographic wettability tests were carried out at 0.2 ml/min and the flood of magnesium chloride at high temperature was performed at 1 PV/day.

4.3.2.1 Triaxial Cell: Rubber Sleeve

Mixed wet core K9 was placed into a triaxial cell and sealed using a rubber sleeve. The initial water saturation of the core was 28.23%. The S_{or} after being flooded by SW-0T was measured to be 44.73% and oil produced was 8.50 ml. Nevertheless, this test failed during second magnesium chloride flooding cycle due to leakage of confining oil into the core; thus, the test had to be stopped and therefore the core removed. However, early results are very promising. Chromatographic wettability tests show the potential of magnesium chloride to change the chromatographic wettability index. For instance, the initial wetting state was quantified to be almost neutral wettability with a wetting index of 0.54. After flooding magnesium chloride for 10 days at 130°C, the wetting index measured was 0.95, indicating a more water wet wetting state according to this kind of wettability measurement. Despite that, the wetting index measured with the chromatographic wettability test increases while flooding magnesium chloride, this does not necessarily mean that the wetting state is changing; the chromatographic wettability test is based on the water wet adsorption area, thus, there are strong suggestions that this area can be modified by precipitation of new minerals, in this case, magnesite. See **Figure 53**. The plot shows a translation to the right side in the x axis while the wetting area between thiocyanide and sulphate increases (curves blue and yellow).

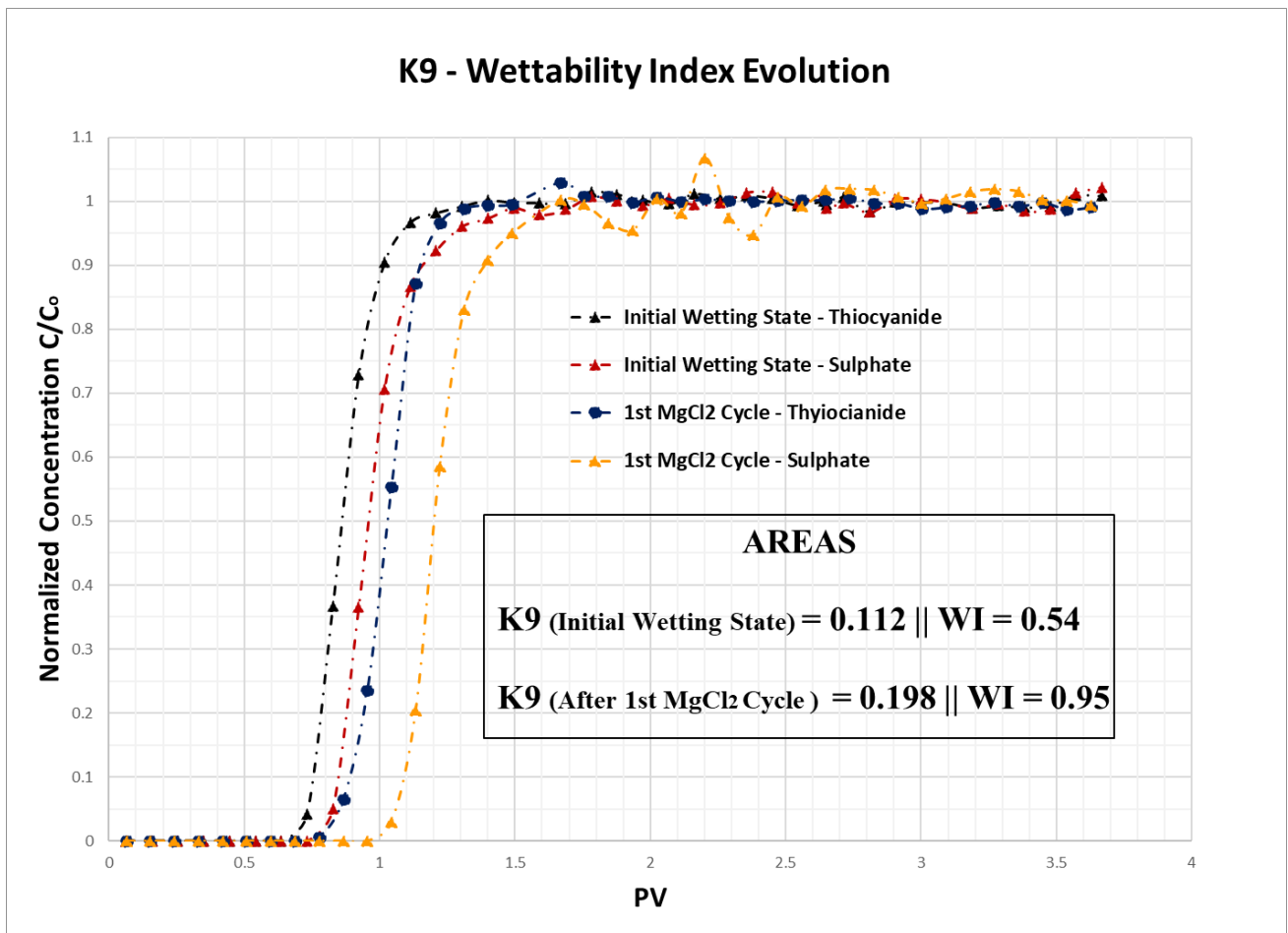


Figure 53: Chromatographic wettability tests performed on mixed wet core K9 in the Triaxial Cell. Wettability Index Evolution after the 1st MgCl₂ cycle.

While flooding magnesium chloride at high temperature, effluent samples were taken every other day. The chemical composition analysis of the samples taken are shown in **Figure 54**. Several changes can be inferred from the analysis. First, retention of magnesium takes place in the chalk surface. The retention is higher when the flood of magnesium chloride starts, magnesium concentration gradually increases, stabilizing around 0.200 [mol/l]. Secondly, loss of calcium from the calcite surface. The loss of calcium takes a maximum when the retention of magnesium is maximum and slowly decreases, reaching a plateau around 0.013 [mol/l]. The plot also shows that the sum of concentrations of magnesium and calcium oscillate around the original concentration of magnesium in the brine (0.219[mol/l]), suggesting perhaps a substitution reaction; however, this is most likely related to a dissolution of Calcite surface and precipitation of new magnesium bearing minerals process. Nevertheless, several mechanisms could potentially be involved. This will be discussed later.

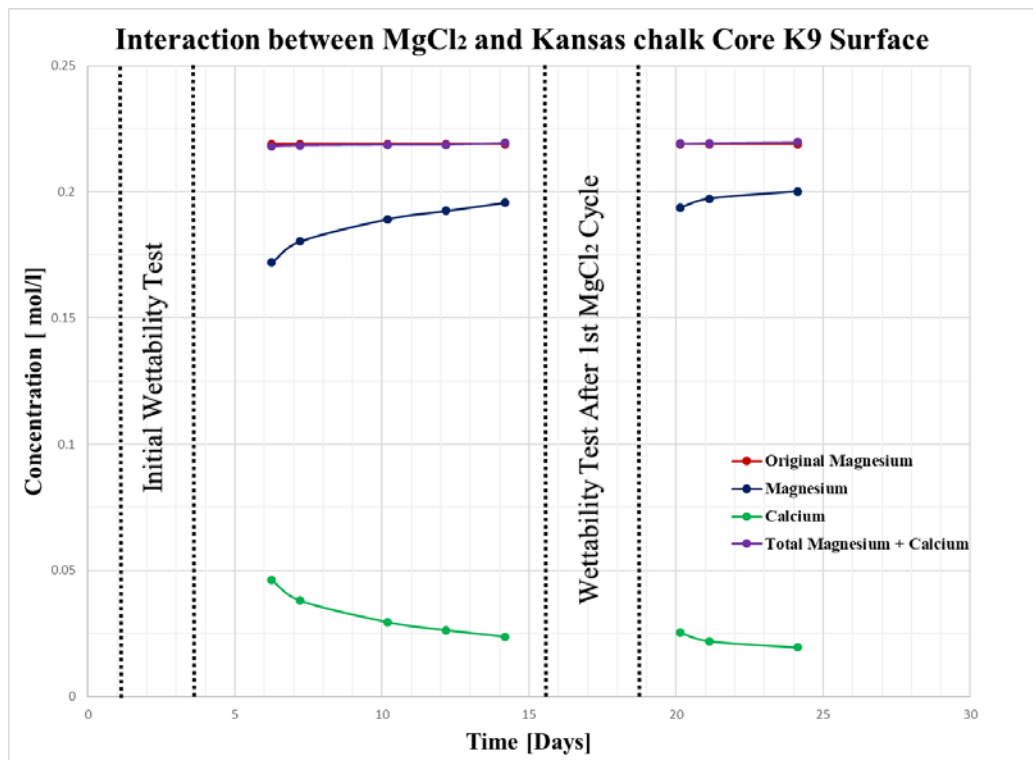


Figure 54: Interaction between MgCl₂ and Kansas chalk core K9 surface.

