Wettability Modification in Chalk

Systematic Evaluation of Salinity, Brine Composition and Temperature Effects

Sohal, Muhammad Adeel Nassar

DOI (link to publication from Publisher):
10.5278/vbn.phd.engsci.00177

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Sohal, M. A. N. (2016). Wettability Modification in Chalk: Systematic Evaluation of Salinity, Brine Composition and Temperature Effects. Aalborg Universitetsforlag. https://doi.org/10.5278/vbn.phd.engsci.00177

WETTABILITY MODIFICATION IN CHALK

SYSTEMATIC EVALUATION OF SALINITY, BRINE COMPOSITION AND TEMPERATURE EFFECTS

BY
MUHAMMAD ADEEL NASSER SOHAL

DISSERTATION SUBMITTED 2016

AALBORG UNIVERSITY
DENMARK

Wettability Modification in Chalk: Systematic Evaluation of Salinity, Brine Composition and Temperature Effects

Ph.D. Dissertation

Muhammad Adeel Nasser Sohal

AALBORG UNIVERSITY
DENMARK

Dissertation submitted October 31, 2016

Dissertation submitted: October 31, 2016

PhD supervisor: Prof. Erik Gydesen Søgaard
Aalborg University, Denmark

PhD committee: Associate Professor Saqib Sohail Toor (chairman)
Department of Energy Technology
Aalborg University

PhD and Senior Scientist Patrick V. Brady
Sandia National Laboratories
Geoscience Research & Applications Group

PhD and Project Manager Vural Sander Suicmez
Maersk Oil and Gas A/S

PhD Series: Faculty of Engineering and Science, Aalborg University

ISSN (online): 2246-1248
ISBN (online): 978-87-7112-831-4

Published by:
Aalborg University Press
Skjernvej 4A, 2nd floor
DK – 9220 Aalborg Ø
Phone: +45 99407140
aauf@forlag.aau.dk
forlag.aau.dk

Printed in Denmark by Rosendahls, 2016

Preface

This thesis is submitted in partial fulfillment of the requirements for the Doctor of Philosophy at the Department of Chemical Engineering and Biotechnology, Aalborg University, Denmark. The work has been supervised by Professor Erik Gydesen Søgaard and Dr. Geoffrey Thyne from the department of Chemical Engineering and Biotechnology, Aalborg University Denmark and Engineered Salinity, USA. Thesis deals with Wettability Modification in Chalk: Systematic Evaluation of Salinity, Brine Composition and Temperature Effects. The main focus is drawn to developing and using flotation method to measure wettability but some PHREEQC modeling is also incorporated to improve the mechanisms understanding.

Firstly, my sincere gratitude to my supervisors, Prof. Erik Gydesen Søgaard and Dr. Geoffrey Thyne, who have supported me throughout my thesis with their advice, patience and knowledge whilst giving me enough freedom to work in my own way. Especially, I will always remember Dr. Geoffrey Thyne advice *"let's speak the data for you"*. All the faculty and staff members were extremely helpful whenever they were asked for help.

I am grateful to my parents for their uninterrupted support and prayers. Especially, I feel proud of my father who always encourages and supports me in the endeavors of life. I keep praying for both of you that "O Allah! Forgive me and my parents as they have brought me up from my childhood". Words fail me to express my appreciation to my wife whose dedication, love and persistent support has taken the load off my shoulder and during first year of PhD study my daughter *"Ayra Adeel"* was born. I am thankful to my brothers and my sisters for their love and support during my stay in Denmark.

Thesis consists of a summary report and four research papers, written during the period of September 2013 to September 2016. Four research papers are published in international peer-reviewed scientific journals.

Muhammad Adeel Nasser Sohal
Aalborg University, October 31, 2016

Abstract

The wettability alteration process depends on the formation water composition, crude oil chemistry, reservoir temperature, rock surface mineralogy and composition of the injected water. The study of all the parameters is important to understand their role in wettability alteration mechanisms, but injected water chemistry is the only that can be tuned at reservoir scale. Therefore, this study principally focused on the investigation of water chemistry effects on wettability including: a) effect of potential scale forming ions on initial wetting conditions, b) effect of ionic composition and strength, c) influence of temperature, d) impact of oxyanions concentration, and e) interfacial tension.

This study used flotation to measure wettability. Comparisons of wettability trends measured by flotation with imbibition showed flotation produced similar results. The experiments used Dan chalk, reservoir oil and synthetic brines were performed at 23, 50 and 100^{o}C. The flotation technique directly measures the wettability and physically separates oil wet rock from water wet rock. The resulting measurement is expressed as % water wet grains. A flotation wettability index (FWI) was defined and works in the same way as Amott wettability index by expressing the wetting condition with a numerical value between completely oil-wet (-1) and water-wet (+1). The technique also allows determination of the amount of oil retained on water-wet surfaces after wettability alteration. The retained oil offers additional information on the wettability alteration mechanisms compared to other wettability measurement techniques.

The experimental results show that changing water chemistry can improve the oil wetness or water wetness. The first effect, improving oil wetting, was found to be associated with an ionic composition, specifically addition of oxyanions, while reducing the ionic strength (dilution) improved the water-wet conditions of the crude-oil-brine (CBR) system. The addition of the oxyanions sulfate and borate shifted the wettability to more oil wet. All the brines had Ca and Mg present so we could not isolate any specific effects associated with the cations. Sulfate was temperature sensitive with little shift at 23 and 50^{o}C as concentration increased, but at 100^{o}C the wettability shift was pronounced from neutral to oil wet. Borate showed less temperature sensitivity and less ability to shift wettability. The wettability shift for both oxyanions was proportional to concentration. Dilution of the brines increased the water-wet conditions up to 10-fold dilution, but further dilutions did not increase water wetting. Dilution changed wettability for formation brines from -0.50 to -0.75 (oil wet) to -0.25 & 0.0. Increase in temperature shifted the CBR system towards more oil wet for all the brines tested including the brines without sulfate or borate. The wettability shifted from near neutral-wet to more oil-wet conditions when the temperature increased from 23^{o}C to 100^{o}C. The temperature effect was different depending on oxyanion. Sulfate showed no temperature effect between 23 and 50^{o}C, but showed significant shifting at 100^{o}C with greater shift to oil wet with increasing sulfate concentration. In contrast, borate showed a systematic increase in oil wetting as temperature increased.

The interfacial tension (IFT) between crude oil and advanced fluids was measured at 23 and 90^{o}C. IFT increased for seawater and seawater without sulfate as temperature increased from 23^{o}C to 100^{o}C, but decreased for seawater with borate. The dilutions of all the brines increased the IFT at constant temperature. The lowest IFT was 11.5 mN/m, which is not low enough to improve oil recovery independently without wettability alteration.

Resumé

Det niveau til hvilket kalk vædes af enten brine eller olie afhænger af den ioniske sammensætning af brine, råolie kemi, reservoir temperatur, overflade mineralogi og sammensætning af det til water flooding injicerede vand. Studiet af alle parametre er vigtige til at forstå deres rolle i de ændringer af grænsefladerne mellem mineral, brine og olie, der skyldes injektion af modificeret havvand med henblik på forøget olieudvinding. Imidlertid er netop vandets kemiske sammensætning den eneste, der kan afstemmes ved reservoir skala. Derfor er dette studium primært fokuseret på at undersøge de vandkemiske effekter på befugtelighed af kalkmineraler, herunder: a) Indflydelsen af potentielt precipitat dannende ioner på de eksisterende befugtnings betingelser. b) effekten af den ioniske sammensætning af det anvendte vand og dets styrke til at gøre kalken mere vandmættet c) indflydelse af temperatur, d) virkningen af oxyanioners koncentration, og e) grænsefladespændingen. Denne undersøgelse anvendte flotation til at måle niveauet af befugtning af calciumkarbonat. Forsøgene anvendte Dan Kalk, reservoir olie og syntetiske saltopløsninger (brines) og blev udført ved 23, 50 og 100^{o}C. Den pågældende flotation teknik måler direkte befugtningen og adskiller fysisk olie befugtede partikler fra vand befugtede partikler. Den resulterende måling udtrykkes som % vand våde partikler. Et flotation befugtningsevne indeks (FWI) blev defineret og fungerer på samme måde som Amott befugtningsevne indeks ved at udtrykke befugtning tilstand med en numerisk værdi mellem helt olie-våd (-1) og vand-våd (1). Teknikken tillader også bestemmelse af mængden af olie, der beholdes på ellers vand-våde overflader efter ændring af befugtningsidentitet. Den tilbageværende olie giver yderligere oplysninger om styrken mellem forekommende oliekomponenter og vandmættet kalk. De eksperimentelle resultater viser, at skiftende vand kemi kan variere olie befugtning eller vand befugtning på calciumkarbonatoverflader. Den første virkning, formindsket oliebefugtning, viste sig at være forbundet med en ionisk sammensætning, specifikt tilsætning af oxyanioner og samtidig reduktion af ionstyrken gennem fortynding dermed resulterende i forbedrede vand-våde betingelser for karbonat-råolie-saltvand (CBR) systemet. Tilsætningen af oxyanionerne sulfat og borat flyttede befugteligheden til mere olie våd. Alle brinetyper havde Ca og Mg til stede, så man ikke kunne isolere specifikke virkninger forbundet med disse kationer. Sulfat var temperaturfølsomt med lille forskydning ved 23 og 50^{o}C, efterhånden som koncentrationen øges, men ved 100^{o}C var der et skift fra udtalt neutral våd til olie våd. Borat viste mindre temperaturfølsomhed og mindre mulighed for at skifte befugtelighed. Muligheden for skift af befugtningstype for begge oxyanioner var proportional med koncentrationen. Fortynding af saltopløsninger øgede de vandvåde betingelser op til 10 ganges fortynding, men yderligere fortyndinger forøgede ikke vand befugtning. Fortynding ændrede befugtningsevnen i af brine fra -0,50 til -0,75 (olie våd) til -0,25 0,0 (neutral våd). Stigning i temperatur flyttede CBR-systemet i retning af mere olie våd for alle de testede brines uden sulfat eller borat indhold. Befugtningsmuligheden skiftede fra nær neutral-våd til mere olie-våd betingelser, når temperaturen steg fra 23^{o}C til 100^{o}C. Temperaturens effekt på befugtningstendensen var forskellig afhængigt af typen af oxyanion. Sulfat viste ingen temperatur effekt mellem 23 og 50^{o}C, men viste signifikant forskydning ved 100^{o}C med større skift til olie våd med stigende sulfat koncentration. I modsætning hertil udviste borat en systematisk forøgelse oliebefugtning, efterhånden som temperaturen øges. Grænsefladespændingen (IFT) mellem råolie og de ionmodificerede brinetyper blev målt ved 23 og 90^{o}C. IFT steg for havvand og havvand uden sulfat, som temperaturen steg fra 23^{o}C til 100^{o}C, men faldt for havvand med borat. Fortyndinger af alle saltopløsninger (brines) øgede IFT ved konstant temperatur. Den laveste IFT var 11,5 mN / m, hvilket ikke er lavt nok til at forbedre olieudvinding selvstændigt uden at ændre befugtning til mere vand-våd.

Thesis Details

Thesis Title:	Wettability Modication in Chalk: Systematic Evaluation of Salinity, Brine Composition and Temperature Effects
Ph.D. Student:	Muhammad Adeel Nasser Sohal
Supervisors:	Prof. Erik Gydsen Søgaard, Aalborg University, Denmark Dr. Geoffrey Thyne, Engineered Salinity, Wyoming, USA

Main body of the thesis consist of a summary report and the following journal articles.

[A] Sohal, M. Adeel, Geoffrey Thyne, and Erik G. Søgaard. "Review of recovery mechanisms of ionically modified waterflood in carbonate reservoirs." Energy & Fuels 30.3 (2016): 1904-1914.

[B] Sohal, Muhammad Adeel Nasser, Geoffrey Thyne, and Erik Gydesen Søgaard. "A novel application of the flotation technique to measure the wettability changes by ionically modified water for improved oil recovery in carbonates." Energy Fuels 2016 30 (8), 6306-6320.

[C] Sohal, Muhammad Adeel Nasser, Sergey Kucheryavskiy, Geoffrey Thyne, and Erik Gydesen Søgaard. "Study of ionically modified water performance in carbonates by multivariate data analysis supplemented with necessary measurements." Journal of Energy & Fuels (under review).

[D] Sohal, Muhammad Adeel Nasser, Geoffrey Thyne, and Erik Gydesen Søgaard. "Effect of temperature on wettability and optimum wetting conditions for maximum oil recovery in carbonate reservoir system." Journal of Energy & Fuels (under review).

The thesis has been submitted for assessment in partial fulfillment of the PhD degree. It is based on the submitted and published scientific papers which are listed above. Parts of the papers are used directly or indirectly in the extended summary report of the thesis. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the faculty. The thesis is not in its present form acceptable for open publication but only in limited and closed circulation as copyright may not be ensured.

Contents

I Thesis Frame Work and Background 1

List of Figures

List of Tables

Nomenclature

γ_{ow}	Oil water interfacial tension
γ_{so}	Solid oil interfacial tension
γ_{sw}	Solid water interfacial tension
$\hbar$	Planck constant (m^2 kg/s)
κ^{-1}	Debye length (nm)
λ	London wavelength (m^{-1})
λ^{-}	Characteristic thickness of hydration layer (Å)
ϕ	Porosity
Π	Disjoining pressure (kPa)
Ψ_o	Surface potential (mV)
σ_o	Surface charge density (C/m^2)
θ	Contact angle
v_e	Plasma frequency of free electron gas (Hz)
ε_1	Static dielectric constant (permitvity) for medium 1
ε_2	Static dielectric constant (permitvity) for medium 2
ε_3	Static dielectric constant (permitvity) for medium 3
I_o	Decay length of structural component (0.05 nm)
$>\mathrm{CaOH}^{o}$	Neutral exposed calcium surface site
$>\mathrm{CaOH}_2^{+}$	Protonated exposed calcium surface site of $CaCO_3$
$>\mathrm{CaSO}_4^{-}$	Adsorption of sulfate ion at exposed calcium surface site of $CaCO_3$

$>CO_3H^o$	Neutral exposed carbonate surface site
Π_E	Electrostatic component of disjoining pressure
Π_M	Molecular component of disjoining pressure
Π_S	Structural component of disjoining pressure
A	Hamaker constant (J)
A_d	Adhesion
A_k	Structural force coefficient (Pa)
AFM	Atomic force microscopy
ANOVA	Analysis of variance
AOR	Additional oil recovery
CBR	Crude brine rock
DIW	De-ionized water
DLVO	Derjaguin, Landau, Verwey, and Overbeek
e	Electron charge 1.60×10^{-19} Coulomb
EDL	Electrical double layer
EFW	Ekofisk formation water
EOR	Enhanced oil recovery
FTIR	Fourier transform infrared spectroscopy
FW	Formation water
FWI	Flotation wetting index
G	Gibbs free energy (kJ)
h	Thin aqueous film (EDL) thickness (nm)
IEP	Iso-electric point
IFT	Interfacial tension (mN/m)
IHP	Inner Helmholtz plane
k_{abs}	Absolute permeability
k_B	Boltzman constant (J/K)

k_{eo}	Oil effective permeability
k_{ew}	Water effective permeability
k_{ro}	Oil relative permeability
k_{rw}	Water relative permeability
LSW	Low salinity water
ME(II)	Divalent metal cations
n_1	Refractive index of first phase
n_2	Refractive index of second phase
n_3	Refractive index of third phase
NMR	Nuclear magnetic resonance
OHP	Outer Helmholtz plane
OOIP	Original oil in place
Pc	Capillary pressure
PCA	Principal component analysis
PCs	Principle components
PDAs	Potential determining anions
PDIs	Potential determining ions
PLS-R	Partial least squares regression
R_1 & R_2	Principle orthogonal radii of total mean curvature of a sphere
r_t	Radius of the pore or capillary tube
RMSE	Root mean square error
ROS	Remaining oil saturation
S_o	Oil saturation
S_{oi}	Initial oil saturation
S_{or}	Residual oil saturation
S_w	Water saturation
S_{wi}	Initial water saturation

SW	Seawater
SW*0S	Seawater without sulfate
SW*B*0S	Seawater enriched with borate instead of sulfate
T	Temperature (K)
TDS	Total dissolved solids (g/l)
V_b	Bulk volume of core
W_{ext}	External work
WAG	Water alternating gas
WI	Wetting index
XRF	X-ray fluorescence

Part I

Thesis Frame Work and Background

Introduction

1 Introduction

1.1 Background and Motivation

More than 60% of the world's oil reservers are stored in carbonates (chalk, limestone and dolomites) [1]. Carbonates tend to be oil-wet or mixed-wet and usually include abundant natural fractures [2]. Ultimate oil recovery factor is less often than 25% [3] in these reservoirs as illustrated in Figure 1.1. In the North Sea much of the total produced oil is recovered from naturally fractured chalk. The matrix porosity of chalk is quite high whereas the matrix permeability is very low. Thus, the fluid flow takes place mainly through the fractures. The ultimate oil recovery by reservoir energy and waterflood is relatively low and about 2/3 of the original oil in place (OOIP) is left behind in the reservoir. This significant amount of residual oil is the challenging target of enhanced oil recovery (EOR) methods.