4.3.2.2 Triaxial Cell: Shrinking Sleeve and Reproducibility

Core K7 and K8 were both tested in a triaxial cell using a shrinking sleeve as a sealing material. Both cores were placed in the same triaxial cell. The wetting index evolution of cores K7 and K8 can be found in **Figure 55** and **Figure 56** respectively. The characteristics two jumps shape were found for the initial wetting state of both core. The wetting index measured were 0.28 for core K7, indicating an oil wet system and 0.49 for core K8 suggesting a neutral system. Wetting Index evolution of both cores are shown in the same figures. After increasing temperature, during all the magnesium chloride cycles, the shape of the curve totally changed in core K7 (See **Figure 55**). This confirms the effect of temperature in the sealing properties of the shrinking sleeve surrounding the core (See **Figure 50**). However, on core K8, even though the shape of the initial wetting state curves were modified by increasing temperature, the effect was not as strong as the one obtained in core K7. Notice the gradually transition between two jumps to 1 jump in curves related to magnesium chloride cycles (See **Figure 56**). This phenomenon is most likely related to the inefficiency of shrinking sleeve to seal the core even after increasing temperature. Regardless of the small differences in shapes behaviour, the changes in wetting index due to the flooding of magnesium chloride are not a random occurrence and can therefore be reproduced. Initial water saturation of 27.19% for core K7 and 27.32% for core K8 were measured. Also, S_{or} were calculated for both cores after being flooded with SW-0T, 49.47% for core K7 and 37.06% for core K8. Oil produced was measured to be 7.05 ml for

core K7 and 11.1 ml for core K8.

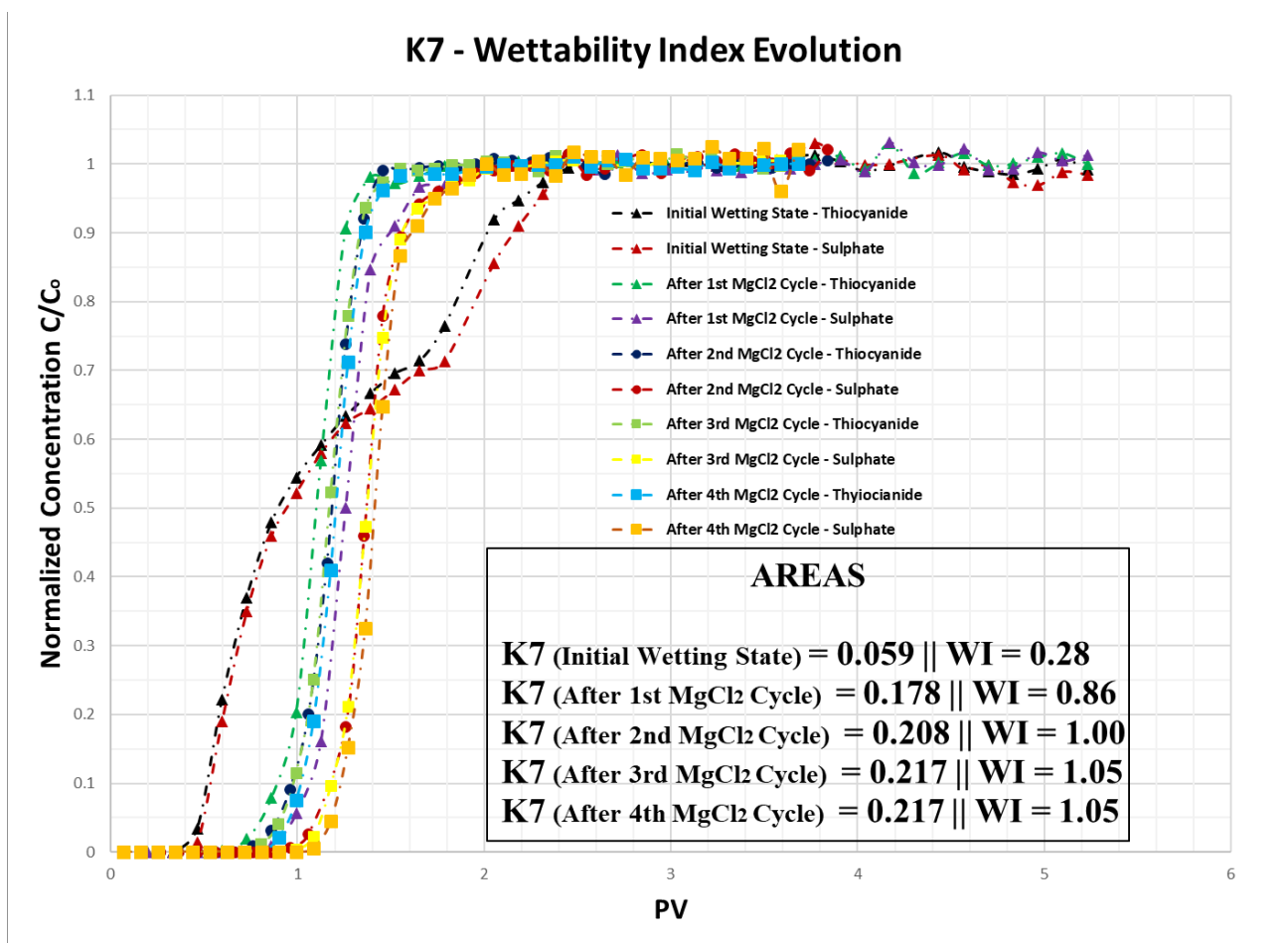


Figure 55: Chromatographic wettability tests performed on mixed wet core K7 in the Triaxial Cell. Wettability Index Evolution after four MgCl₂ cycles.

Effluents analysis of both cores are respectively presented in **Figure 57** and **Figure 58**. Four flooding cycles of magnesium chloride were performed in core K7 and two in core K8. The effluent analysis corroborates previous results found in core K9. Retention of magnesium into the chalk surface and production of calcium removed from the calcite surface. Magnesium concentration gradually increases and stabilizes around 0.2 [mol/l] but never reaches the original concentration for both cores, thus, moles retained are around 0.019 [mol/l]. Once the retention of magnesium starts taking place in the same core, production of calcium is obtained in the effluent, it takes a maximum when retention of magnesium is the highest and again slowly decreases until it stabilizes for both core around the same value, 0.013 [mol/l]. These two phenomena could induce changes in the core mineralogy that could potentially affect the specific surface area of the core. It is worth noting that uncertainties present during the dilution of the samples or IC analysis can lead to small differences between original concentration of magnesium and the sum of concentration of magnesium and calcium.

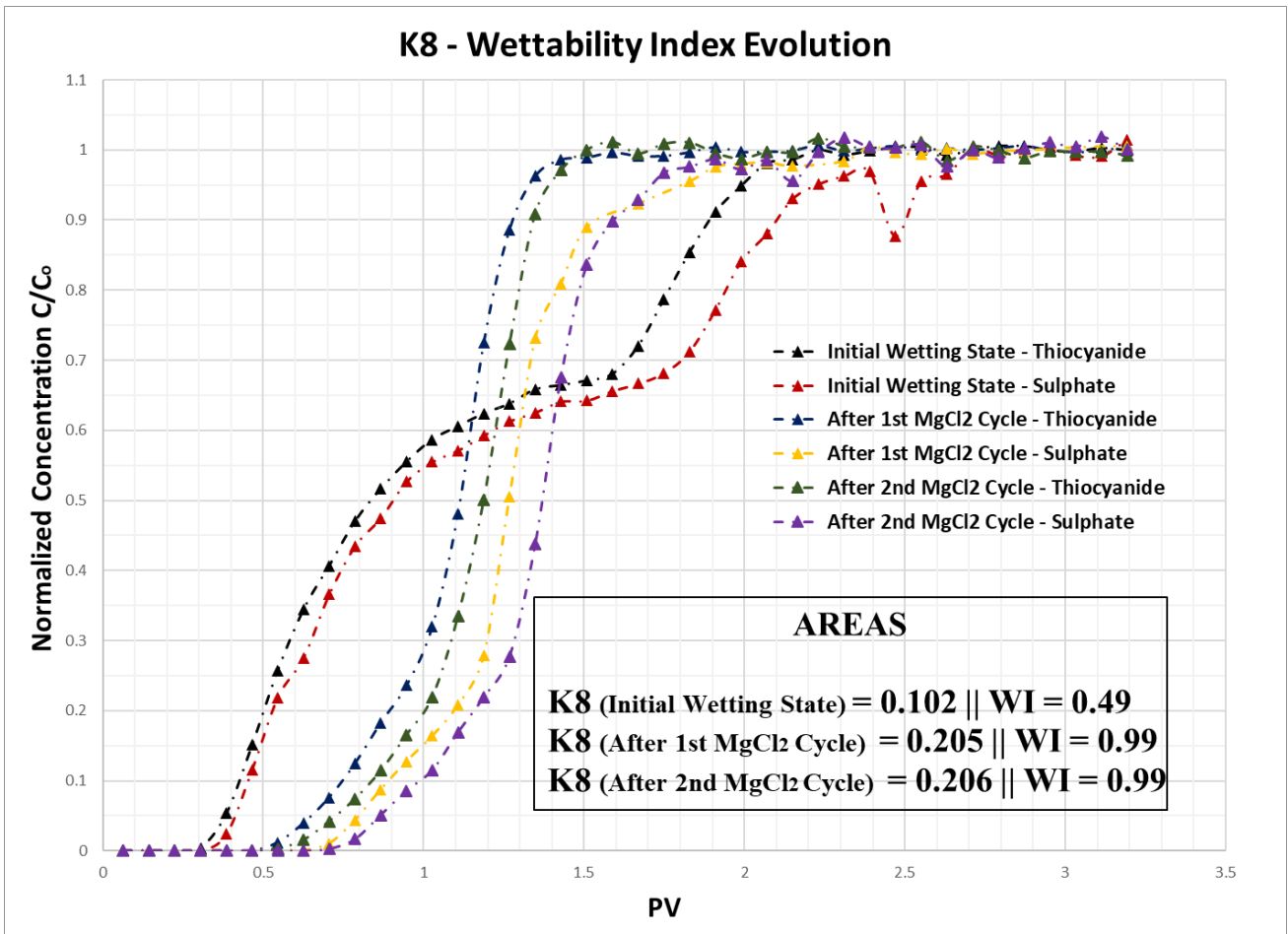


Figure 56: Chromatographic wettability tests performed on mixed wet core K8 in the Triaxial Cell. Wettability Index Evolution after two $MgCl_2$ cycles.

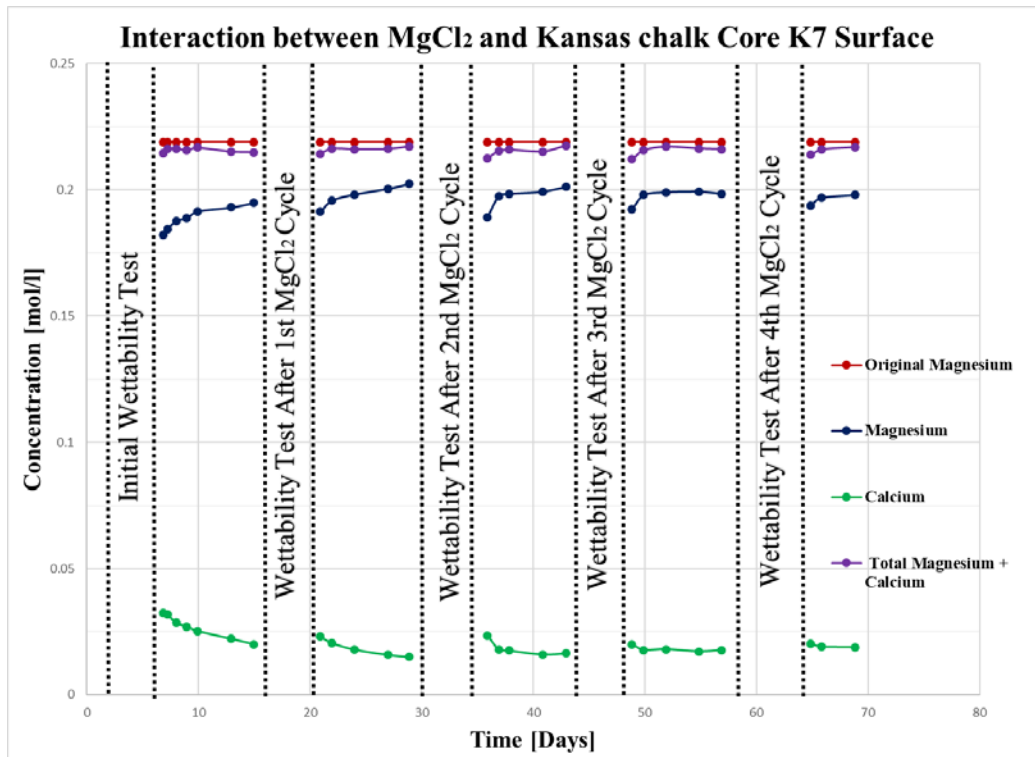


Figure 57: Interaction between $MgCl_2$ and Kansas chalk core K7 surface.

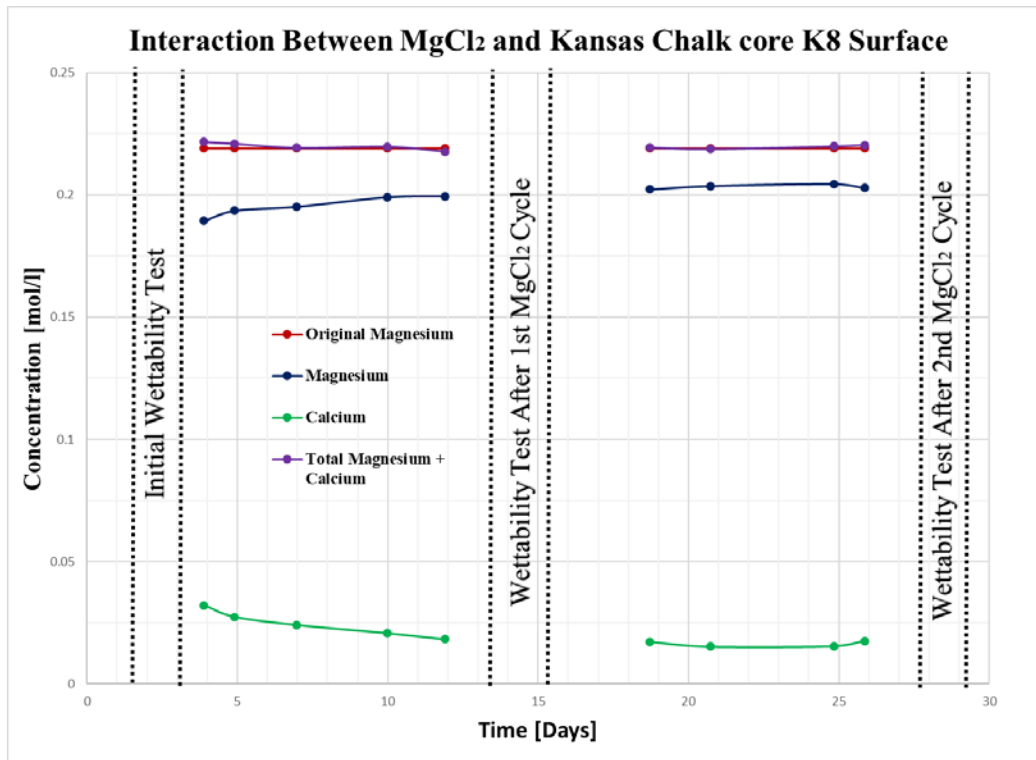


Figure 58: Interaction between MgCl₂ and Kansas chalk core K8 surface.

A brief summary of results obtained in mixed wet cores is presented in **Table 13**, emphasizing in the setup and sealing materials chosen to perform the core flooding experiments. Wetted areas between thiocyanide and sulphate are also shown and their respective wetting indexes. Mixed wet cores and water wet cores results will now be discussed in chapter five.

Table 13: Summary of results obtained in mixed wet cores used to establish the initial wetting state of mixed wet Kansas cores and evaluate the potential of MgCl₂ as a wettability modifier agent.

CORE	SETUP	SEALING	SHAPE	AREA THIOCYANIDE - SULPHATE	WI
K7 Initial Wetting State	Triaxial Cell	Shrinking Sleeve	2 Jumps	0.059	0.28
K7 After 1 st MgCl ₂ Cycle			1 Jump	0.178	0.86
K7 After 2 nd MgCl ₂ Cycle				0.208	1.00
K7 After 3 rd MgCl ₂ Cycle				0.217	1.05
K7 After 4 th MgCl ₂ Cycle				0.217	1.05
K8 Initial Wetting State			2 Jumps	0.102	0.49
K8 After 1 st MgCl ₂ Cycle		0.205		0.99	
K8 After 2 nd MgCl ₂ Cycle		1 Jump	0.206	0.99	
K9 Initial Wetting State			Rubber	0.112	0.54
K9 After 1 st MgCl ₂ Cycle				0.198	0.95
K10 Initial Wetting State	Hassler Cell			0.137	0.66

Finally, when the experimental work started, the initial wettability tests were performed flooding more than 5.5 PV of SW-1T through the core. This was done by sampling for 10 minutes and wasting for 10 more minutes. However, these initial conditions were inefficient and time consuming. Thus, they were gradually improved by reducing the wasting time between samples. Toward the end of the experimental work, a total of 40 samples were taken, sampling for 10 minutes and just wasting for 2.5 minutes, which provides a total flood slightly over 3 PV of SW-1T, allowing to carry out the core flooding experiment in just 8.3 hours. All these tests were carried out using a flooding rate of 0.2 ml/min.

It is worth mentioning all the chromatographic wettability test areas were calculated using the trapezium method.

CHAPTER 5

DISCUSSION

Several observations were made during the experimental work and will be the subject of discussion in this chapter along with the main results of chapter 4.