Increasing global energy demand and declining rate of new oil discoveries are the primary motives behind development of economically viable EOR methods to recover this retained remaining oil. Reservoir lithology and fluid properties served as a screening tool in the selection of an EOR technique for trapped oil recovery [4]. The most commonly implemented EOR methods in carbonates based on the global EOR database are shown in Figure 1.2.

According to this database 10% of the total applied methods are gas injection in carbonates [5]. These methods are still considered very attractive for carbonates but mainly depends on the availability of cheap gas (e.g., CO_2) sources. The second most commonly used EOR method in carbonates are chemically based EOR methods. In chemical flooding, polymers have been successfully used for mobility control in the early stage of water injection [5]. But polymers have not been a choice for low permeability (< 5 mD) chalk reservoirs. Surfactants have also been tested to improve the oil recovery by changing wettability and IFT but this approach is growing very slowly [6, 7]. Moreover, chemical EOR methods are the most expensive to apply at field scale. Thermal methods are 3% of the total applied EOR methods & proved insignificant in carbonates. According to the North Sea EOR survey five major EOR technologies have been tested in the region and different forms of the water alternating gas (WAG) injection have been applied extensively [8]. But CO_2 was not the part of these WAG processes due to limited availability. Waterflooding is the best possible choice for North Sea chalk reservoirs to improve the oil recovery based on the above information. It is the cheapest and most widely used method to replenish the reservoir energy after primary depletion. But due to oil-wet nature of chalk reservoirs traditional waterflooding is not a plausible option to improve the recovery. Oil wetness of chalk hinders the water imbibition through fractures and large amounts (> 75%) of oil remain trapped in matrix interstices. Hence, the total recovered oil at secondary stage is much less than the oil which is normally recovered in clastic rocks as a result of conventional waterflood.

Injection of the seawater in Ekofisk chalk oil field of North Sea recovered more oil that is normally produced by the established waterflood technique. This fact turned the focus to identify the hidden mechanisms behind the additional produced oil in chalk [9, 10]. So, after extensive research work that spans two decades it was revealed that it is the water chemistry which caused this enormous recovery [11–22]. Composition of the injected water that is different from formation brine brings the CBR system into a new equilibrium state that favors the improved oil recovery. There are some auxiliary benefits of chemically tuned water technology compared to other EOR methods [23, 24]. (1) Low capital investment and operating cost make it the most economical EOR method.

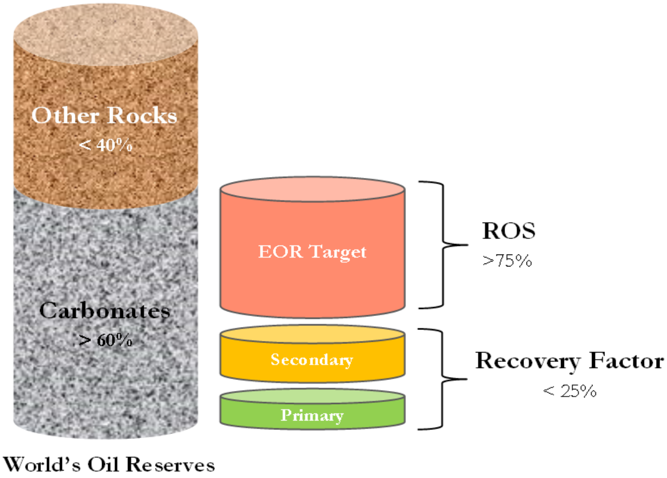


Fig. 1.1: Percent of total oil reserves and recovery factor in carbonates. Data Source: [1]

(2) It can be applied at any recovery stage of the reservoir but sooner is better. (3) There are no environmental issues associated with this technique. (4) The return on the investment is high given the low capital and low operating costs. The lab based results for imbibition and coreflooding experiments proved successful and point toward shifts in wettability to more water-wet conditions as the cause. But months are required to complete one set of experiments using one CBR system. Understanding different CBR systems and the conditions required to optimize wettability in the reservoir would require years of experiments. Therefore, a fast robust and reliable method was needed to achieve this task in a reasonable time frame. In order to meet this challenge, a new method of wettability measurement using flotation has been investigated and tested in this PhD study.

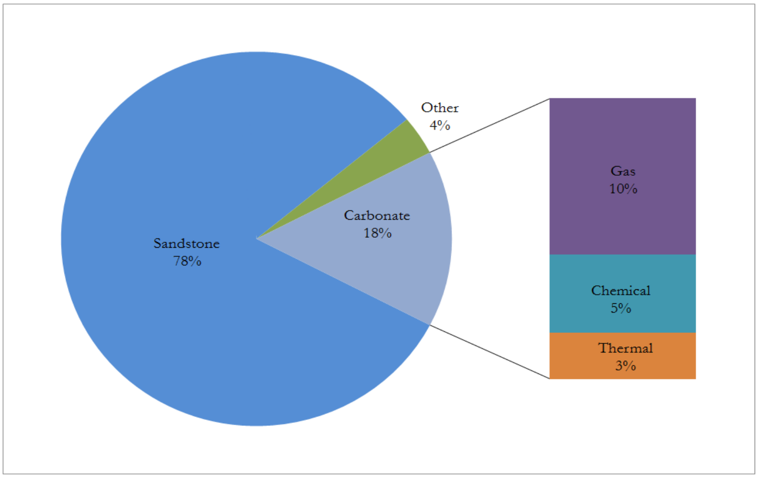


Fig. 1.2: Type of EOR field projects in carbonates. Data Source: [5]

1.2 Objectives and Contribution

The enhanced oil recovery by ionically modified water is primarily based on the tuning of reservoir wettability. All the efforts have been made to adjust wettability by changing the injected or imbibed water chemistry. A substantial amount of data was produced in last two decades by using different CBR systems under a variety of operating conditions. In all these studies wettability changes have been mainly judged by production. Additional amount of oil coupled with wettability measurements by contact angles, chromatography and nuclear magnetic resonance (NMR) techniques. In chromatography, adsorption of ions onto rock surface from injected water are calculated by chemical analysis of effluent. Then, the difference in concentration is converted to water-wet surface area to find the change in wettability. In NMR technique pore coupling is calculated by protons relaxation time which caused by dissolution. The connectivity of micro and macro pores improves permeability which is considered the effect of wettability alteration. But, no single study has been reported to date in which the wettability alteration has been directly measured at pore or grain scale level. Basically, there was a need of an innovative method that could directly measure the wettability alteration. So, a flotation method which quantitatively measured the wettability changes was developed. This is a major contribution of this PhD research work. I began this work with, a carbonate coreflood and imbibition experiments database was built based on published journal and conference papers. The database was analyzed with the help of multivariate data analysis technique to identify the factors that influence additional oil recovery (AOR) the most. Finally, flotation experiments were conducted with reservoir oil to determine the effect of temperature, brine composition and dilution on chalk wettability and briefly summarized as:

- What is the role of potential scale forming ions on wetting conditions? Understanding of the initial wetting condition is crucial for optimum oil recovery. The optimum wetting conditions exist close to the neutral-wet conditions. So, it depends on the initial wetting conditions in which direction (oil-wet to water-wet or vice versa) system wettability has to be shifted for maximum oil recovery. Petroleum reservoirs brines contain solute such as barium that form scales and are usually excluded from experiments.

- Separate the effect of low salinity and potential determining ions (PDIs) on wettability. This effect has been a challenge for most experiments that injecting/imbibing ionically modified water. Anhydrite dissolution is an internal source of ${SO_4}^{2-}$ and considered a key feature of low salinity chemical mechanisms behind EOR in carbonates. This sulfate works in the same way together with Ca^{2+}, and Mg^{2+} as externally injected sulfate. It has always been a debate in literature that the additional produced oil is a low salinity effect or PDIs effect.

- Assess the relative and individual potential of ${SO_4}^{2-}$ and ${BO_3}^{3-}$ (potential anions) to change the chalk wetting conditions; investigation of the optimum concentration to maximize the wettability shift.

- The role of different concentrations of potential anions on IFT and how temperature effects the IFT of different brines? Is there any relation between IFT and wettability?

- Effect of temperature on chalk wettability.

1.3 Thesis Outline

The work presented in this research is organized into following two major parts.

- Introduction
- Papers

The introduction consists of several sections that give a basic overview of the research. The second part consist of four published and submitted journal articles that were produced during the PhD. A schematic overview of the experimental work that explains the sequence of attained objectives is shown in Figure 1.3.

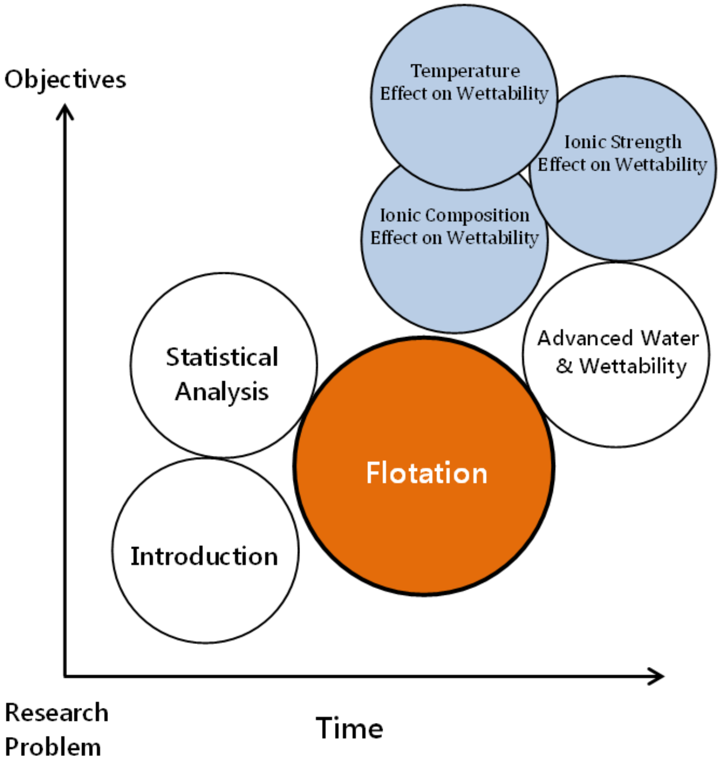


Fig. 1.3: A schematic overview of the PhD work.

1.3.1 Introduction

The details of all the sections included in introduction part are given as following.

- **Section 1** gives a brief introduction of the project and describes its industrial importance. It also delineate the goals and objectives of the work.
- **Section 2** provides a literature review of the advanced water in carbonates. In this section, history of the advanced water and the lab processes that have been used to test its potential are described. It also describes the current identified recovery mechanisms of advanced water and some auxiliary effects.
- **Section 3** begins with morphology and composition of the chalk including its crystal system, surface chemistry and surface charge. Then interaction of chalk with crude oil and brine is described with some brief explanation of its physical properties. At the end role of initial wetting conditions in shifting of wettability from oil-wet to water-wet or vice versa are discussed for optimum oil recovery.
- **Section 4** elaborates the material and methods that were used to achieve the desired outcomes. It explains all the methods that were used to characterize the physical and chemical properties of rock, crude and brine. The importance and need to measure physicochemical properties of these parameters and their role in overall wettability process is discussed. In this section importance and significance of flotation technique is explained that has been used to conduct this study. Its the flotation that made it possible to achieve this massive list of objectives in such a short period of time otherwise years were required to accomplish it.
- **Section 5** explains all the produced results and discusses them in the light of already published results. It also describes new findings that have not been discussed in the literature so far. The role of potential scale forming ions in the restoration of initial wettability and why their exclusion in lab experiment would mislead the wettability alteration process at the field scale level. The role of each individual potential anion to change wettability at different operating conditions. The comparison of borate and sulfate anions potential to alter the wettability. The contribution of dilution or low salinity compared to potential anions and total dissolved solids (TDS) to improve water-wetness at different temperatures. The increasing concentration of sulfate make the chalk more oil-wet instead of water-wet. The overall effect of temperature on

wetting conditions in the used CBR system. The influence of temperature and potential anions on IFT. Finally the relation between IFT and wettability are described.

- **Section 6** provides the overall conclusions and recommendations for future work.

1.3.2 Papers

The following is a list of published and submitted journal articles that were produced from this PhD study and authored by the author of this thesis.

[A] Sohal, M. Adeel, Geoffrey Thyne, and Erik G. Søgaard. ″Review of recovery mechanisms of ionically modified waterflood in carbonate reservoirs.″ Energy & Fuels 30.3 (2016): 1904-1914.

[B] Sohal, Muhammad Adeel Nasser, Geoffrey Thyne, and Erik Gydesen Søgaard. ″A novel application of the flotation technique to measure the wettability changes by ionically modified water for improved oil recovery in carbonates.″ Energy & Fuels 2016 30 (8), 6306-6320.

[C] Sohal, Muhammad Adeel Nasser, Sergey Kucheryavskiy, Geoffrey Thyne, and Erik Gydesen Søgaard. ″Study of ionically modified water performance in carbonates by multivariate data analysis supplemented with necessary measurements.″ Energy & Fuels (2016).

[D] Sohal, Muhammad Adeel Nasser, Geoffrey Thyne, and Erik Gydesen Søgaard. ″Effect of temperature on wettability and optimum wetting conditions for maximum oil recovery in carbonate reservoir system.″ Energy & Fuels (2016).

2 Advanced Water

The injected water that has different ionic strength and composition compared to formation water (FW) is known as advanced water. So, injection of advanced water in oil reservoirs to improve oil recovery is an EOR process according to the definition of Larry W. Lake [25]. It has been known by different names like LoSal^{TM}, designer water, smart water, ionically modified water and advanced ion management in the published literature. But basically its name was derived from traditional waterflood which is a well established recovery method. In carbonates the first large scale application was the injection of seawater in Ekofisk chalk oil field of the North Sea [9, 10]. Injection of seawater recovered more oil that was expected by traditional waterflood. Since, that a substantial amount of lab experiments have been performed to understand the hidden recovery mechanisms which caused this unexpected additional recovery. So, in most of the published studies wettability alteration has been found a principle cause of this effect [12, 14, 15, 20, 21, 26–38]. Therefore, advanced water has been identified as a wettability alteration agent. In lab recovery experiments composition of the advanced water tuned in two different ways to improve the water wetness as depicted in Figure 2.1. In one approach ionic strength of the injected water was decreased. While in the other approach ionic composition of the injected water was adjusted [39]. Therefore, recovery experiments were performed using brines of different ionic compositions and strength at different operating conditions.