5.1 Establishing Initial Wetting State: Insight of Aging and Core Restoration

5.1.1 Initial Wetting State of mixed wet Kansas chalk cores

Core restoration processes are not yet standardized. Thus, there are several procedures reported in the literature about how to establish the initial wetting state of outcrop cores. Trying to simulate millions of years of interactions between the crude oil, formation water and rock reservoir in a short restoration process have been and will be very challenging. Before oil accumulates into the reservoir rock, the rock is presumed to be completely water wet. However, when oil is trapped in the reservoir rock a new chemical equilibrium takes place in the reservoir lasting for millions of years. Sadly, reservoirs cores are rarely available. Thus, outcrop cores are used to mimic reservoir conditions.

Kansas outcrop chalk was used in this study. Water wet Kansas outcrop chalk cores were flooded with oil to change the wetting state, simulating the interaction taken place when oil invaded the initially water wet reservoir rock. Aiming to get same conditions after respectively aging process, mixed wet cores used in this dissertation were all prepared using the same methodology, flooding 2 PV of this oil in each direction, aging the core in the same oven at the same temperature during the same time span.

Despite the efforts to keep all operation parameter as constant as possible, establishing the initial wetting state was a herculean task. The initial wetting state of all the four cores tested vary from oil wet state to water wet state; cores K8 and K9 exhibit neutral wettability. One of them tested in the Hassler's Cell Setup and three of them tested in triaxial cell, one of this with rubber sleeve instead of shrinking sleeve. See **Table 13**.

Deeping into all the operation variables of the core tested, one small difference was noted in the mixed wet cores tested. After 3 weeks, the aging cell containing the mixed wet cores were taken out.

However, the cores were not immediately tested. Some variations in time regarding the number of days that cores remained inside of the aging cell at room temperature before being tested. A recapitulation of some results and the small difference noted are presented in **Table 14**.

Table 14: Mixed Wet Cores observed and measured parameters.

CORE	WETTING INDEX (WI)	INITIAL WATER SATURATION [%] (S _{wi})	RESIDUAL OIL SATURATION [%] (S _{or})	DAYS AGED AT ROOM TEMPERATURE
K7	0.28	27.19	49.47	76
K8	0.49	27.32	37.06	50
K9	0.54	28.23	44.73	1
K10	0.66	27.07	36.79	17

Small variation in initial water saturation between the four cores were found, but they do not differ more than 1.16%. On the other hand, the time that cores remained inside of the cell aging at room temperature before being tested highly varied.

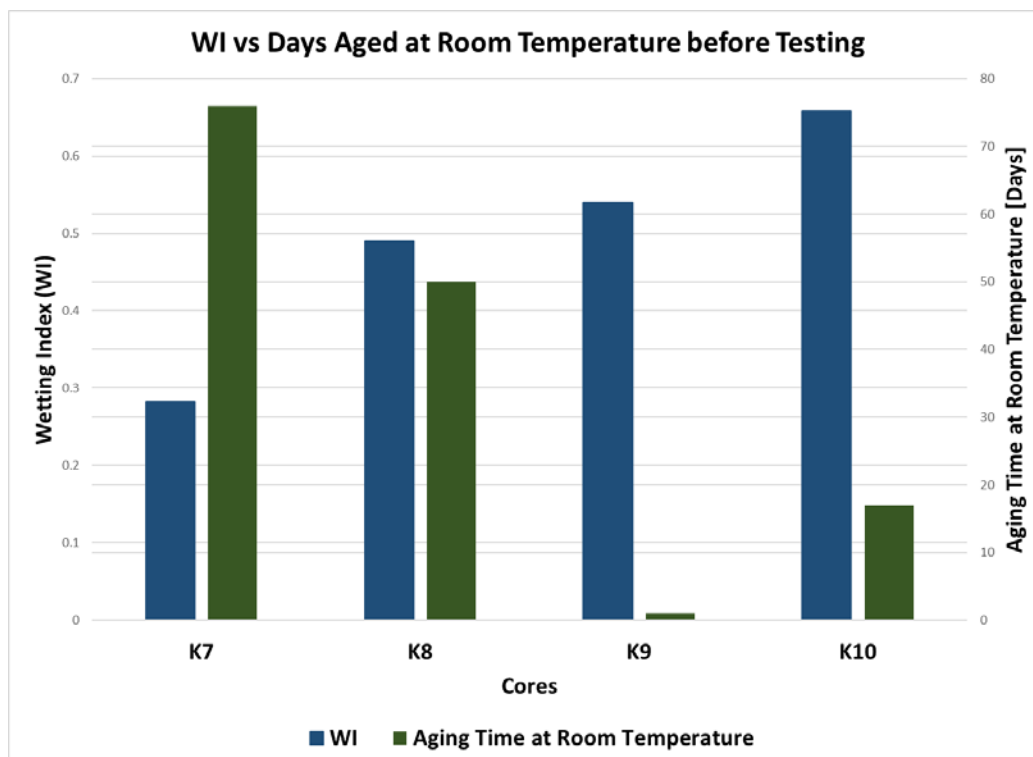


Figure 59: Wetting Index vs Days aged at room temperature for mixed wet cores tested. All cores were initially aged at 90°C for 21 days.

Cores K7, with a low wetting index of 0.28, after 21 days aging at 90°C remained 76 days without being tested. Suggesting, perhaps the aging process and adsorption of oil components in the matrix continue at low temperature. Core K8, tested under the same conditions of core K7, but differing in numbers of days aged at room temperature before testing, provides a higher wetting index of 0.49 indicating neutral wettability. Both cores were tested in triaxial cell using a shrinking sleeve as a sealing material. Core K9 was also tested in the triaxial cell setup but using a rubber sleeve as a sealing material. And lastly, core K10 was tested in the Hassler’s Cell.

The three cores tested in the triaxial cell, K7, K8 and K9 show a good correlation regarding the initial wetting state with the number of days aged at room temperature. See **Figure 59**. The same trend is observed regarding the residual oil saturation obtained after being flooded with SW-OT for cores K7 and K8. Higher values of residual oil saturation are found in core with lowest wetting index. See **Figure 60**.

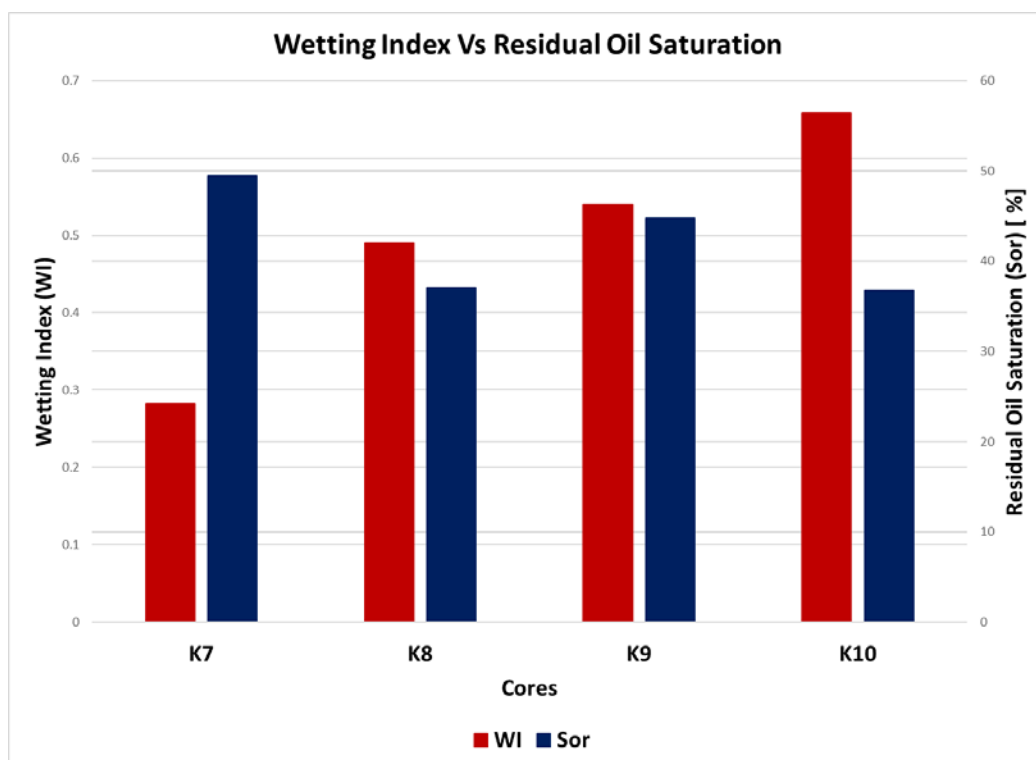


Figure 60: Wetting Index vs Residual Oil Saturation for mixed wet cores tested.

However, residual oil saturation is not just a function of initial wetting state of the core but also of heterogeneities presented in the cores. Carbonate reservoirs are highly heterogeneous and naturally fractured. Outcrop Kansas chalk is not the exception.

Core K10 tested in the Hassler cell indicates a slightly water wet mixed system. This was the highest wetting index achieved in all four cores. Core K10 results do not fit in any trend with the cores tested in the triaxial cell. It is worth noting that this core was tested with a low flow rate of 0.1 ml/min. The produced oil is highly influenced by the flooding rate. Thus, oil flooded out increases with increasing flooding rate. Therefore, oil produced is expected to be higher with a flooding rate of 0.2 ml/min, decreasing the S_{or} previously obtained.

Results obtained in different mixed wet cores can also be influenced by design parameters of each setup. See **Table 10**. The influence of sealing material was widely studied during this dissertation, however, the effect of differences in confining pressure and flooding direction through the core were not tested, thus, the impact of these variations in the results are unknown.

The initial wetting state of all mixed cores suggest that the aging process is a continuous process, where the oil wetness state increases with the aging time, facilitating the adsorption of acidic polar components even at room temperature; however, changes in the initial wetting state can also be linked to outcrop Kansas chalk heterogeneities. Regardless, these preliminary observations seem to contradict the theory proposed by Hopkins et al. 2016, where acidic polar components in the crude oil adsorbed onto the rock surface immediately upon contact and resulted in a mixed-wet rock surface, even without core aging.

5.1.2 Sulphate Content in Kansas Chalk

Anderson (1986) suggested that in order to attempt the restoration of cleaned cores to its original wettability, the core should initially be saturated with brine, oil flooded, and then aged at the reservoir conditions for 1000 hours, allowing a mixed wetting state to be restored. However, these conditions were slightly modified, specially the aging time. Cores were not cleaned during this dissertation, leading to potential miscalculation in wetting indexes of restored cores. Unfortunately, this was observed later in the development of the experimental work.

Punternvold et al. 2007, found that some of the quarry close to the sea contained initial sulphate due to the constant influx of seawater. They also found the initial sulphate present in the cores increases the water wetness of the core by preventing the carboxylic material in crude oil from absorbing. Punternvold et al. 2007, recommended to pre-flush the outcrop chalk cores with at least 4 PV distilled water or a brine without sulphate to remove dissolvable sulphate that could affect the initial wetting state.

Therefore, it was decided to flush a Kansas core with 4 PV of distilled water to analyse if considerable amount of sulphate was present in a randomly chosen core. The physical properties of core K11 are found in **Table 15**. Sulphate analysis was carried using the Dionex IC S-5000+ Ion Chromatography System and results are shown in **Figure 61**.

Table 15: Physical properties of core K11 used to determine the presence of sulphate in outcrop Kansas core.

Core	K11
Core Length [mm]	64.46
Core Diameter [mm]	38.13
Dry Mass [g]	128.69
Pore Volume (PV) [ml]	25.85
Porosity (ϕ) [%]	35.12

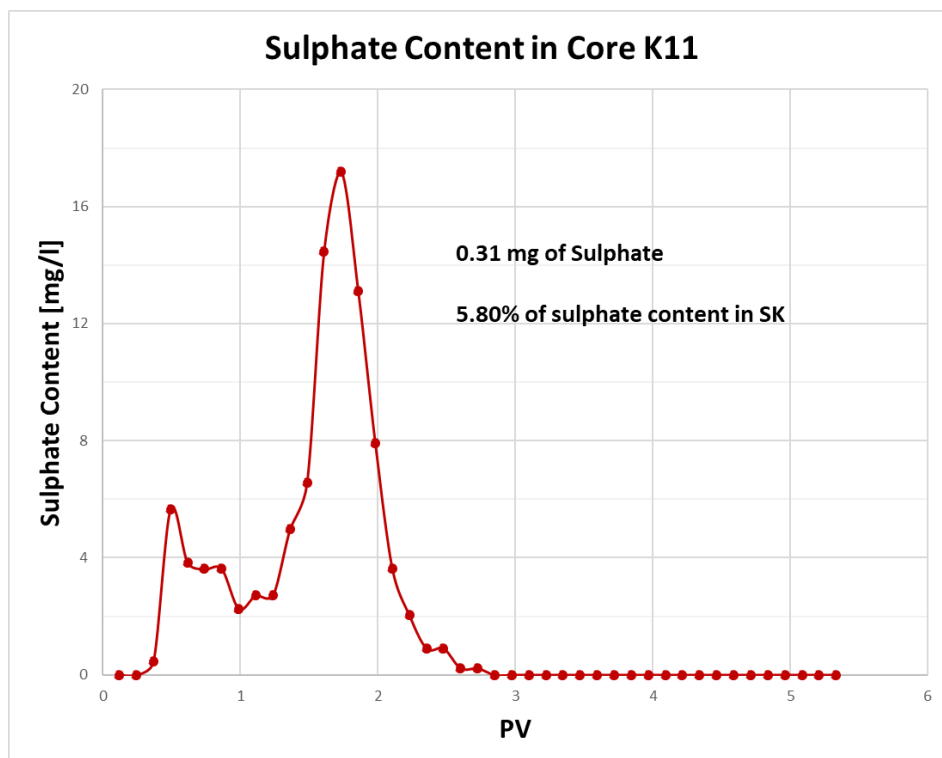


Figure 61: Effluent sulphate content of core K11 flooded with distilled water at room temperature.

A total of 0.31 mg of sulphate was found in this core. This was obtained calculating the area below the curve from **Figure 61**. The area was found using the trapezium method. The test was performed at room temperature. Tests conducted by Puntervold et al. 2007, found that the average sulphate content in Stevns Klint outcrop chalk cores were 5.35 mg, tests conducted at 50°C. The amount of sulphate found in Kansas core corresponds to 5.8% of average sulphate content found in Stevns Klint cores. The influence of temperature to remove dissolvable sulphate from the chalk surface was not studied.

The differences in sulphate content in the outcrop chalks are mainly related to the natural depositional environment of each system. Even though both chalks formation indicated marine environments, Stevns Klint outcrop chalk is located close to the sea just right on the coast; on the opposite side, Kansas outcrop chalk is located inland. The biggest difference is perhaps the constant influx of seawater (containing sulphate) near the depositional environment of Stevns Klint quarry in Denmark; this does not happen for Kansas outcrop chalks present in Niobrara formation in United States.

Despite small traces of sulphate present in the Kansas core tested, it is strongly recommended to clean the core before wettability restoration. Initial content of sulphate in the core increases the water wetness of the core, thus, current procedure to alterate wettability must be modified. After saturating the core with 1.1 M NaCl, the core should be place into the rig at 50°C and flood with at least 4 PV of 1.1 M NaCl before start flooding oil through the core.

5.2 Effect of Flooding Magnesium Chloride and Sodium Chloride through Kansas Chalk Cores at 130°C

5.2.1 Can Magnesium Chloride (MgCl₂) modify the wetting state?

After having flooded magnesium chloride through three mixed wet cores, early results suggest the strong possibility of this reactive brine to decrease the oil wetness of the cores. This suggestion was made based on the evolution of the wetting index of the three cores tested. See **Table 13**. The wetting index is related to the wetted area measured by the chromatographic separation between non-adsorbing thiocyanide ion and adsorbing sulphate ion toward the water wet area. The chromatographic wettability test is of adsorbing nature. Thus, it is fairly to assume that results obtained by using the chromatographic separation test are influenced by variations in the specific surface area.

Evolution of wetting index for core K7, K8 and K9 suggest the increase of water wetness based on preliminary results obtained by using the chromatographic wettability tests. See **Figure 53**, **Figure 55** and **Figure 56**. However, while flooding magnesium chloride at high temperature, no extra oil production was noted, just traces of oil were obtained in the effluent. These traces of oil produced while flooding the reactive brine at high temperature are attributed to decrease of oil viscosity with increasing temperature. The reduction of viscosity allows to displace more oil with the same driven

energy; however, it can also be related to small changes in the wetting state because the cores tested were either oil wet or neutral wet, and the changes in the wetting state could have been minimum causing that just traces of oil were observed. So, if there is no considerable extra production of oil during the flooding of magnesium chloride, why is the wetting index based on the chromatographic test suggesting an increase in the water wetting state of the cores?

No extra production of oil was later confirmed when the cores were extracted from the triaxial cell. Cores K7 and K8 were preserved in distilled water for analysis. Imbibition studies carried out by Zhang et al. (2007) found that adding magnesium to the imbibing fluid increased the oil recovery around 5% at 100°C, suggesting the possibility of magnesium to potentially be able to modify the wetting state. This study also found that the effect of magnesium increases with increasing the concentration of sulphate present in the imbibing fluid. Thus, could magnesium sulphate being able to modify the wetting state? Furthermore, core K9 was accidentally destroyed and could not be preserved. Cores K7 and K8 are shown in **Figure 62**. Notice the particular brownish colour of both cores, suggesting the presence of oil trapped inside the cores. The cores were preserved for future testing using scanning electron microscope (SEM) analysis, Energy-dispersive X-ray spectroscopy (EDS) and X-ray powder diffraction (XRD). None of these tests have been carried out yet.



Figure 62: Mixed wet cores K7 and K8 preserved in distilled water after being removed from the triaxial cell.