2.1 Recovery Process

The recovery processes that were used in laboratory studies to test the potential of both ionic composition and ionic strength of imbibed/injected water are classified into imbibition and coreflood experiments. In low-permeability fractured carbonate reservoirs where most of the oil is stored in rock matrix, imbibition technique was preferred. In imbibition experiments capillarity is the principle driving force which allows the fluid to imbibe in matrix micropores. Water imbibed more strongly in core plugs as water wetness improved and displaced the oil in both counter and co-current fashion. The mechanism is exactly the same for coreflooding in fractured carbonates but the only difference is, fluid is forced to displace the oil. Whereas, in imbibition it is driven only by capillary force. It is the force that originates by the combined effect of IFT, wettability and pore geometry. In the petroleum literature it is commonly written as capillary pressure (Pc).

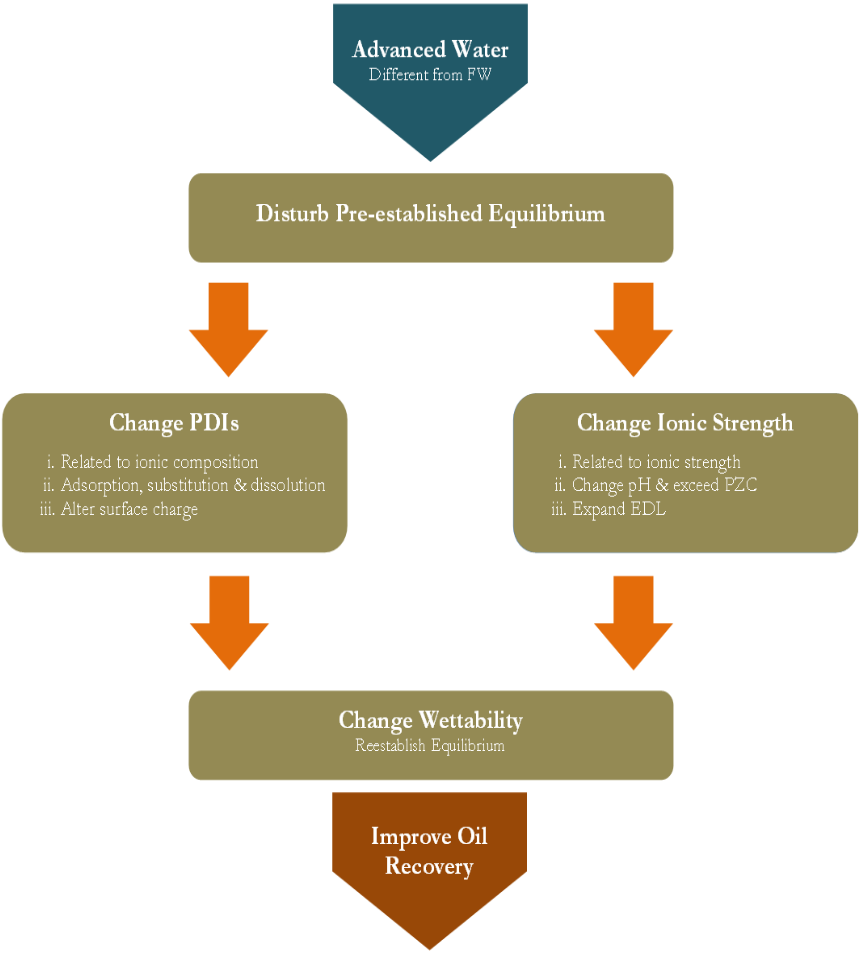


Fig. 2.1: Flowchart of advanced water wettability alteration mechanisms in carbonates.

2.1.1 Imbibition

The absorption of a wetting phase into a porous rock without applying pressure is known as spontaneous imbibition otherwise imbibition. In this process wetting phase displaced the non-wetting phase under the influence of capillary force. It is used to measure the initial rock wettability in the lab [40] and actively displace the non-wetting phase from matrix of a fractured rock. Imbibition was used to test the potential of advanced water in outcrop chalk mainly by Austad and co-workers [22, 26, 27, 29]. They focused on the ionic composition aspect of the advanced water by changing the concentrations of Ca^{2+}, Mg^{2+} and $SO_4{}^{2-}$ in synthetic seawater at different operating conditions. But, Al-Harrasi et al. [14] recovered less oil by advanced water in coreflooding experiments compared to imbibition. Therefore, they recommended not to use imbibition data at field scale especially for fractured rocks.

2.1.2 Coreflooding

In this process fluid(s) is forcefully injected in a core to displace the oil. It is the most commonly used lab method to test the potential of advanced water and best matched with the field simulations. It provides the relative permeability and capillary pressure data that is used in reservoir simulation models. The coreflood experiments are mostly performed at reservoir injection rates ($\backsim$ 1 ft/day) and incorporate the imbibition effect. But in short core plugs it may induce capillary end effects and lead to overestimation of remaining oil saturation (ROS) [41]. The recommended procedure is to use a short period of high injection rate to overcome this problem as critical capillary number or bond number for oil-wet carbonates is quite high. But this effect is decreased as wettability changes to water-wet conditions [14]. Zhang and Sarma [38] concluded from low salinity soaking experiments that decrease in injection rates amplify the low salinity water (LSW) effect.

2.2 Recovery Mechanisms

According to Sohal et al. [24] the most popular oil recovery mechanisms in carbonates could be divided into following two categories. The contribution of each of these proposed mechanisms according to the published studies is shown in Figure 2.2. In majority of the observed results, EOR is attributed to improved water wetness [20, 22, 32, 35, 36] but in a number of studies it was linked to neutral-wet state [15, 42, 43].

1. Wettability alteration
    - (a) Ionic composition effect
    - (b) Ionic strength effect
2. Auxiliary effects
    - (a) Rock dissolution
    - (b) IFT reduction
    - (c) pH & viscosity change

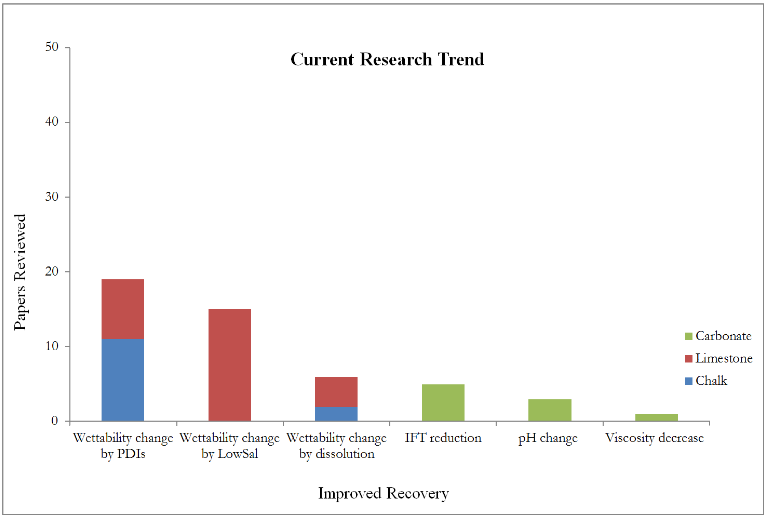


Fig. 2.2: Proposed recovery mechanisms of improved oil recovery in carbonates by advanced water. Source: [24]

2.2.1 Ionic Composition

Advanced water enriched with potential determining ions (Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$, $PO_4{}^{3-}$, $BO_3{}^{3-}$) but lower in salinity compared to formation brine is often injected/imbibed in carbonate rock experiments. It brings the rock-brine interface into a new equilibrium state by ions adsorption, substitution and dissolution or precipitation on mineral surface. This can alter the carbonate surface charge to negative which was initially positive at reservoir conditions ($pH \leq 7$) [44]. Because, the crude oil brine interface is negatively charged at $pH > 3.5$ as found in zeta potential measurements by Buckley [45]. Otherwise, there would be a strong electrostatic attraction between two oppositely charged interfaces that bring the oil in direct contact with the mineral surface as stated by Hirasaki and Zhang [46].

Sulfate or other potential anions adsorb at positively charged surface sites ($>Ca^{+}$) while Mg^{2+} and Ca^{2+} adsorb at negatively charged surface sites ($>CO_3^{-}$) of the carbonate. In carbonate formation water concentration of sulfate and other potential anions is relatively low. These surface sites were partially occupied by the crude oil acidic and basic components at original reservoir conditions in oil-wet carbonates. PDIs compete for the surface sites with the oil polar components. When the water chemistry changes these ions may adsorb to mineral surface specifically or through the intervening layer of water molecules (solvation shell) and also form complexes with released polar components. In ionic composition aspect of the advanced water, role of pH change may not that significant because the surface binding sites are crowded by PDIs compared to H^+ and OH^- ions. But relatively less important than low salinity aspect because some of the H^+ and OH^- ions also react with ${SO_4}^{2-}$, Ca^{2+}, and Mg^{2+} as described by Mahani et al. [47].

It was proposed in chalk imbibition experiments that sulfate from seawater adsorbed at the surface and replaced the carboxylic acid group then Ca^{2+} complex with it [21]. Zhang el al. [21] also claimed the process became more active at high temperature then Mg^{2+} replaced the Ca^{2+}. Strand et al. [19] observed the same and also found that adsorption of ${SO_4}^{2-}$ increased with temperature in chromatographic separation technique. The same effect was observed in Stevns Klint chalk by increasing temperature and removing NaCl from synthetic seawater [27, 32–34]. The same chalk was used in all of the experiments, however, Ferno et al. [48] observed that different chalks did not respond the same way. They used different chalks (Stevns Klint, Rørdal and Niobrara) in imbibition experiments to test the sulfate concentration effect and observed additional oil recovery only in Stevns Klint. The sulfate effect was smaller compared to previous studies and seems lithology dependent. In some carbonate coreflooding studies Mg^{2+} and SO_4^{2-} were found to be more active than Ca^{2+} [2, 49]. Gupta et al. [12] recovered 15 to 20% more oil using borate and phosphate ions in synthetic seawater compared to sulfate in Middle Eastern limestone coreflood experiments.

There is another effect associated with PDIs that is the ionic strength. The concentration of PDIs in injected/imbibed brine influence the ionic strength more than monovalent ions. So, under higher ionic strength and valence electrical double layer shrinks dramatically as described by Crittenden et al. [50]. So, this aspect of the ionic composition of injected/imbibed brine promotes the oil wetting.

2.2.2 Ionic Strength

This aspect of the advanced water deal with fluid species and chiefly low salinity or diluted seawater is injected/imbibed in carbonates. It is believed that it disturbs the pre-established equilibrium and brings the CBR system into a new state by stabilizing the thin water film between oil and rock phases. It also dissolves minerals like anhydrite ($CaSO_4$) and calcite ($CaCO_3$) to counteract the decrease in concentration of dissolved ions. Stability of the water film can be enhanced by expansion of electrical double layer (EDL). Thick water film effect the electrostatic component that increases the disjoining pressure, so this way water wetting improves. Mineral dissolution may improve oil recovery by increasing the connectivity of the pores so that the reservoir becomes more permeable to flow [51, 52]. The pH change significantly influence the surface charge characteristics. Mahani et al. [53] measured more negative charge (zeta potential) on chalk surface with 25 times diluted seawater (25dSW) compared to SW at the entire range of reservoir pH. The more negativity of surface charge with 25dSW than SW at same pH may be linked to relative less amount of available PDIs. Yousef et al. [36] injected 2, 10, 20 and 100 times diluted seawater in carbonate reservoir cores and produced substantial amount of additional oil. Al Harrasi et al. [14] also recovered 5 to 21% additional oil by injecting 2, 5, 10 and 100 times diluted versions of synthetic reservoir brine in imbibition and coreflood experiments on Middle Eastern carbonate reservoir core plugs. Shehata et al. [49] produced additional oil by injecting deionized water (DIW) after seawater in long (20 in.) limestone reservoir core. Gupta et al. [12] recovered 7-9% of OOIP by decreasing the hardness (divalent cations) of injected water.

Electrical Double Layer

When a charged surface contacts the electrolyte solution, counter ions (ions of opposite charge) from the solution approach it as a result of coulomb attraction to neutralize it. But this phenomenon also creates an osmotic or diffusive force that works in the opposite fashion. Consequently, layers of ions along the interface develop that are different from the bulk solution [54]. This special structure of ions distributed along the interface is known as electrical double layer as shown in Figure 2.3. The EDL comprises of two layers that are known as the Stern and diffuse layers. The Stern layer mostly consist of counter ions and is very compact with a thickness of $\sim$1 nm [55]. The counter ions specifically adsorb in the inner part of Stern layer which constitute the inner Helmholtz plane (IHP). The next layer consists of non-specifically adsorbed ions and an imaginary plane that passes through their centers is known as outer Helmholtz plane (OHP). This plane is considered the starting point of the diffuse layer which is also called Gouy-Chapman layer. The thickness of diffuse layer is Debye length ($1/\kappa$) and it ends where surface effect is not felt by the ions of bulk solution. Debye length is highly dependent on concentration of electrolyte in solution. The extent/thickness of the double layer decreases with increasing electrolyte concentration because more ions are available to shield the surface charge. The ions of higher valence (e.g., trivalent) screen the surface charge more effectively and compress it to a greater extent than monovalent ions [56]. The next imaginary plane is the shear or slipping plane and located inside the EDL at a distance approximately equal to the thickness of the stationary Stern layer [55]. The potential difference between this plane & bulk solution is known as zeta-potential (ζ) and is always less than the surface potential (ψ_o). Basically, it measures the type and net amount of charge on the surface after adsorption of ions bounded in shear plane.

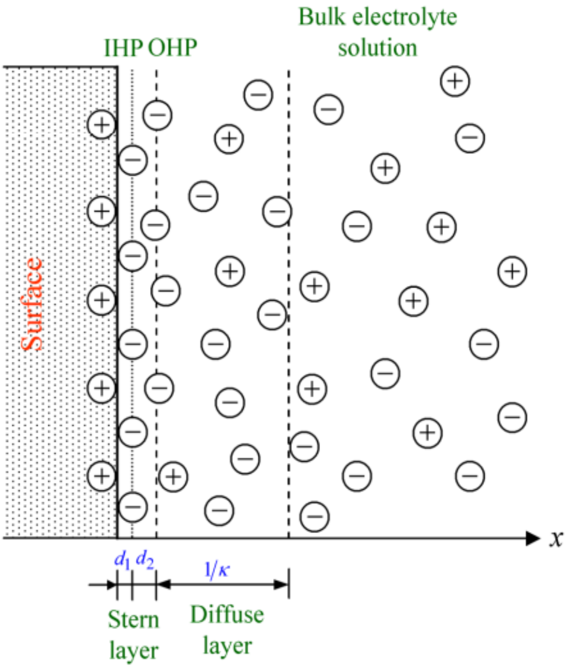


Fig. 2.3: Electrical double layer of ions. Source: [55]

Disjoining Pressure

The disjoining pressure is the change in Gibbs free energy with distance and per unit area at constant temperature, volume and cross-sectional area as described in Equation 2.1 [57]. But, Starov et al. [58] defined it more simply, it's the surface force per unit area. Basically, it is the excess pressure within aqueous film wiht respect to the outer bulk liquid. It tends to disjoin or separate the two interfaces while a negative disjoining pressure attracts the two interfaces [59].

$$\Pi = -\frac{1}{A}.\frac{\partial G}{\partial x}\bigg|_{A,T,V} \tag{2.1}$$

The thickness range of disjoining (or surface forces) action $t_s = 10^{-5}$ cm [58]. The most common forces that contribute to the stability of thin water film on a solid surface and constitute the disjoining pressure are as following.