Thus, trying to understand changes taking place inside the core. It was decided to flood a water wet Kansas chalk core initially with sodium chloride (NaCl) and subsequently with magnesium chloride (MgCl₂). Core tested was K4. Properties of the core are shown in **Table 7**. The changes in wetting index, evaluated using the chromatographic separation tests can be found in **Table 12**. The results suggest that flooding sodium chloride through Kansas chalk cores leads to reduction the wetted area of the core. However, this reduction is not entirely clear, Madland et al. 2011, showed that there is no precipitation of new mineral by flooding NaCl through chalks material; this can also be related to uncertainties obtained during the dilution procedure or while calculating the respective area. On the opposite side, flooding magnesium chloride through Kansas chalk cores increase the wetted area of the core. Thus, effluent analysis, density and specific surface area measurements were carried out to obtain insights of mineralogical changes taking place inside the core.

Effluent analysis of core K4 can be appreciated in **Figure 63**. During the sodium chloride cycle, it can be noticed that there is no retention of sodium inside the core, with average concentration equal to the initial of sodium injected, 0.657 M. Also, chloride behaves inertly to the calcite surface, chloride concentration is equal to the initial concentration injected, 0.657 M. This sodium chloride behaviour is in accordance with studies performed before, Madland et al. 2011, Megawati et al. 2015. Small fluctuations were obtained but these are most likely related to dilution discrepancies. Moreover, small traces of calcium are obtained in the effluent while flooding sodium chloride through the core.

During the magnesium chloride cycles, magnesium is retained inside the chalk core. The same behaviour was obtained while flooding magnesium chloride through mixed wet cores. Also, calcium is produced due to dissolution of calcite. Similar results were obtained in mixed wet cores. See **Figure 54**, **Figure 57** and **Figure 58**. The original magnesium concentration is never reached, stabilizing around 0.2 M concentration, calcium concentration stabilized around 0.013 M. Similar behaviour has been widely reported in other experimental studies (Madland et al. 2011, Neramoen et al. 2015; Zimmermann et al. 2015).

Dissolution of calcite directly affects the mechanical strength of chalk rocks (Korsnes, 2007; Korsnes et al., 2006a, b, 2008; Madland et al., 2008; Zangiabadi et al., 2009). Retention of magnesium triggers mineralogical changes in the chalk framework (Madland et al. 2011, Neramoen et al. 2015; Zimmermann et al. 2015).

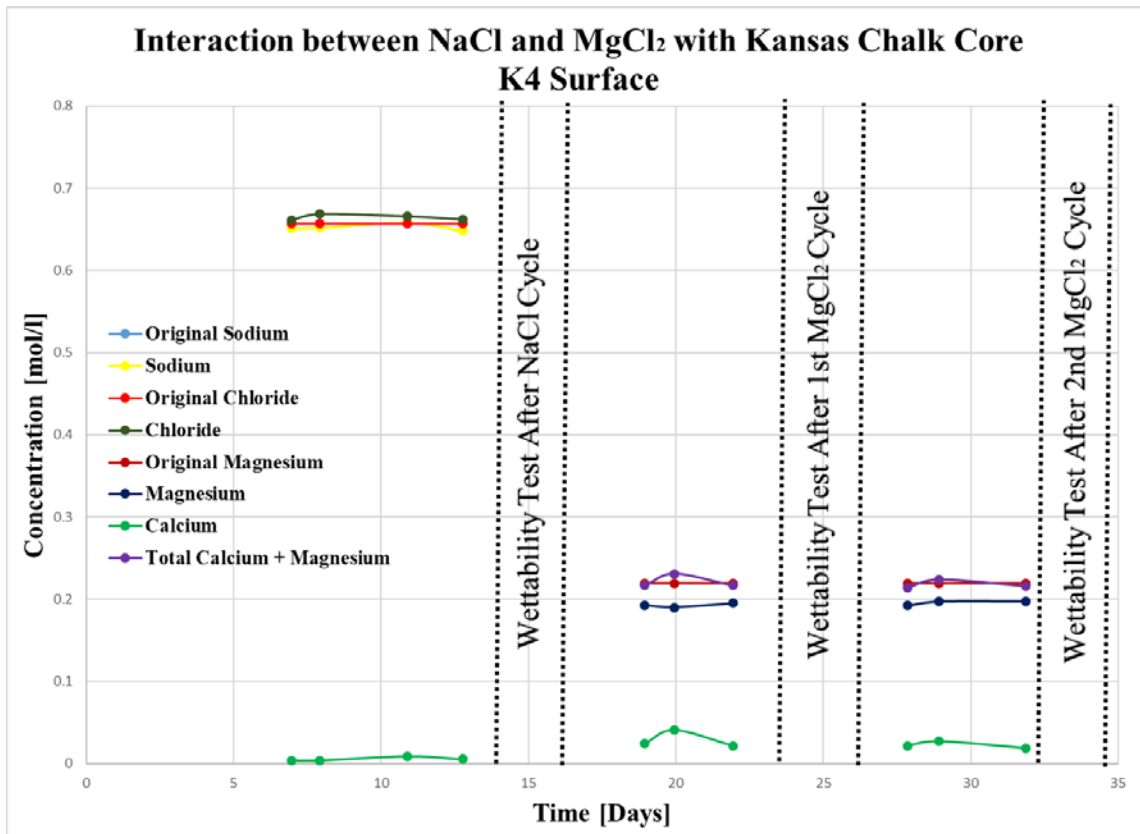


Figure 63: Interaction between flooding brines (NaCl and MgCl₂) and Kansas chalk core K4 surface.

5.2.2 Changes in Mineralogy

Trying to address these changes triggered in the calcite surface, density measurements using AccuPyc II 1340 Gas Pycnometer and specific surface area (SSA) measurements using Micrometrics TriStar II: Surface Area and Porosity were carried out in core K4. Properties of this core before and after testing are presented in **Table 16**. Notice the loss of mass of 0.8 grams in just three weeks. The increase in density of the core from 2.695 to 2.703 g/ml. The overall increase in core's density is attributed to precipitation of new magnesium bearing minerals, specially magnesite (Madland et al. 2011, Zimmerman et al. 2015, Nermoen et al. 2015, Minde et al. 2017, Egeland et al. 2017).

Pure calcite density is 2.71 g/ml and magnesite density is 3 g/ml. However, outcrop Kansas chalk is not completely pure, whereas calcite content is in the range of 95 to 97%, decreasing the density in the range of 2.69 to 2.70 g/ml. A dissolution of the calcite surface and precipitation of new magnesium bearing minerals lead to a magnesium enrichment inside the chalk framework, therefore, a chalk density increase from calcite range till magnesite range is expected.

Table 16: physical properties of core K4 before and after testing.

Core K4	Before testing	After Testing
Core Length [mm]	68.61	68.56
Core Diameter [mm]	38.12	38.08
Dry Mass [g]	136.82	136.02
Saturated Weight with water [ml]	164.36	163.77
Bulk Volume [ml]	78.30	78.08
Pore Volume [ml]	27.54	27.75
Porosity [%]	35.17	35.54
Bulk Density [g/ml]	2.695	2.703



Figure 64: Core K4 Inlet removed from the rest of the core for density and specific surface area analysis.

In order to look into the mineralogical changes inside the core, the inlet of the core was cut off and initially tested for density. This inlet density measurement was compared to the rest of the core. Physical properties and measured densities of the inlet and rest of the core can be found in **Table 17**.

Table 17: Physical properties of inlet and rest of the core K4.

Core K4	Inlet	Rest of the Core
Dry Mass [g]	11.216	122.026
Measured Volume [ml]	4.098	45.146
Density [g/ml]	2.737	2.704

Notice the biggest change in density is achieved in the inlet. The inlet density was measured to be 2.737 g/ml compared to the rest of the core which is 2.704 g/ml. The weighted average density was calculated using the following relation:

$$\rho = \frac{m_1 \cdot \rho_1 + m_2 \cdot \rho_2}{m_1 + m_2} \quad \text{Eq. 10.}$$

where m is the mass measure of each part and ρ is the respective density of each part.

Weighted density averaged was 2.707 g/ml.

Early results suggest that precipitation of new magnesium bearing mineral is a transient process, which starts taking place in the core's inlet and slowly propagates through the outlet. It is worth noting that these changes were observed after flooding magnesium chloride at 130°C for 2 weeks at 1 PV/day. These results completely agree with research studies presented by Nermoen et al. 2015 and Nermoen et al. 2016, where density of the core was increased in long term flooding experiments through chalk cores.

5.2.3 Changes in Specific Surface Area, SEM and EDS analysis

Precipitation of new minerals can obliterate the adsorption surface of the initial calcite surface; thus, specific surface area measurements were carried out mainly in core K4 and in its respective unflooded end-pieces. Others SSA measurements were performed in Kansas cores in order to determine the grade of heterogeneity of this kind of chalk, these results were compared to pure calcite outcrop Stevns Klint chalk.

Table 18: Specific surface area measurements obtained in core K4.

Core K4	Unflooded end-piece Inlet	Core's Inlet	Left Section before Middle of the Core	Middle of the Core	Right Section after Middle of the Core	Left Section before Core's Outlet	Core's Outlet	Unflooded end-piece outlet
Average Specific Surface Area (SSA) [m ² /g]	2.192	2.344	2.599	2.809	2.762	1.652	1.289	2.189

Notice, the increase of the specific surface in the inlet compared to the unflooded end-piece inlet. Average specific surface area increased from 2.192 to 2.344 m²/g. Apparently, the flood of magnesium chloride modifies the specific surface area by increasing it. These results agree with unpublished IOR Centre-work (Wang et al. 2017), where the flood of magnesium chloride increases the specific surface area of Kansas chalk cores. That study also found that the biggest increase in specific surface area is obtained in the inlet of the core and decreases till the outlet of the core.

Furthermore, unpublished work by Wang et al. 2017, also found that flooding sodium chloride through a Kansas Chalk core, reduce the specific surface area, where the lowest SSA is located in the inlet and increases till the outlet. However, SSA measurements obtained in the middle and outlet of the core do not agree with this unpublished work. It appears to be a specific surface area gradient through the core where the SSA increases reaching a peak in the middle of the core and then starts decreasing taking a minimum in the outlet. Thus, further studies are currently under schedule to understand this behaviour and analyse possible heterogeneities that might be present in the core. Scanning electron microscope (SEM) was carried out in the outlet of the core to understand why lowest SSA measurements were obtained in this section.

SEM analysis of flooded core's outlet K4 showed coccolithophore rings, typical unicellular eukaryotic phytoplankton alga which is commonly found in chalk reservoirs. See **Figure 65** left. The analysis also showed that the main constituents are calcite, no magnesite was present in the outlet. This was expected; magnesite precipitation is mainly focused in the core's inlet. See **Figure 65** right. Largest pore showed in **Figure 66** was analysed for elements composition. Energy-dispersive X-ray spectroscopy (EDS) (See **Figure 68**) confirmed that main constituent element was calcium. Potassium was found to cover the pore and impurities of iron were noticed.

However, SEM and EDS analysis did not show any anomaly that could help us to explain the lowest values obtained in core's outlet K4. The Si content is not predominant. Hjuler and Fabricius (2009) showed that SSA measurements were low when Si element was predominant, indicating the presence of feldspars and quartz, main components of sandstones. Thus, no reasons for low values have been found so far.

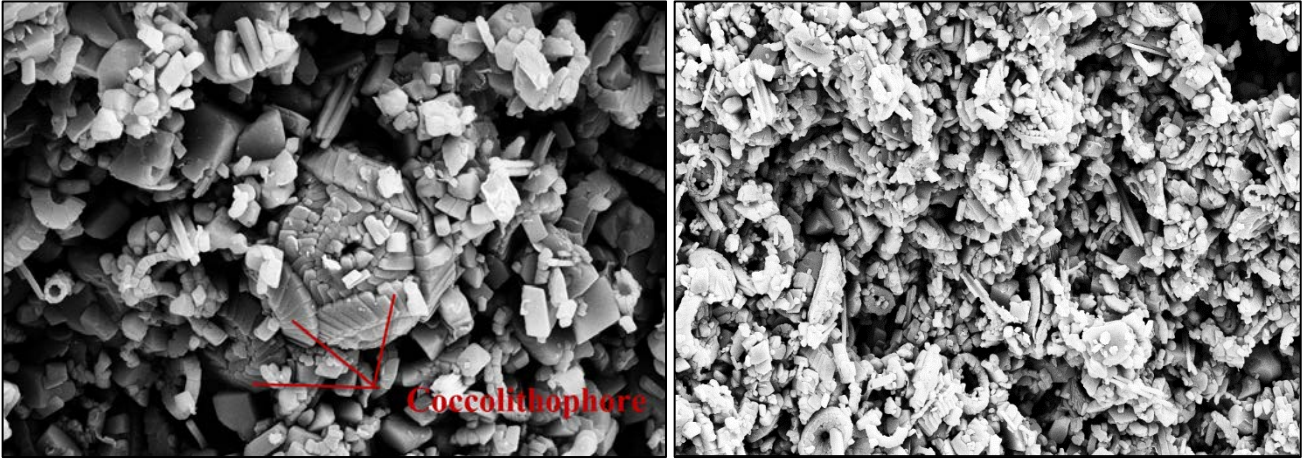


Figure 65: Left: Typical Cocolith structure present in outcrop Kansas chalk core's outlet K4 [1 μ m] scale. Right: SEM analysis after NaCl and MgCl₂ flooding cycles in Core's outlet K4 [10 μ m] scale.

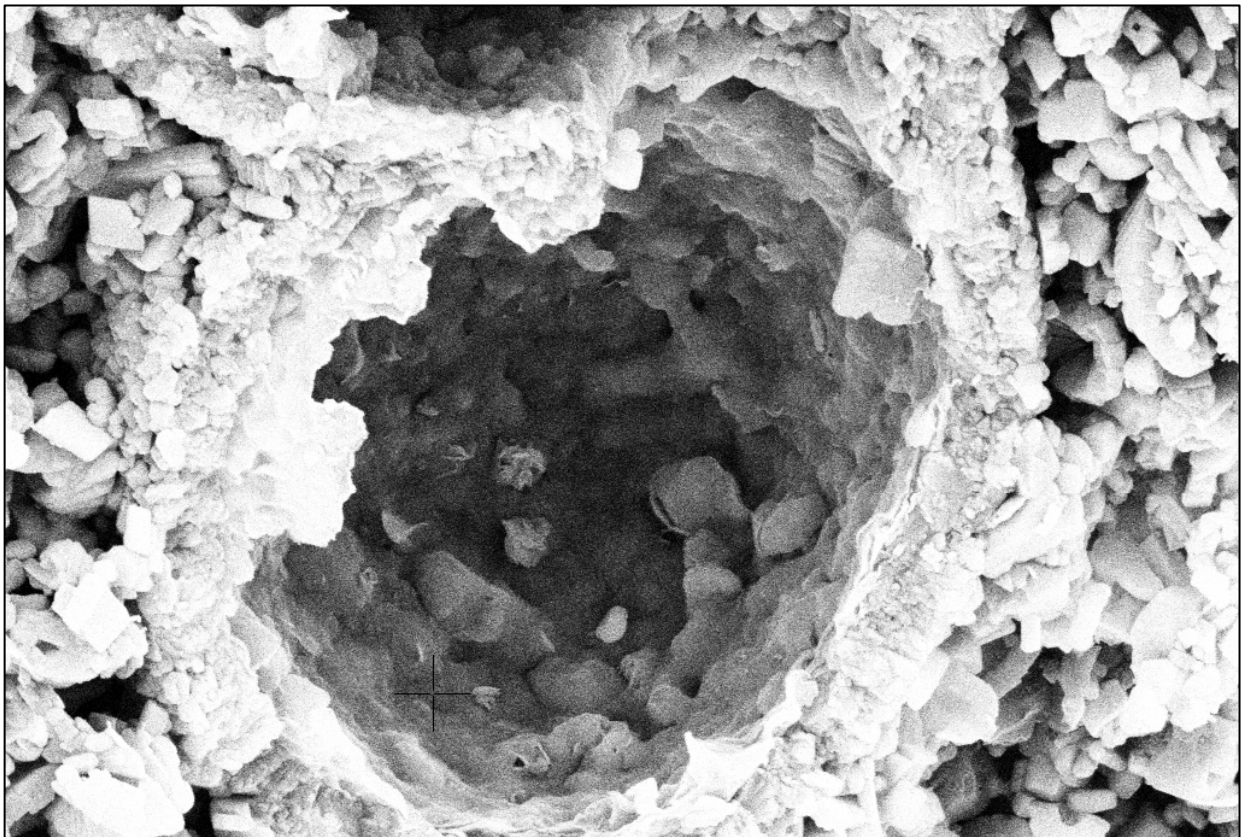


Figure 66: SEM analysis in largest pores present in Core's outlet K4 [2 μ m] scale.