Table 2.1: Hydration number and hydration radii for different ions. Source: [60]

Ions	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Li^{+}	Cl^{-}	PO_4^{3-}	SO_4^{2-}
Hydration Number	8.5	8	6.6	5.9	5	3.69	-	-
Hydration Radius (nm)	0.412	0.428	0.331	0.358	0.36	0.332	0.339	0.3

$$\left.\begin{array}{l}\text{1. Molecular/Dispersion component } (\Pi_M)\\ \text{2. Electrostatic component } (\Pi_E)\end{array}\right\}\text{DLVO}$$

3. Structural component (Π_S)

The classical theory of Derjaguin and Landau (1941), and Verwey and Overbeek (1948), DLVO explains the stability of colloids in suspension as well as static and kinetics of wetting. According to this theory the total disjoining pressure is the sum of the electrostatic repulsive and Van Der Waals attractive forces. But later it was understood that these two components are insufficient for explaining the phenomenon, therefore strong repulsive (structural) forces that are very active at small separations (<5 nm) were included. These forces are caused by hydrated cations which are bound to negative surface sites. The strength and range of repulsion is calculated by hydration number. This number for most common ions that found in pore water of petroleum reservoir rocks with decreasing order is given in Table 2.1.

The molecular component (Van Der Waals Forces) describes the interaction of neutral molecules at relatively large distances (10^{-8}cm) and its contribution to disjoining pressure can be calculated by Hamaker constant. But the original equation of Hamaker constant works only in vacuum (without any intervening media) and it was modified by Lifshitz in 1956. So, properties of the three phase system were added as dielectric constants (ε) and refractive indices (n) as shown in Equation 2.2 according to Israelachvili [61].

$$\mathrm{A} \approx \frac{3}{4}\kappa_B T \frac{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)} + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{\sqrt{n_1^2+n_3^2}\sqrt{n_2^2+n_3^2}\left(\sqrt{n_1^2+n_3^2}+\sqrt{n_2^2+n_3^2}\right)} \tag{2.2}$$

The contribution of molecular component to disjoining pressure isotherm for petroleum reservoirs is given by Equation 2.3. It is inversely proportional to the cube of film thickness and its valid when film thickness is small compared to characteristic wavelength of adsorption spectra of the bodies. The relationship between disjoining pressure and film thickness is known as the disjoining pressure isotherm [62].

$$\Pi_M(h) = \frac{-A(15.96\frac{h}{\lambda}+2)}{12\pi h^3(1+5.32\frac{h}{\lambda})^2} \tag{2.3}$$

The electrostatic component is related to the overlapping of two charged surfaces when the separation between them is less compared to their EDL. If the double layers of both surfaces keep same kind of charge then repulsion appears as a result of their overlapping. Thus, electrostatic component is positive otherwise negative. The electrostatic component as shown in Equation 2.4 derived from [61] in published results [62, 63].

$$\Pi_E(h) = -\left(\frac{\sigma_{o_i}^2}{2\varepsilon\varepsilon_o}\right) + 4n_o kT\left[sinh\left(\frac{y_{oi}}{2}\right)\right]^2 \tag{2.4}$$

$$y_{oi} = \frac{e\Psi_{oi}}{kT} \tag{2.5}$$

The structural component of disjoining pressure caused by the orientation of water molecules in the vicinity of brine-solid interface as stated by Starov et al. [58]. Depending on the surface charge, positive or negative, part of water molecules are attracted and the next layer follows the same pattern. This way water molecules orientate themselves in a finite thin layer (hydration layer) where the structure of water dipoles are different from bulk aqueous phase. However, thermal fluctuations will try to destroy this orientation. So far, only semiempirical equations exist that links structural component of the disjoining pressure with the thickness of liquid film as shown in Equation 2.6 [62].

$$\Pi_S(h) = A_k e^{\left(\frac{-h}{l_o}\right)} \tag{2.6}$$

Currently, it is assumed that the disjoining pressure of thin aqueous films is equal to the sum of following three components as shown in Equation 2.7.

$$\Pi_{DisjoiningPressure} = \Pi_M + \Pi_E + \Pi_S \tag{2.7}$$

Schematic representation of a disjoining pressure isotherm is shown in Figure 2.4. Thick black curve represents the net result of all the involved forces. The disjoining pressure would be negative if the net resultant force is attractive and that is possible when TDS is high or there is a high concentration of divalent ions compress the EDL [64]. Moreover, increase in electrolyte concentration diminish the range of electrostatic repulsion and van der Waals attractions become more important [65].

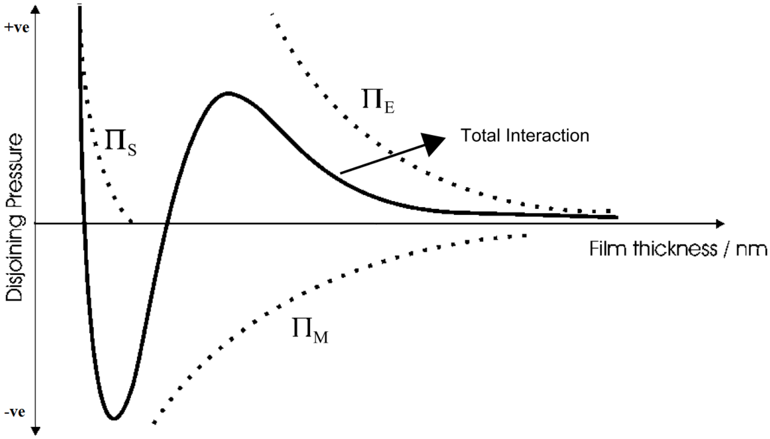


Fig. 2.4: A schematic representation of a disjoining pressure isotherm. Source: [66]

2.3 Auxiliary Effects

There are some supplementary effects of advanced water which may influence the performance of the EOR process. In the low salinity aspect of the advanced water, scaling problems could be avoided as the concentration of PDIs is relatively low. The scale formation reduces the reservoir pore throats and can cause serious flow restrictions. In the ionic composition aspect of the advanced water, sulfate in injected water can readily precipitate with barium, strontium, and calcium in formation water to produce barite ($BaSO_4$), celestine ($SrSO_4$), and anhydrite ($CaSO_4$) scales, respectively [24]. Moreover, higher concentrations of sulfate, such as in seawater, may convert sweet oil fields into sour oil fields and produce highly corrosive and toxic H_2S gas [67].

2.3.1 Mineral Dissolution

Advanced water with low ionic strength may dissolve the $CaCO_3$ and $CaSO_4$ and change the wetting conditions. So, dissolution of surface species possibly takes place at water-wet sites as the oil-wet sites are covered with thin oil layer/drops. It has been observed in carbonate coreflooding experiments that the microscopic dissolution enhanced the connectivity between micro and macropores [35, 52]. So, dissolution was linked to increased reservoir permeability which improved the oil recovery through ease of flow. Gupta et al. [12] desorbed small amounts of oil by injecting soft water in reservoir carbonate core plugs and linked additional recovery to rock dissolution. Kasha et al. [68] observed calcite dissolution in the form of clear rhombohedral crystals in seawater using atomic force microscopy (AFM) and optical microscope. This enhanced the oil snap-off mechanism to recover oil as observed by Gandomkar and Rahimpour [69]. Zahid et al. [70] suggested that the rock dissolution is one of the possible reasons to improve oil recovery in Stevns Klint chalk cores by injecting seawater. Hiorth et al. [71] found in geochemical modeling that the calcite dissolution is a possible reason of enhanced oil recovery in chalk imbibition and coreflooding experiments that were performed by Austad and coworkers.

2.3.2 pH

In the published results pH value of injected/imbibed advanced water is mostly greater than 7. The high pH values increase the oil recovery by changing the carbonate surface charge. It has been observed in zeta potential measurements increasing the pH value of advanced water changes the surface charge of both rock-brine and oil-brine interfaces [45, 47, 53]. Mahani et al. [47] described that the surface charge by low ionic strength brine is mainly controlled by the concentration of H^+ and OH^- (pH) ions as amount of PDIs is relatively less.

Dubey and Doe [72] stated that if oil-brine and mineral-brine interfaces have like charges, an electrostatic force of repulsion increases the disjoining pressure and results in a thicker water film bounded by two interfaces. This situation is more likely to produce water-wet surfaces. Conversely, if two interfaces have opposite charges, then electrostatic interaction is attractive and thins the water film which promotes the oil-wet surfaces. Takamura and Chow [73] explained that increasing pH beyond the carbonate iso-electric point (IEP) makes the solid-water interface change from positive to negative and the charge at the oil-water interface is already negative at that pH. Thus, a repulsive electrostatic force emerges that maintains a high disjoining pressure and expands the EDL to support the water-wet conditions.

2.3.3 IFT

Interfacial tension is the force of repulsion that exist between interface of two immiscible fluids. If it is reduced by several orders of magnitude compared to normal reservoir conditions, the oil and water become miscible enhancing oil dispacement. IFT is directly related to capillary pressure and negatively affects the capillary-dominated flow if decreased [7, 74]. In published research the IFT between advanced water and crude oil is always greater than one mN/m or dyne/cm whereas the value required for complete miscible displacement is in the range of 10^{-2} to 10^{-3} mN/m or dyne/cm. Therefore, it seems that the IFT value which is achieved by advanced water does not contribute in improved oil recovery.

Al-Attar et al. [15] found that interfacial tension may not be responsible for the increase in oil recovery due to the injection of low-salinity water. Sohal et al. [75] determined that there is a positive correlation between wettability alteration and increase in IFT by advanced water. But the positive correlation between IFT and improvement in water-wet conditions held only for a certain level of dilution in their CBR system. The effect of different ions in advanced water on IFT has also been investigated but none of these studies linked decrease in IFT with EOR [14, 76–80].

3 Chalk Reservoirs

The chalk oil reservoirs of the North Sea are located in the central Graben structure that is located between Denmark, Norway and the United Kingdom. These chalk formations of the north west Europe were deposited during late Cretaceous to early Paleocene (100-61 Ma) and largely consists of thick (2000 m) intervals of white chalk sediments [81]. The deposition of chalk was accompanied by rise of ridges, domes and anticlines due to halokinetic movements and tectonic inversion of the pre-Cretaceous extensional faults [82]. These activities extensively fractured the chalk formations and developed structural traps for hydrocarbon storage. These fractures enable the commercial flow of hydrocarbons because otherwise matrix permeability is too low. The hydrocarbon fields are all located over thick areas of Kimmeridge and Oxford clay source rocks. So, hydrocarbons entered the chalk reservoirs through fractures as a result of buoyancy and/or pressure generated by shales [83]. Early diagentic changes such as compaction by dewatering and loss of aragonite reduced porosity. But the filling with hydrocarbons and Mg^{2+} in pore water retarded the diagenesis to decrease porosity. As a result all chalk fields show anomalously high values of porosity ($\sim$ 50%). However, the permeability is in the range of 1-10 mD due to small pore throat sizes that range from 0.1-1 microns in diameter [83, 84].

3.1 Morphology and Composition

Chalk forms microporous reservoir structure and primarily consists of minute skeletal remains of coccolithophorid algae. These calcareous nannofossils are composed of individual plates called coccoliths. These coccoliths form clay to silt sized spherical bodies which are called coccospheres as shown in Figure 3.1. Complete coccospheres are occasionally found in chalk but majority of them are broken into single cocoliths or laths (0.5 to 3μm). North Sea chalk primarily deposited as a result of pelagic rain of cocoliths in marine environment. It deposited on sea floor as a highly water saturated calcareous ooze. These thixotropic chalk oozes had no unbalanced electric charges or platy interlock, hence there was little or no cohesion. Therefore, remobilization and downslope movement of the incohesive chalk material deposited as allochthonous blocks. The other calcareous material that found in North Sea chalk reservoirs are derived from calcispheres, foraminifers, macrofossil mollusc debris, bryozoan, brachiopos debris and ostracods [81].

Central graben chalk is primarily composed of calcite coccoliths (>96%) and low in magnesium content which improved its chemical stability to pore fluids [83]. Chalk also contains other non-biogenic terrigenous fractions like clay and quartz but these two constituents comprise less than 5% of the rock. So, chalk is very pure and mechanically very weak. Cretaceous chalks are dom-

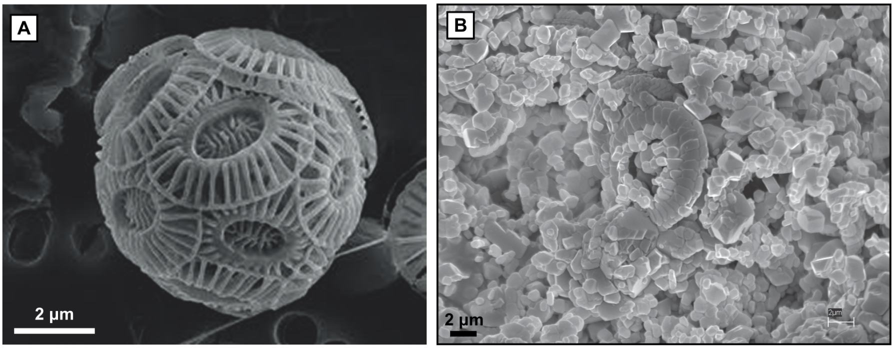


Fig. 3.1: (A) Coccolithophore. (B) Scanning-electron micrographs showing fragments of Coccoliths from the Ekofisk formation. Source: [81]

inantly composed of low-magnesium calcite, that is calcite with less than 5 mole percent Mg in the lattice [85]. The other calcium carbonate minerals such as aragonite and high-magnesium calcite, are less stable at ordinary temperatures and pressures than calcite.

3.1.1 Crystal Structure

Chalk is mainly composed of calcite crystals that are held together either by organic material or through mechanical interlocking. The other two polymorphs of $CaCO_3$ are aragonite and vaterite that are less common in chalk than calcite. These three polymorphs differ by the arrangement of CO_3 ions in their crystal structures. The shape of the calcite crystals depends on temperature, pressure and solution composition during formation. The crystal structure of calcite is rhombohedral as determined using X-ray diffraction by Bragg in 1914 [86]. The rhombohedral unit cell of calcite is shown in Figure 3.2 and defined by hexagonal axes. The hexagonal unit cell has carbonate ions lying flat on the basal plane and has a = b = 4.990Å and c = 17.061Å $\alpha = \beta = 90^o$ and $\gamma = 120^o$ [87]. The calcium and carbonate ions in calcite are held together through ionic bonding. Calcite mostly cleaves along the lowest energy plane $10\bar{1}4$ when an external force is applied. Cleavage along the $10\bar{1}4$ plane splits calcite in a characteristic rhombohedral shape. This plane contains equal number of Ca^{2+} and CO_3^{2-} ions which produce neutral surface charge. It is the most stable and low energy surface with highest density of ions compared to other possible neutral planes [88].

3.1.2 Surface Chemistry

The calcite surface unit cell is rectangular, containing two calcium and two carbonate ions. But carbonate units, CO_3^{2-} form the basic building blocks of

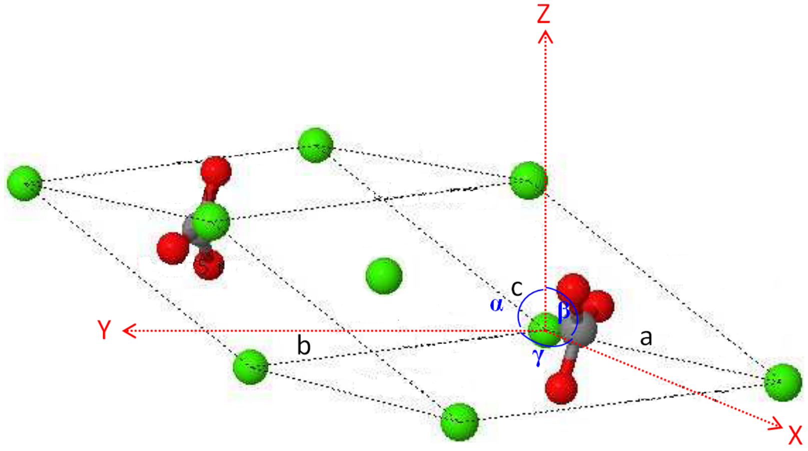


Fig. 3.2: Calcite rhombohedral unit cell, calcium (Ca) ions are green, carbon (C) are grey and oxygen (O) are red. Source: [87]

all type of carbonate minerals, to which the divalent metal ions (Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, etc.) are coordinated [89]. The crystallographic density of $>Ca^{+}$, and $>CO_3^{-}$ sites on $10\bar{1}4$ face is 4.95 nm^{-2} or 8.22 x 10^{-6} mole/m^2 [90]. The pristine surface of a carbonate mineral consists of oxygen atoms which are either coordinated to carbon atoms within the carbonate groups or to metal ions. Exposed metal and carbonate sites along the water interface are coordinated to oxygen and hydrogen of OH^{-} and H^{+} groups or water molecules respectively. The surface sites may deviate from 1:1 stoichiometry if faces other than $10\bar{1}4$ are exposed. The exposed surface sites at face, edge and corner of a cleavage rohmbohedron are shown in Figure 3.3 [89]. The coordination of exposed carbonate and metal groups to bulk lattice depends on its position at corner, edge or face. Therefore, charge neutralization is position dependent. For example, Ca^{2+} in the bulk lattice has six fold coordination with oxygen which means it neutralizes 1/3 charge per bond as shown in Figure 3.4. But at the exposed face, edge and corner it looses one, two and three coordinations that put +1/3, +2/3 and +1 charge respectively. Similarly, CO_3^{2-} group will loose the same number of coordination with Ca^{2+} and acquire -1/3, -2/3 and -1 charge on face, edge and corner sites. Thus, polar surfaces are unstable and commonly adsorb ions to diminish the dipole moment.

3.2 Chalk Water Interaction

It has been investigated with electrokinetic experiments that the surface charge of calcite in aqueous conditions is controlled by Ca^{2+} and CO_3^{2-} surface ions [92]. Theoretical calculations show that $10\bar{1}4$ is the dominating cleaved

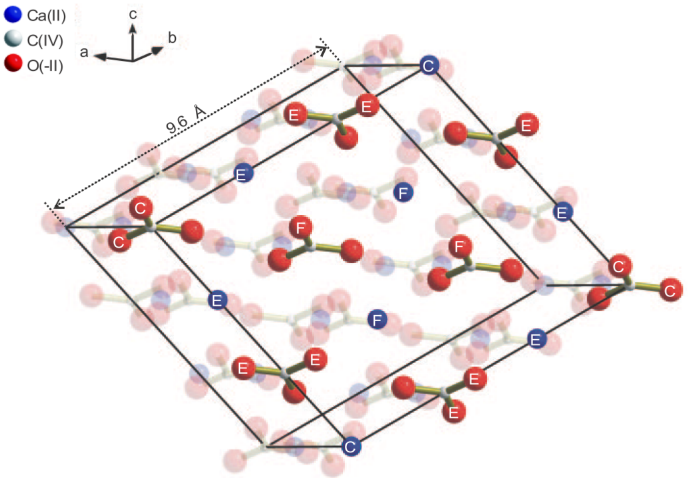


Fig. 3.3: A smallest rhombohedral crystal of calcite, consisting of $10\bar{1}4$ faces. For the front face, atoms are opaque and corner (C), edge (E) and face (F) sites are indicated for the oxygen in CO_3 and the calcium atom that form CaO groups (oxygen atoms for the latter are not shown). Source: [89]

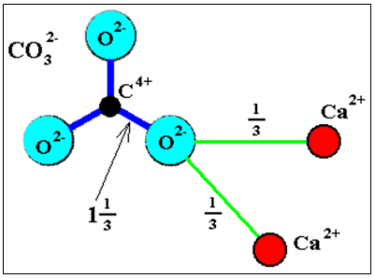


Fig. 3.4: Charge distribution between CO_3^{2-} and Ca^{2+} groups in calcite crystal lattice. Source: [91]

plane and has lowest surface energy. The adsorption of water on $10\bar{1}4$ surface of calcite follow a distinct order which is confirmed by theoretical and experimental studies. The first ordered layer adsorbed at a height of 2.3±0.1Å from surface plane and the second one weakly adsorbed at 3.45±0.2Å as shown in Figure 3.5 [89]. The structure of these water layers was significantly different from bulk water up to 10Å from solid surface. X-ray and IR spectroscopic measurements suggested that water dissociates into H^+ and OH^- ions on calcite surface [93]. Therefore, hydroxyl ions on calcium and protonation of carbonate groups produce >$CaOH^o$ and >CO_3H^o surface sites at hydrated calcite crystals respectively. Bond valance calculations and energy minimization of calcite surfaces favor the molecularly or non-dissociatively adsorbed water. Hydrogen adsorbed to the surface are generally considered the part of solid surface rather than the Stern layer [94]. Surface titrations of carbonates at different values of divalent metal cations (Me(II)= Ca^{2+}, Mg^{2+}, Mn^{2+}, etc.) in bulk solution; adsorb onto the mineral surface and significantly effect the surface charge [89].

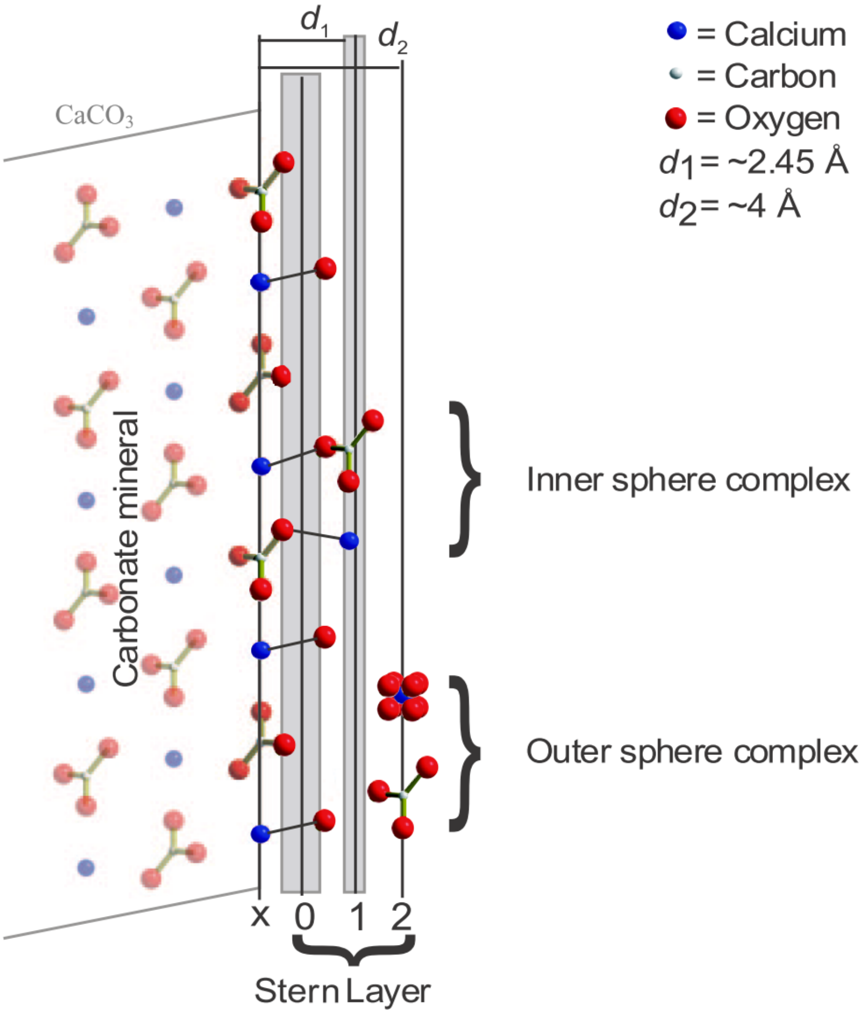


Fig. 3.5: A sketch of crystal plane truncation (x) location and the three planes that together describe the Stern layer: the 0-plane, cutting through the oxygen atoms in surface and adsorbed carbonate groups and hydroxylated surface metal ions; the 1-plane for inner sphere complexes; and the 2-plane for outer sphere complexation. Atoms are not to scale. Source: [89]

3.2.1 Surface Charge

Carbonate surfaces develop electrical charge on contact with electrolyte solutions for three reasons. (1) Complexation reactions between the surface and dissolved species. (2) Lattice imperfections as well as substitution with in the crystal lattice. (3) Dissolution of surface groups. The exposed calcite surface along $10\bar{1}4$ face consists of two exposed surface sites $>Ca^+$ and $>CO_3^-$ as described above. The different modes of adsorption/adhesion of ions, organic molecules and complexes are illustrated in Figure 3.6. This aspect of the surface charge is pH dependent. The two surface sites neutralize on hydration at a pH of zero surface charge (pH_{zpc}) as shown in Equation (3.1) & (3.2) [95]. The stabilization of surface charge also depends on brine composition. In a highly saline brine surface sites are crowded with PDIs (Ca^{2+}, Mg^{2+},CO_3^{2-}, SO_4^{2-}, etc.) and these ions compete for surface sites. Therefore, pH change does not effect surface charge significantly and it is mainly controlled by adsorption of brine species.

$$>CaOH^o + H^+ \leftrightarrow \ >CaOH_2^+ \tag{3.1}$$

$$>CO_3H^o \ \leftrightarrow \ >CO_3^- + H^+ \tag{3.2}$$

The other calcite surfaces/planes $01\bar{1}2$ & $000\bar{1}$ are polar. They terminate either by a layer of calcium ions or a layer of carbonate ions, leading to a positively or negatively charged surfaces respectively. The dissolution rate of calcite depends on a number of factors, these include the pH and composition of the dissolving solution. Dissolution rates have been observed to be high in solutions with low pH. The solution pH gradually increases as dissolution occurs leading to slower dissolution [96].

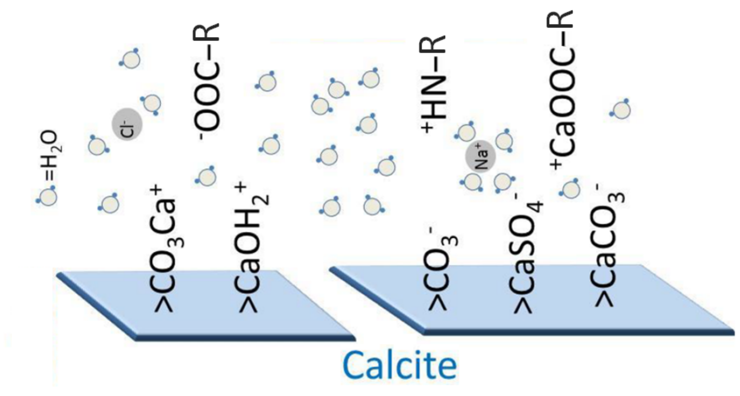


Fig. 3.6: Calcite surface charge along $10\bar{1}4$ face with adsorption of pore fluid species. Source: [97]

3.3 Chalk Oil Interaction

Crude oil invades the pores of reservoir rock that are already coated with water and try to directly attach the rock surfaces. So, depending on the balance of surface forces which based on oil, solid and brine compositions, water film hinders its direct adhesion. Hence, direct oil adhesion depends on instability of water film as explained in the previous section. Water film stability has important association with subsequent alteration of wetting in a reservoir. The role of crude oil components that are likely to adsorb and alter the wettability are discussed in this section. Crude oil is a mixture of naturally occurring hydrocarbons and other organic materials. It composed of hundreds of components ranging in size from one carbon atom to one hundred or even more. Therefore, crude oils are often characterized by dividing the components into few groups based on physical and chemical separations as described by Buckley, 1997 [98]. Not all of the components of crude oil adhere or adsorb to the exposed solid surfaces. Only polar heteroatoms (such as organic acids & bases) and the asphaltenes wet the solid surfaces. Therefore, according to standard procedure for separating asphaltenes from crude oils (ASTM D2007-80); it can be divided into following two groups and shown in Figure 3.7.

- Maltenes
- Asphaltenes

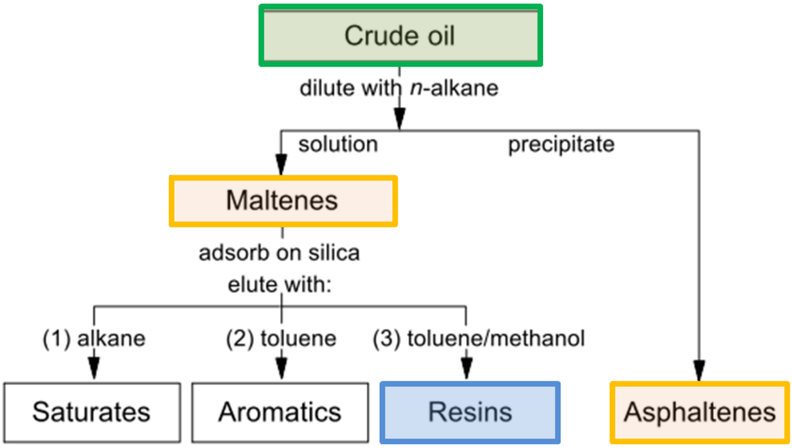


Fig. 3.7: SARA separation scheme which divides crude oil into saturates, aromatics, resins (or polars) and asphaltenes. Source: [98]

3.3.1 Asphaltenes

Asphaltenes are the heaviest, most polar and insoluble in low molecular weight paraffins. If one volume of crude oil is mixed with 40 volumes of *n*-pentane, the resulting precipitate is defined as the asphaltene fraction of the crude oil as described by Buckley, 1997 [98]. She also reported that the chemical composition of asphaltenes depends on the source of crude oil and the method by which it was separated from the remaining crude oil. The molecular weight, polarity and aromaticity of asphaltenes depends on the diluting agents (n-alkane) as explained by Buckley, 1997 [98] and shown in Figure 3.8. Speight, 1991 [99] introduced an empirical formula $C_{100}H_{115}N_1S_3O_2$ to calculate the ratio of elements in the *n*-pentane precipitate of asphaltenes. He stated the degree of aromaticity depends on carbon to hydrogen ratio; oxygen and sulfur content are more variable compared to nitrogen. He found that the extent of polar functionality of these molecules contributes to oil/brine interface.

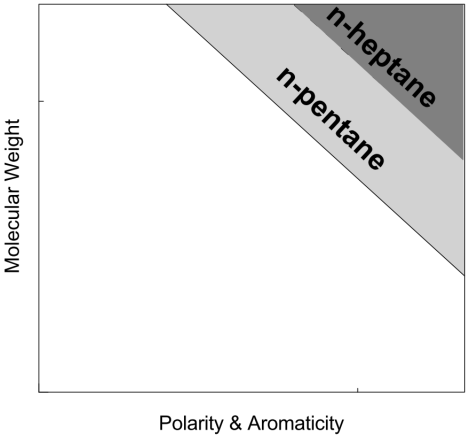


Fig. 3.8: Characteristics of asphaltenes precipitated by n-pentane or n-heptane. Source: [98]

3.3.2 Maltenes

The part of crude oil that is soluble in solvent (n-pentane or n-hexane) is known as maltenes. Maltenes can be separated chromatographically as saturates, aromatics and resins on the basis of polarity. Saturates are open chain or cyclic alkanes and least polar fraction of hydrocarbons followed by aromatics. The final fraction of maltenes is called resins (polars) and consists of hydrocarbons with small percentages of polar heteroatoms (other than hydrogen and carbon, mainly oxygen, nitrogen and sulfur). The hydrocarbon compounds that contain oxygen are considered organic acids whereas nitrogen containing compounds are considered bases. Chiefly, these compounds of crude oil show an affinity to adhere to rock surface and turn it oil-wet. It was confirmed by Andersen et al. [100] that the species containing carboxylic acids functionality adsorb at the oil-water interface by Fourier transform infrared spectroscopy (FTIR) spectra.