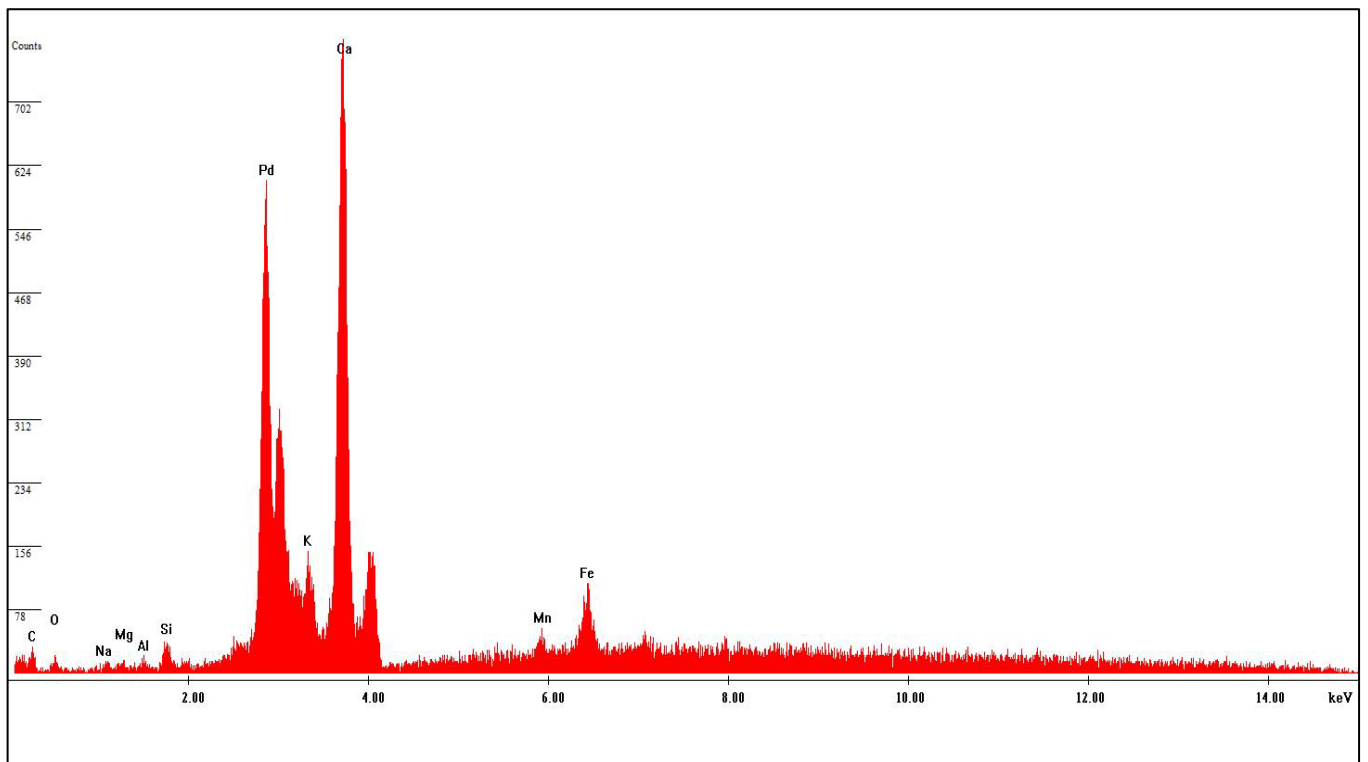


Figure 67: EDS analysis of largest pore present in core's outlet K4.

Moreover, unpublished results by Wang et al. (2017) could help to explain the behaviour of the wetted area in the chromatographic wettability test. See **Table 12**. Therefore, the sodium chloride cycle through core K4, could have initially reduced the specific surface, however, when the flood of magnesium chloride starts, the effect is highly reduced because of the first sodium chloride cycle, notice just the change in areas from 0.197 to 0.200 in the chromatographic test. So, when magnesium chloride overcomes the effect of sodium chloride, the area drastically increased to a value of 0.247, highest water wet area obtained during this experimental work. Specific surface area decreases with decreasing the water wet area of the core available for adsorption. On other words, an increase in the specific surface area can be reflected in an increase in the water wet area available for adsorption measured by the chromatographic separation between thiocyanide and sulphate ion. The fact that the chromatographic separation test allows to determine changes in the specific surface is not fortuitous. Specific surface area is extremely important in adsorption processes, allowing to quantify the mass adsorbed per area unit. Thus, the question missing to answer is how the specific surface area is related to the water wet area measured by the chromatographic wettability test?

Furthermore, specific surface area measurements were carried out on different Kansas chalk cores, finding out that results obtained vary from core to core. Specific surface area measured on outcrop

Kansas chalk vary between 2 to 3 m²/g, obtaining values as low as 2 and as high as 2.98 m²/g. Past studies have reported values of 2.95 m²/g for Kansas chalk (Megawati et al. 2015), and unpublished study of Wang et al. (2017) have reported values of 3 m²/g. Moreover, three random unflooded pieces belonging to Stevns Klint cores were tested for specific surface area, values measure vary between 2.2 to 2.3 m²/g, previous values reported of 1.89 m²/g were found by Megawati et al. (2015) and 2 m²/g by Wang et al. (2017). Notice that the variation between SSA measurements is higher for outcrop Kansas chalk compared to outcrop Stevns Klint. Stevns Klint possesses a higher purity than Kansas, with carbonate content higher than 99% compared to Kansas ranging between 95 to 97%. Specific surface area could help to understand the heterogeneities present in different outcrop chalks. This, however, is still under investigation.

Finally, water wet reference areas reported in Stevns Klint chalk cores while flooding SW-0T and SW-1T at room temperature were between 0.168 to 0.171, averaging 0.1705 (Strand et al. 2016). Water wet reference areas found in outcrop Kansas chalk cores while working with the same flooding brines and performing the chromatographic test at room temperature, vary between 0.184 to 0.227, averaging 0.207. See **Table 11**. Thus, in average, specific surface area of outcrop Kansas chalk is higher than outcrop Stevns Klint chalk, confirming the average water wet reference area of Kansas chalk to be higher than the average water wet reference area in Stevns Klint; suggesting a possible link between the specific surface area and the area measured by the chromatographic wettability test.

CHAPTER 6

CONCLUDING REMARKS AND FUTURE WORKS

The flood of magnesium chloride (MgCl_2) through outcrop Kansas chalk cores induces mineralogical changes due to precipitation of new magnesium bearing minerals in the initially rich in calcium porous material, between other phenomena. Moreover, magnesium chloride potential to modify the initial wetting state of mixed wet Kansas chalk cores is minimum; traces of oil obtained while flooding magnesium chloride at 130°C are attributed to a reduction of oil viscosity and to a minimum change in the wetting state of the oil wet core and mixed wet cores tested. Several observations were made during the development of this experimental work. Thus, the main conclusions based on the experimental work are presented in this chapter. Also, recommendations for future works are suggested.

6.1 Concluding Remarks

- Shrinking Sleeve sealing properties increase with increasing temperature. Rubber sleeve offers better sealing properties than the shrinking sleeve. However, when using shrinking sleeve in any core flooding experiment, it is strongly recommended to increase the temperature to 130°C to increase the adherence of the shrinking sleeve to the core, improving the sealing properties of itself and ensuring the total flood of the brine right through the cross-sectional area of the core and not through the lateral walls.
- Water wet area of the core measured by the chromatographic wettability test is not affected by performing it with a flooding rate of 0.1 ml/min or 0.2 ml/min. However, flooding rate higher than 0.2 ml/min, the area measured becomes lower.
- For future chromatographic wettability tests performed in a triaxial cell setup, a total of 40 samples are suggested, with a sampling time of 10 minutes and a wasting time of 2.5 minutes while using a flooding rate of 0.2 ml/min.
- The flood of distilled water through a Kansas core at 130°C does not affect the water wet area of the core measured by the chromatographic wettability test.
- Chromatographic wettability test developed by Strand et al. (2006) provides a quick a

good estimation of the initial wetting state of mixed wet Kansas cores. However, it is not reliable to quantify changes in the wetting state while flooding a reactive brine (Magnesium Chloride) through the core due to mineralogical changes inside of it.

- Water wet area measured by the chromatographic wettability test is strongly related to specific surface area (SSA) of the core. Preliminary results suggest that Sodium Chloride (NaCl) flood through the core could lead to a reduction of the wetting area measured by the chromatographic test, and thus, could reduce the SSA based on measurements reported in unpublished work by Wang et al. (2017); on the opposite side, flooding Magnesium Chloride ($MgCl_2$) through the core leads to an increase in the specific surface area based on observed increment in the wetting area measured by the same test and SSA measurements showed by Wang et al. (2017) and by this dissertation.
- Change in density toward a calcite rich in magnesium was observed in the inlet of core K4. An increment in the specific surface area of the core's inlet was observed compared to the unflooded end piece of the core.
- Sulphate content found in a randomly chosen Kansas core looks to be neglectable with a value around 5.8% of averaged values reported by Puntervold et al. (2007) in Stevns Klint cores. However, to ensure that no traces of sulphate are inside the core, the outcrop Kansas cores must be initially flooded with 4 PV of 1.1 M NaCl at 50°C before the wettability alteration process starts.
- Just traces of oil produced were observed while flooding Magnesium Chloride ($MgCl_2$) at 130°C through a mixed wet core. Thus, it was concluded that magnesium chloride potential to modify the initial wetting state of the mixed wet core is minimum. These observations agree with previous observations reported by Zhang et al. (2007) in a series of imbibition experiments where magnesium seemed to increase the oil recovery when was present in the imbibing fluid.
- An increase in wetting index measured by the chromatographic wettability test was observed while flooding Magnesium Chloride through mixed wet cores, suggesting the increase of the water wetness of the cores. However, this can be related to a combination of two main processes: changes in the specific surface area of the core by precipitation of new magnesium bearing minerals inside the core and minimum wettability alteration effects taking place inside the core.

6.2 Future Works

- Evaluate the effect of flooding a non-reactive brine (NaCl) through mixed wet Kansas chalk cores based on the evolution of the wetting index over time.
- Evaluate the effect of flooding a reactive brine (MgCl₂) and non-reactive brine (NaCl) through a pure calcite outcrop chalk cores, like Mons or Stevns Klint.
- Evaluate the potential of magnesium sulphate (MgSO₄) to modify the wetting state of mixed wet outcrop chalk cores.
- Establish the influence of pre-flushing water wet Kansas cores before wettability alteration.
- Close the causal gap between specific surface (SSA) and the chromatographic separation area between thiocyanide and sulphate.

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