3.4 Wettability

In the petroleum reservoir system the forces that are active between liquid and solid surfaces are equally important as the interfacial or surface tensions between liquid-liquid or liquid-gas phases respectively. Solids and liquids are ubiquitously in contact in the reservoir so intermolecular interactions are active between the phases and can change the surface properties. The liquid wet (adhere) to the solid surface if adhesive forces are stronger than the cohesive forces. The degree of wetting (wettability) is determined by the balance of these two forces and can be summarized as following according to Abhijit [101].

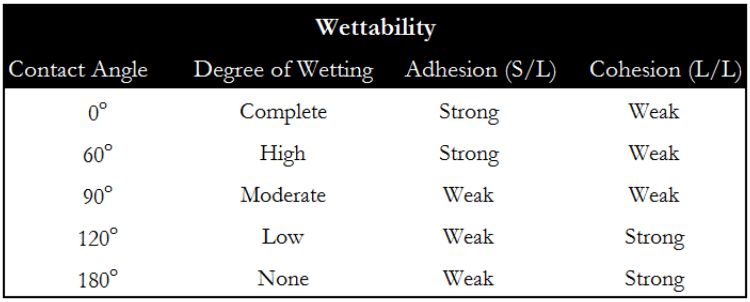
- The relative ability of a fluid to spread on a solid surface in the presence of another fluid, e.g., water spreading more than oil and vice versa.
- The tendency of surfaces to be preferentially wet by one fluid phase e.g., water or oil preferentially wetting.
- The tendency of one fluid of a fluid pair (oil-water) to coat the surface of a solid spontaneously.

To characterize the wettability, how strongly or weakly a liquid adhere to the solid surface, the contact angle is measured. So, as the tendency of a liquid drop to spread out over a solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability as described by Shafrin et al. [102]. The contact angle based on cohesive (liquid/liquid) and adhesive (solid/liquid) forces according to [103] is shown in Table 3.1. Njobuenwu et al. [104] explained different wetting conditions based on contact angle of a liquid drop on solid surface as shown in Figure 3.9.

3.4.1 Contact Angle Measurements

The adhesion (A_d) is a function of interfacial tension and determines the wetting tendencies of fluid rock system as firstly explained by Benner et al. [105]. The adhesion between two immiscible fluids (oil & water) present in the pores of a reservoir rock is defined by Equation 3.3 according to Abhijit [101]. The contact angle between liquid and solid surface is shown in Figure 3.10 and measured through the denser liquid phase by convention. The contact angle

Table 3.1: Contact angles based on cohesive (liquid/liquid) and adhesive (solid/liquid) forces. Source: [103]



Wettability			
Contact Angle	Degree of Wetting	Adhesion (S/L)	Cohesion (L/L)
0°	Complete	Strong	Weak
60°	High	Strong	Weak
90°	Moderate	Weak	Weak
120°	Low	Weak	Strong
180°	None	Weak	Strong

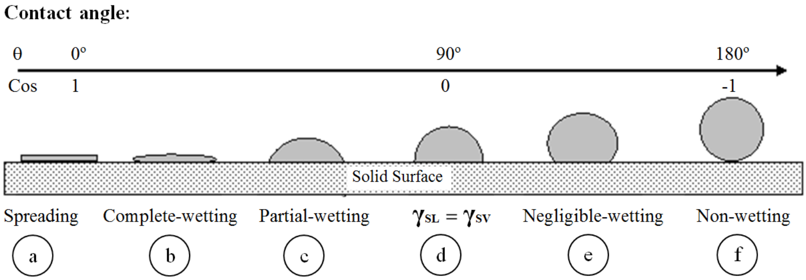


Fig. 3.9: Different wetting behaviours based on contact angles of a liquid drop with solid surface. Source: [104]

can be measured by rearranging the Young's Equation 3.4. If the oil-water interfacial tension and contact angle with solid surface is known, then A_d can be calculated by Equation 3.5. It is positive for water-wet ($\theta = 0^o$) system and negative for oil-wet ($\theta = 180^o$) system whereas zero ($\theta = 90^o$) indicates the equal affinity of both phases to solid surface.
Where, γ_{so} is the interfacial tension between solid-oil interface, γ_{sw} is the interfacial tension between solid-water interface and γ_{ow} is the interfacial tension between oil-water interface.

$$A_d = \gamma_{so} - \gamma_{sw} \tag{3.3}$$

$$cos\theta_{ow} = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} \tag{3.4}$$

$$A_d = \gamma_{ow} cos\theta_{ow} \tag{3.5}$$

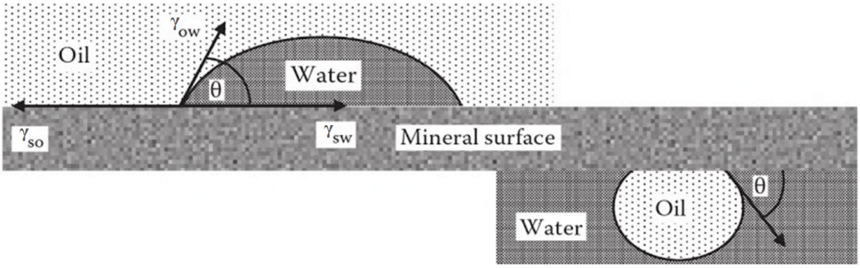


Fig. 3.10: Schematic of oil and water contact with solid surface together with acive interfacial forces. Source: [101]

3.4.2 Wettability Types

The contact angle is based on the affinity of both solid and liquid phases which originates from their compositions. The composition of solid phase (rock) depends on the rock forming minerals. Therefore, on the basis of mineralogical composition of a rock it was classified into following two main types by Radke et al. [106].

- Homogeneous
- Heterogeneous

If the entire rock surface has a uniform molecular affinity towards the liquid phase then it is considered homogeneous and classified by Craig [107] as water-wet, intermediate-wet and oil-wet on the basis of contact angles as described above.
When the rock surface shows nonuniform molecular affinity towards the liquid phases then it is considered heterogeneous and divided into following two types by Craig [107].

- ○ In petroleum systems if the larger rock pores are oil-wet and only smaller pores are water-wet then the rock is considered *mixed-wet* as described by Faruk [108].
- ○ But if the rock has sites of different surface characteristics due to the differences in the type of surface mineralogy it is known as *fractional-wet* as explianed by Faruk [108].

Several methods in the literature has been described to measure the wettability changes but in this research only flotation is used and explained below. It can quantitatively measure the fraction of rock that has affinity for water (brine) phase and oil phase.

3.5 Significance of Wettability

The wettability of a porous medium controls the relative distribution of fluids in pores and considerably influences the fluid flow. The important reservoir properties such a capillary pressure, relative permeability, connate water saturation and residual oil saturation depend on the wettability. It is used to judge, describe or explain the behavior of a particular recovery process such as the performance of a waterflood. For example, core analysis frequently show oil recoveries from preferentially water-wet rock are significantly greater than those from preferentially oil-wet rock as explained by Bobek et al. [109]. In reservoir calculations/simulations wettability is indirectly added through relative permeability and capillary pressure functions that control the fluid flow.

3.5.1 The Effect of Wettability on Pc & Kr

The pressure difference across a curved interface between two immiscible fluids is known as the capillary pressure and caused by wettability and interfacial tension [110]. The curvature of the interface depends on the contact angle of the wetting fluid, stronger wetting deepens the curvature. A spherical interface exists between oil and water phases inside a capillary tube (analogus to a pore geometry) as shown in Figure 3.11 and capillary pressure across this curved interface is calculated by Equation 3.6. A deeply curved interface shows higher pressure difference (Pc) between two immiscible fluids. Aderson [110] investigated the effect of wettability on capillary pressure by calculating the change in external work required to displace the oil in strongly water-wet and oil-wet rocks as given in Equation (3.7) & (3.8).

$$P_c = \gamma_{ow}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \frac{2\gamma_{ow}\cos\theta}{r_t} \tag{3.6}$$

$$\Delta W_{ext} = -\phi V_b \int_{S_{w1}}^{S_{w2}} P_c dS_w \tag{3.7}$$

$$\Delta W_{ext} = \phi V_b \int_{S_{o1}}^{S_{o2}} P_c dS_o \tag{3.8}$$

Where, θ is the contact angle, γ_{ow} the oil water interfacial tension, R_1 & R_2 are the principle orthogonal radii of total mean curvature of a sphere, r_t the radius of the capillary tube (pore), V_b the bulk volume of core, ϕ the porosity, W_{ext} the external work, S_o the oil saturation and S_w is the water saturation. Anderson found that area under the drainage curve was larger for water-wet system but area under the imbibition curve for same system was relatively smaller. This shows more work is required for oil to displace the water (drainage process) in water-wet system and vice versa. When oil is

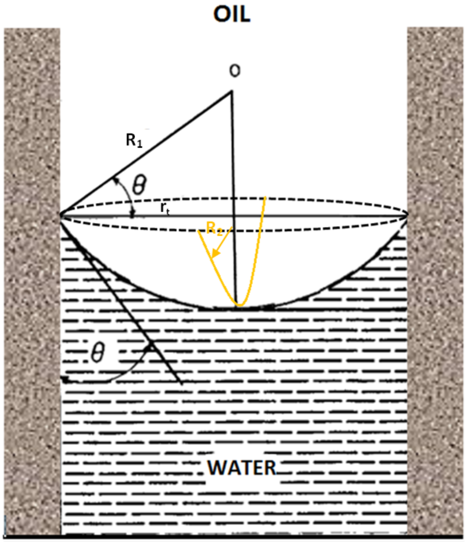


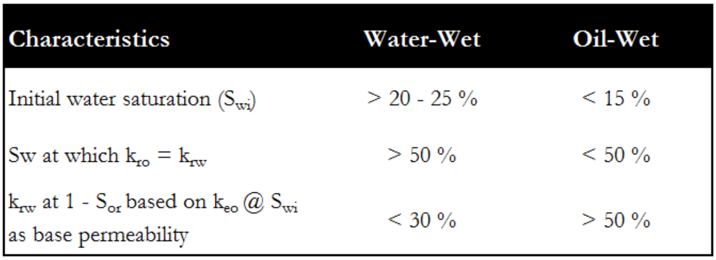
Fig. 3.11: Schematic of an oil water interface inside a capillary tube. Source: [110]

the strongly wetting fluid then role of water in a strongly water-wet system is replaced with oil. He also stated that less external work is required for neutral-wet system as area under the drainage curve is reduced because system has equal affinity for both phases. So, when strongly wet systems change to neutral-wet conditions then non-wetting phase can easily enter the system and reach the smaller pores. Therefore, residual saturation of wetting phase is always higher than the non-wetting phase.

Relative permeability is a dimensionless function of saturation and describes the simultaneous flow of immiscible fluids through the porous medium. It is usually expressed by the ratio of effective permeability to absolute permeability and written as the fraction or percentage. It is significantly effected by wettability that controls the fluid distribution in the pores. Anderson [111] stated that difference in relative permeabilities of strongly water-wet and oil-wet systems are caused by fluid distribution which based on wettability. For example, in a strongly water-wet system at initial water saturation (S_{wi}) water exists in small pores without effecting the flow of oil and effective permeability of oil (k_{eo}) often close to absolute permeability (k_{abs}). Whereas, the effective permeability of water (k_{ew}) at residual oil saturation (S_{or}) is hindered by the trapped oil ganglia in larger pores. Therefore, k_{eo} at S_{wi} is larger than k_{ew} at S_{or} in the same water-wet system. However, in a strongly oil-wet system k_{ew} at S_{or} is relatively higher than k_{eo} at S_{wi} because S_{or} is located in smaller pores in the form of a continuous film where it has little effect on flow of water. Fatt and Klikoff [112] prepared sandpacks by mixing treated and un-

treated sand grains to measure the ratio of water to oil relative permeability (k_{rw}/k_{ro}). They found k_{rw}/k_{ro} decreased as the weight fraction of oil-wet sand grains decreased from 100% to 0% at a given water saturation.
Craig [107] presented several rules of thumb that describe the differences in relative permeability characteristics of strongly water-wet and oil-wet cores as shown in Table 3.2.

Table 3.2: Rules of thumb relating wettability and relative permeability. Source: [107]



Characteristics	Water-Wet	Oil-Wet
Initial water saturation (S_{wi})	> 20 - 25 %	< 15 %
Sw at which $k_{ro} = k_{rw}$	> 50 %	< 50 %
k_{rw} at 1 - S_{or} based on k_{eo} @ S_{wi} as base permeability	< 30 %	> 50 %

3.5.2 Optimum Wettability

Importance of the wettability has been identified by several authors [113, 114] who have found that waterflood recovered more oil from water-wet rocks than oil-wet rocks. Therefore, major focus has been to improve the water wetness of reservoir cores for maximum oil recovery [19, 20, 32, 36]. But some authors [115, 116] indicated that waterflood oil recovery may be greater in intermediate-wet cores compared to either strongly water-wet or oil-wet rock cores. Thus, shifting the wettability to neutral-wet conditions improved the oil recovery to maximum level as described by [15, 42, 43]. Jadhunandan and Morrow [117] stated that the maximum oil recovery near neutral wettability is more appealing because it can be argued that capillary forces are minimized. Abhijit [101] described that higher oil recovery and low S_{or} are obtained with in the range of weakly water-wet to neutral-wet conditions as shown in Figure 3.12. Salathiel [118] stated that if oil paths are continuous in mixed-wet system water could displace oil from larger pores with little or no oil held by capillary forces in small pores. Therefore, it is imperative to know the initial wetting conditions of the reservoir rock before the starting of a wettability alteration EOR process. It will help to decide which way wettability has to be shifted for optimum recovery.

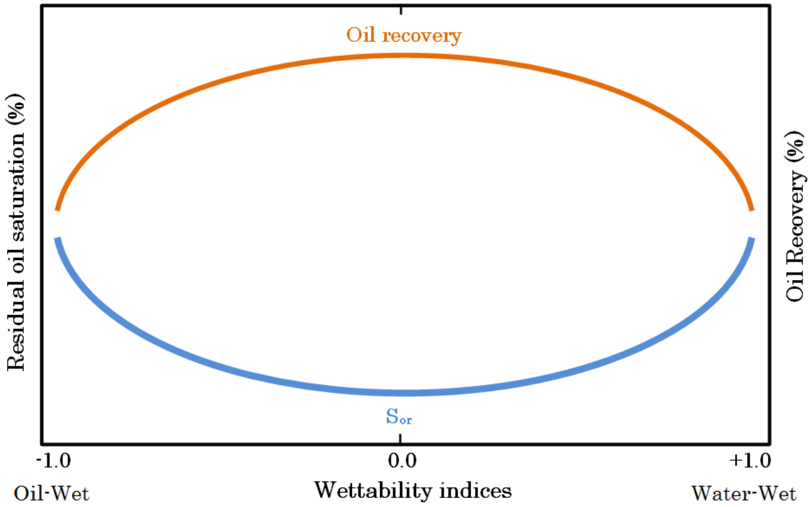


Fig. 3.12: Relationship between wettability, residual oil saturation or oil recovery. Source: [101]

4 Materials and Methods

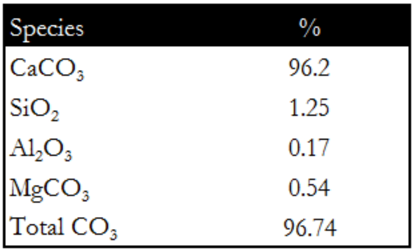
4.1 Materials

In this experimental study the effect of temperature, brines ionic compositions and strengths on chalk wettability has been investigated with the help of flotation technique. The stock tank crude oil from a chalk reservoir of the Danish North Sea was used to investigate the oil-wetting characteristics. The details of the chalk, crude oil and brines used are explained in the following sections. The description of the method (flotation) to understand the effect of above stated parameters on wettability using given CBR system is explained in methods section.

4.1.1 Dan Chalk

The outcrop Dan chalk was provided by Dankalk A/S, Denmark. It was broken into small pieces and ground with the help of a ball mill. The wettability of a reservoir system depends on rock, brine and crude oil properties. Therefore, it was important to know the chemical composition of Dan chalk to understand its contribution in overall wettability process. The elemental composition of chalk was determined by X-ray fluorescence (XRF) technique. The details of the method are stated in Sohal et al. [75] and the composition of Dan chalk is given in Table 4.1. The properties of the Dan chalk are quite similar to the coccolithic chalk oil reservoirs of the North Sea. Therefore, the results from Dan chalk could be directly extrapolated to the chalk reservoirs of the region or any other chalk reservoir with similar properties. The chalk sample that has to be used in flotation experiments must be uncontaminated (original) and dried for the accuracy of produced results. Thus, the samples that used in this study were clean and completely dried (almost zero moisture). The grain size is the second most important factor that could influence the results as explained in appendix A, so the sieving process was used to select a specific range of grain size. More than 90% of the grain sizes range between 50 to 100 μm.

Table 4.1: XRF analysis of outcrop Dan chalk. Source: [75]

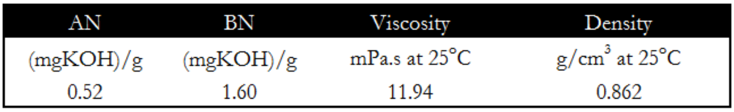


Species	%
$CaCO_3$	96.2
SiO_2	1.25
Al_2O_3	0.17
$MgCO_3$	0.54
Total CO_3	96.74

4.1.2 Crude Oil

Crude oil is a significant factor that affects the reservoir wettability. Therefore, it is imperative to accurately determine the crude oil components that influence the rock wetting characteristics. The crude oil is a mixture of naturally occurring hydrocarbons and not all of its components have affinity to adhere (wet) the rock surface. It is well-known that the polar components of crude oil wet the rock surface and consist of acidic and basic compounds [119]. Dubey and Doe [72] initially developed the method to measure the crude oil acid and base numbers that was revisited by Fan and Buckley [120]. In the latter method strong acid or base is used to neutralize the crude oil polar components and then calculated by the quantity of acid or base consumed. The stock tank crude oil from a chalk reservoir of Danish North Sea is used in this experimental study. The details of the measuring equipment as well as physical and chemical properties of the crude oil are described in Sohal et al. [75] and given in Table 4.2.

Table 4.2: Properties of the used crude oil. Source: [75]



AN	BN	Viscosity	Density
(mgKOH)/g	(mgKOH)/g	mPa.s at 25°C	g/cm^3 at 25°C
0.52	1.60	11.94	0.862

4.1.3 Brines

The composition and salinity of reservoir brine significantly affect the wetting properties of CBR system. This is the only parameter that could be tuned in ionically modified waterflood process to alter the wetting characteristics of a reservoir rock. The carbonate reservoir brines are often highly saline and rich with divalent cations. Therefore, the composition of advanced water should be compatible with pore water and must be tested by aqueous stability testing or geochemical modeling before using in coreflooding or imbibition experiments. In this experimental study synthetic brines were prepared by mixing the reagent grade salts in DIW. Compositions of the synthetic brines were taken from published studies. The details of all the methods that used to measure the properties of brines are explained in Sohal et al. [75] and given in Table 4.3. Brines are based on formation water (Valhall and Ekofisk), seawater (SW), seawater augmented with 2 to 4 times sulfate (SW*2S & SW*4S), seawater without sulfate (SW*0S) and seawater containing borate instead of sulfate (SW*B*0S). In addition 2 to 100 times dilutions of these brines were also tested (prepared by adding DIW). Potential scale forming ions Sr^{2+} and Ba^{2+} were also added separately in FW in order to understand their effect on initial wetting conditions.

Table 4.3: The ionic composition (mmol/l), ionic strength (I_c), total dissolved solids and density of all the used brines. Source: [75]

Brines	Ca^{+2}	Mg^{+2}	SO_4^{-2}	Na^+	Cl^-	HCO_3^-	K^+	Ba^{2+}	Sr^{2+}	$[B_4O_5(OH)_4]^{2-}$	I_c (mole/l)	TDS (g/l)	Density (g/cm^3)
VB	29.249	7.870	0.704	995.962	1064.559	8.928	4.695	0.000	0.000	0.000	1.113	62.798	1.041
EFW	99.922	21.889	0.000	1155.561	1423.306	3.952	7.364	1.842	8.514	0.000	1.559	83.091	1.056
EFW*0Sr	99.922	21.889	0.000	1155.561	1406.278	3.952	7.364	1.842	0.000	0.000	1.534	81.742	1.055
EFW*0Ba	99.922	21.889	0.000	1155.561	1419.622	3.952	7.364	0.000	8.514	0.000	1.554	82.708	1.056
EFW*0(Sr*Ba)	99.922	21.889	0.000	1155.561	1402.594	3.952	7.364	0.000	0.000	0.000	1.528	81.358	1.055
SW*B*0S	12.992	44.515	0.000	420.446	525.142	2.024	10.060	0.000	0.000	9.177	0.612	32.159	1.021
2D*SW*B*0S	6.496	22.257	0.000	210.223	262.571	1.012	5.030	0.000	0.000	4.589	0.306	16.079	1.009
10D*SW*B*0S	1.299	4.451	0.000	42.045	52.514	0.202	1.006	0.000	0.000	0.918	0.061	3.216	1.000
20D*SW*B*0S	0.650	2.226	0.000	21.022	26.257	0.101	0.503	0.000	0.000	0.459	0.031	1.608	1.000
100D*SW*B*0S	0.130	0.445	0.000	4.204	5.251	0.020	0.101	0.000	0.000	0.092	0.006	0.322	0.998
SW	12.992	44.515	24.007	450.107	525.142	2.024	10.060	0.000	0.000	0.000	0.657	33.392	1.022
2D*SW	6.496	22.257	12.004	225.053	262.571	1.012	5.030	0.000	0.000	0.000	0.328	16.696	1.010
10D*SW	1.299	4.451	2.401	45.011	52.514	0.202	1.006	0.000	0.000	0.000	0.066	3.339	1.000
20D*SW	0.650	2.226	1.200	22.505	26.257	0.101	0.503	0.000	0.000	0.000	0.033	1.670	0.999
100D*SW	0.130	0.445	0.240	4.501	5.251	0.020	0.101	0.000	0.000	0.000	0.007	0.334	0.997
SW*0S	12.992	44.515	0.000	460.443	583.493	2.024	10.060	0.000	0.000	0.000	0.643	33.391	1.022
2D*SW*0S	6.496	22.257	0.000	230.221	291.746	1.012	5.030	0.000	0.000	0.000	0.322	16.696	1.010
10D*SW*0S	1.299	4.451	0.000	46.044	58.349	0.202	1.006	0.000	0.000	0.000	0.064	3.339	1.000
20D*SW*0S	0.650	2.226	0.000	23.022	29.175	0.101	0.503	0.000	0.000	0.000	0.032	1.670	0.999
100D*SW*0S	0.130	0.445	0.000	4.604	5.835	0.020	0.101	0.000	0.000	0.000	0.006	0.334	0.998
SW*2S	12.992	44.515	48.015	498.121	525.142	2.024	10.060	0.000	0.000	0.000	0.729	36.802	1.025
2D*SW*2S	6.496	22.257	24.007	249.061	262.571	1.012	5.030	0.000	0.000	0.000	0.364	18.401	1.011
10D*SW*2S	1.299	4.451	4.801	49.812	52.514	0.202	1.006	0.000	0.000	0.000	0.073	3.680	1.000
SW*4S	12.992	44.515	96.029	594.151	525.142	2.024	10.060	0.000	0.000	0.000	0.873	43.622	1.030
2D*SW*4S	6.496	22.257	48.015	297.075	262.571	1.012	5.030	0.000	0.000	0.000	0.436	21.811	1.014
10D*SW*4S	1.299	4.451	9.603	59.415	52.514	0.202	1.006	0.000	0.000	0.000	0.087	4.362	1.001

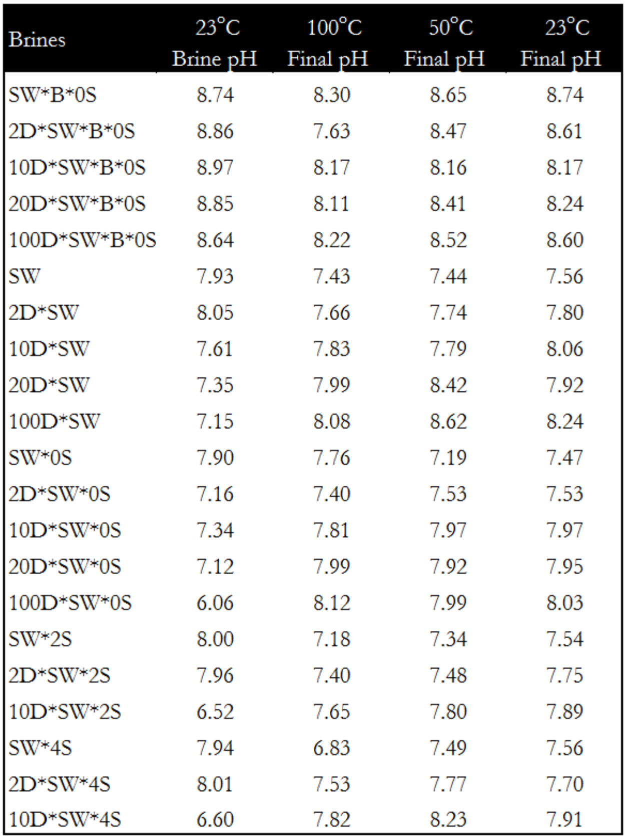
4.1.4 Initial and Final pH

The initial and final pH of all the brines were measured at room temperature (23°C) but the final pH was measured after treating the brines at given temperatures by PHM-210 from Radiometer Analytical. The borate brines showed higher pH values compared to seawater and seawater without sulfate. The pH of all the brines before using in flotation experiments was measured at room temperature and the final pH of all the treated brines (23, 50 & 100°C) was measured at 23°C. The collected samples showed clearly the effect of temperature on pH as it can be seen in Table 4.4. The variation in pH value between initial and final values is an indication of dissolution of $CaCO_3$.

4.1.5 Interfacial Tension

Interfacial tension is the force of repulsion between two immiscible fluids and it is one of the components of the capillary forces that can trap the crude oil in porous media. In low tension EOR methods it is significantly reduced by

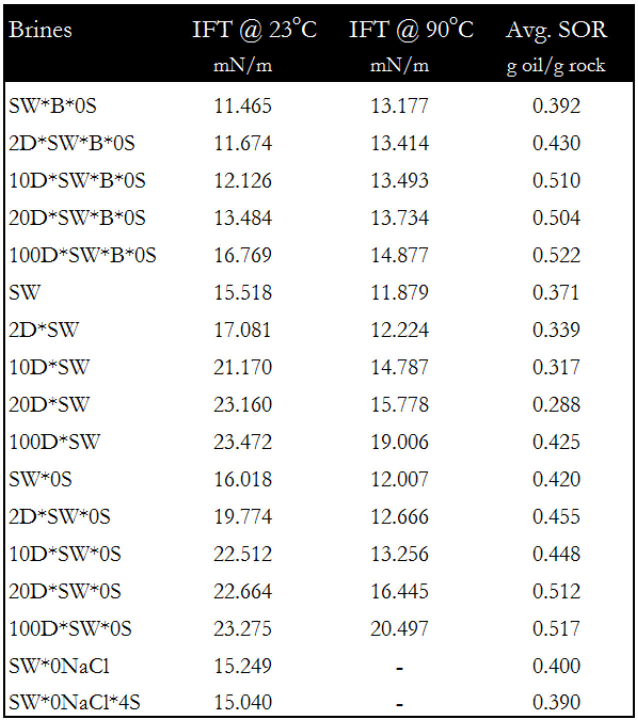
Table 4.4: The initial and final pH of brines at 23°C, final pH measured after treating brines at given temperatures.



Brines	23°C Brine pH	100°C Final pH	50°C Final pH	23°C Final pH
SW*B*0S	8.74	8.30	8.65	8.74
2D*SW*B*0S	8.86	7.63	8.47	8.61
10D*SW*B*0S	8.97	8.17	8.16	8.17
20D*SW*B*0S	8.85	8.11	8.41	8.24
100D*SW*B*0S	8.64	8.22	8.52	8.60
SW	7.93	7.43	7.44	7.56
2D*SW	8.05	7.66	7.74	7.80
10D*SW	7.61	7.83	7.79	8.06
20D*SW	7.35	7.99	8.42	7.92
100D*SW	7.15	8.08	8.62	8.24
SW*0S	7.90	7.76	7.19	7.47
2D*SW*0S	7.16	7.40	7.53	7.53
10D*SW*0S	7.34	7.81	7.97	7.97
20D*SW*0S	7.12	7.99	7.92	7.95
100D*SW*0S	6.06	8.12	7.99	8.03
SW*2S	8.00	7.18	7.34	7.54
2D*SW*2S	7.96	7.40	7.48	7.75
10D*SW*2S	6.52	7.65	7.80	7.89
SW*4S	7.94	6.83	7.49	7.56
2D*SW*4S	8.01	7.53	7.77	7.70
10D*SW*4S	6.60	7.82	8.23	7.91

adding surfactants in injected water to achieve miscibility between crude oil and the injected brine. In advanced waterflooding process some of the ionically modified waters have low tension between oleic and aqueous phases. Although, the decrease in IFT between oil and ionically modified water is not as low as it is in case of surfactant, it may contribute to the process of increased oil recovery. Therefore, the IFT between crude oil and brines that used in flotation experiments was measured at room temperature and 90°C. The explanation of the method that used to measure the IFT between crude oil and brines is given in Sohal et al. [75] and the produced values are listed in Table 4.5.

Table 4.5: IFT at 23 & 90°C and average retained oil at 100°C. Source: [75]



Brines	IFT @ 23°C mN/m	IFT @ 90°C mN/m	Avg. SOR g oil/g rock
SW*B*0S	11.465	13.177	0.392
2D*SW*B*0S	11.674	13.414	0.430
10D*SW*B*0S	12.126	13.493	0.510
20D*SW*B*0S	13.484	13.734	0.504
100D*SW*B*0S	16.769	14.877	0.522
SW	15.518	11.879	0.371
2D*SW	17.081	12.224	0.339
10D*SW	21.170	14.787	0.317
20D*SW	23.160	15.778	0.288
100D*SW	23.472	19.006	0.425
SW*0S	16.018	12.007	0.420
2D*SW*0S	19.774	12.666	0.455
10D*SW*0S	22.512	13.256	0.448
20D*SW*0S	22.664	16.445	0.512
100D*SW*0S	23.275	20.497	0.517
SW*0NaCl	15.249	-	0.400
SW*0NaCl*4S	15.040	-	0.390

4.2 Methods

Several methods have been proposed to measure wettability quantitatively and qualitatively in the literature [44, 121–123]. In general, these methods take the wettability measurements by displacement of fluids in porous medium. The USBM and Amott test are most commonly used and based on water saturation. In these methods a wettability scale -1 to +1 is used that expresses a completely oil-wet to completely water-wet system, and is used to quantify the wetting state of a rock. In this study a novel application of flotation is introduced to quantitatively measure the wettability and explained in next section. Moreover, a newly defined wettability index based on flotation results, the flotation wettability index is also presented. It varies from completely oil-wet to completely water-wet and has values between -1 and +1.

4.2.1 Flotation

All the steps of flotation method are explained with bullets in a sequence as it was practiced in the laboratory according to Sohal et al. [75].

- One gram of the chalk sample (50 – 100 μm grain sizes) was aged in 10 ml of brine at respective temperature (23, 50 or 100^{o}C) for approximately for one day. Then the brine is poured into another test tube for later use. The decanted brine was preserved in a sterilized glass test tube with tight cap and the pH measured.
- The brine-wet grains in the test tube were aged with 5 ml of crude oil for 24 hours at experimental temperature (23, 50 or 100^{o}C) and shaken twice a day for a few seconds with vortex shaker. The oil aging time may be different for different rocks and crude oils.
- After oil aging, the preserved decanted brine was added back into the test tube and gently shaken with the vortex shaker. The mixture was allowed to settle for several hours.
- Finally, the grains attached to oil phase (oil-wet) were removed and the walls of the test tube rinsed with deionized water to clean off any stuck grains. The rinsing step was repeated twice or thrice to remove all the oil-wet grains from the test tube.
- The sunken water-wet grains were coated with oil which could not be removed during the rinsing process. The water-wet oil coated grains were dried and weighed and then washed with a volatile organic solvent to remove the attached oil. The cleaned and dried water-wet grains were subtracted from the original mass to calculate the amount of oil-wet grains.

Experiments were performed to select the best proportions of rock sample, brine, and crude oil, as well as aging time, grain size, rinsing, and mixing steps to determine the conditions for optimum results as given in appendix A. The final amounts were 5 ml of crude oil, 10 ml of brine, and one gram of rock powder. One gram amount of rock sample was chosen as the minimum amount of the rock that produced good reproducibility (± 5%), while minimizing consumption of the most limited resource, reservoir rock. The minimum amount of rock that produced optimum results was selected to carry out the experiments to save resources. A diagram of the experimental setup with major operating steps is shown in Figure 4.1.

4.2.2 Oil Adhesion & Cleaning

It was observed by Sohal at al. [75] that a measurable amount of oil was still attached to water-wet grains after the wettability alteration and the amount was variable for different advanced fluids. The attached /adhered oil is referred to as retained oil. Some components of crude oil will remain strongly

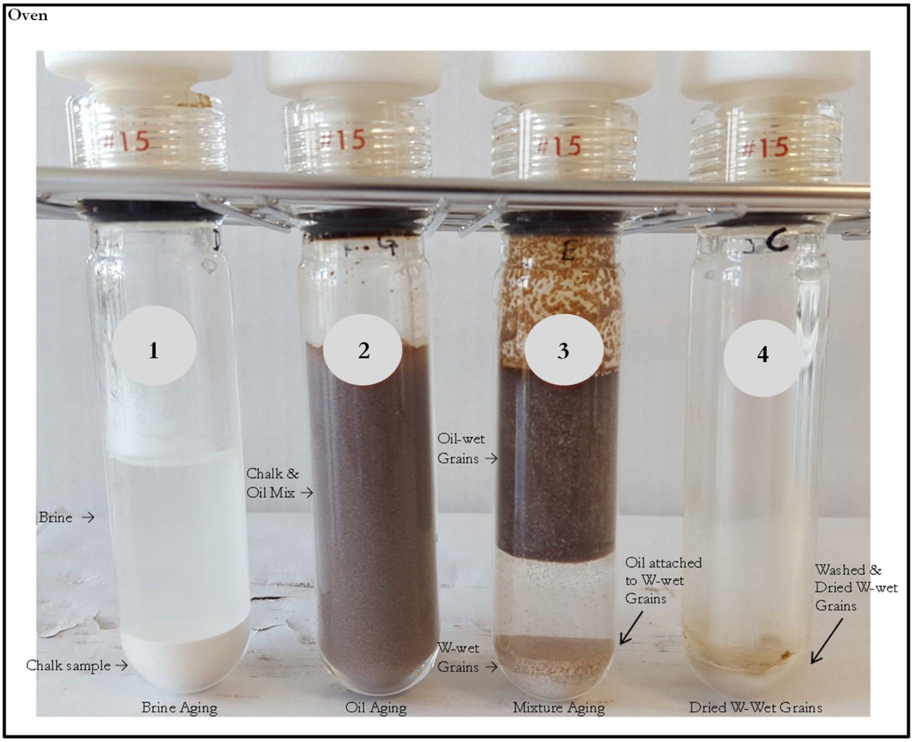


Fig. 4.1: Diagram illustrating the flotation experiment procedure. Sunken rock grains are considered water-wet and the grains attached to the oil phase are oil-wet. Source: [75]

absorbed to the rock surface and can only be removed by solvent extraction [124]. In this study the amount of oil that was attached to water-wet chalk grains after wettability alteration was measured for each type of brine at 23, 50 and 100^{o}C. This amount was measured by the mass difference of washed and dried water-wet grains from unwashed dried oil coated water-wet grains as shown in Figure 4.2. The oil coated water-wet chalk grains were washed by organic solvent without dissolution of chalk.

4.2.3 Statistical Analysis

Statistical analyses were performed on a carbonate coreflooding and imbibition experiments database based on published journal and conference papers. The analysis tried to identify the most influential parameters for further investigation. The data base includes fluid and rock properties as well as diverse operating conditions as shown in Table 4.6. The multivariate data analysis was carried out using the R environment (v.3.3.2) supplemented with mdatools package (doi:10.5281/zenodo.59547) in the following three stages.

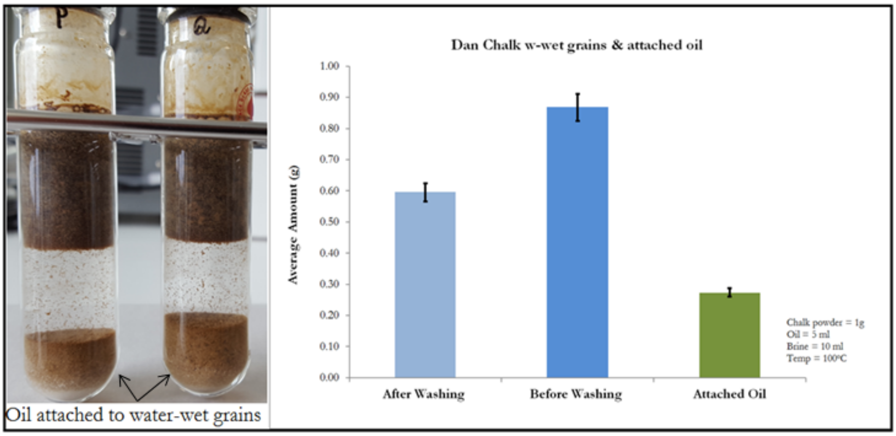


Fig. 4.2: Average amount of Dan chalk water-wet grains before and after washing with organic solvent and amount of oil attached to these grains. Error bars represent ± 5%, the experimental uncertainty associated with the flotation technique. Source: [75]

- ANOVA and Tukey's HSD
- Principal component analysis (PCA)
- Partial Least Squares (PLS) regression

Details of the analysis and outcomes are given in article C in papers section. The first test was performed to investigate the influence of categorical variables, such as Rock Type, Recovery Type, Initial Wettability, and Test Type. After that all the qualitative values were standardized to values between -1 and +1 for PCA. At final stage PLS regression analysis was applied to obtain a predictive model for AOR and to identify which variables contribute the most.

Table 4.6: Carbonates oil recovery experiments database including different parameters with known and missing values.

Rock type	2nd. Recovery Run	Ter. Recovery Run	Oil Acid Nr.	Oil Base Nr.	Oil Density	OIL Viscosity	FW Salinity	FW Ionic Strength	IB Ionic Strength	IB Ionic Strength	Test Temp	S_{wi}	S_{oi}	S_{or}	Recovery Time	AOR	Test Type	Permeability	Contact Angle	Aging Time	Aging Temp	IFT	Source
Chalk	30	0	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Al-Harrasi et al. (2012)
Chalk	6	4	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Alameri et al. (2014)
Chalk	8	26	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Fathi et al. (2012)
Chalk	13	6	yes	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Fathi et al. (2011)
Chalk	0	4	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Fathi et al. (2010a)
Chalk	13	0	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Fathi et al. (2010b)
Limestone	0	10	yes	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	no	yes	yes	no	Gupta et al. (2011)
Carbonate	0	5	yes	no	yes	yes	yes	yes	yes	yes	yes	no	no	no	no	yes	yes	yes*	yes	no	no	no	Hazim et al (2013)
Carbonate	8	8	no	no	yes	yes	yes	yes	yes	yes	yes	no	no	no	no	yes	yes	yes	yes	yes	yes	no	Mohanty et al. (2013)
Limestone	7	1	yes	no	yes	yes	yes	yes	yes	yes	no*	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Romanuka et al. (2012)
Chalk	8	0	yes	yes	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	no	yes	yes	no	Strand et al. (2006)
Carbonate	0	46	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Shehata et al. (2014)
Carbonate	1	4	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	Yousef et al. (2012a)
Carbonate	3	3	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	yes	yes	yes	yes	Yousef et al. (2012b)
Carbonate	0	8	yes	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	Yousef et al. (2011a)
Chalk	4	0	yes	no	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	no	Yousef et al. (2010)
Carbonate	1	22	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	no	yes	yes	no	Yu et al. (2010)
Limestone	0	19	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	no	yes	yes	no	Zhang et al. (2012)
Carbonate	0	9	no	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	Zhang et al. (2007)
Limestone	9	23	no	no	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no*	yes	yes	yes	no	yes	yes	no	Zhang et al. (2006)

5 Results and Discussion

5.1 Statistical Analysis

At the preliminary stage of multivariate data analysis categorical variables were divided into several groups and paired based on (1) lithology, (2) recovery type, (3) wettability type, (4) test type and investigated accordingly. A Spearman correlation coefficient was computed for each pair of these categorical variables to find the relation among them. There was a moderate correlation between rock type and recovery type as well as a relatively strong positive and negative correlation between initial wettability & rock type, test type & rock type, respectively. Several contingency tables were generated to see the association between variables and statistically confirmed by the Chi-square test. The details of these tests and results are given in paper C. During the quantitative analysis, several variables were excluded due to missing or limited number of values to avoid the bias. Therefore, dataset was divided into following four groups and analyzed separately.

1. Secondary vs tertiary recovery in limestone coreflooding
2. Secondary vs tertiary recovery in chalk imbibition
3. Limestone vs chalk in tertiary imbibition recovery
4. Limestone coreflood vs limestone imbibition in tertiary recovery

The difference in AOR depending on qualitative factors with in each group was calculated by analysis of variance (ANOVA) and then post-hoc Tuckey's test was used to compare influence of different combinations factor variables pairwise to see which group mean is significantly different from others. The p-values and confidence intervals were used to evaluate the statistically significant effects. Figure 5.1 shows box plot for logarithm of AOR values for each of the groups together with calculated p-values and confidence intervals. Thus for group 1 in tertiary stage oil recovery only 4.8 to 13.5% of the secondary recovery was recovered.
Box plot and statistics for the second group again show that more oil was recovered at secondary recovery stage compared to tertiary stage recovery. However, tertiary mode chalk recovery is greater than tertiary mode limestone waterfloods.
The analysis for the third group revealed that imbibition recovery is slightly higher in chalk cores compared to limestones.
The analysis of the last group showed that there is no statistically significant difference in mean additional oil recovery values of coreflood and imbibition for limestone in the tertiary recovery mode.

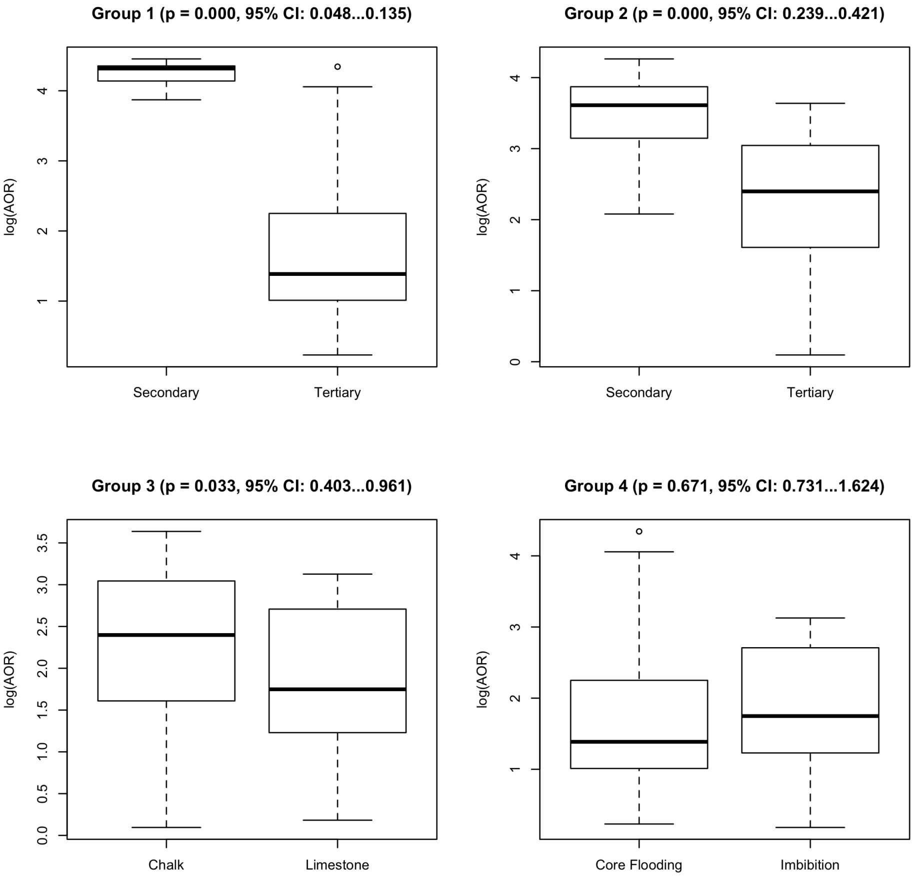


Fig. 5.1: Boxplots for the selected groups. The titles of the plots show a p-value and 95% confidence intervals for the difference in average AOR values.

The multivariate association between the variables were found by applying PCA. The first two principle components (PCs) split the whole dataset into two clusters that mainly based on rock type (chalk & limestone). The description of the method and relevant charts are given in paper C. Additional plots and charts are given in Appendix B. The results of the initial PCA model showed that the biggest difference among AOR was due to the rock type, so it was decided to analyze these two groups separately. A brief explanation of the results of chalk dataset is given in this section whereas a detailed explanation of all other results can be found in paper C. According to the PCA scores and loadings plots, the Mg^{2+} in injected water (AWI.Mg2),

S_{oi}, formation water salinity (FW.Salinity), sodium and chloride content in formation water (FW.Na & FW.Cl) influenced the AOR more than other variables. Among these variables AWI.Mg2 & Soi are positively correlated to AOR while FW.Salinity, FW.Na & FW.Cl are negatively correlated.
Partial least square regression (PLS-R) analysis of the chalk dataset is presented in Figure 5.2. PLS-R results include predicted vs. measured plots, root mean square error (RMSE), regression coefficients and selectivity ratio plots. The PLS model produced reasonable performance (cross-validated R^2 = 0.57) with a clear minimum RMSE at three PLS-components. The analysis of regression coefficients and selectivity ratio plots showed the same results that were observed in PCA. The factors which influence the AOR most are AWI.Mg2, FWNa, FWCl, FW.Salinity, Soi and test type. Their correlation with AOR and importance can be easily identified at regression coefficients and selectivity ratio plots respectively.

5.2 Potential Scale Forming Ions & Wettability

The efficiency of EOR processes that alter the wettability of an oil reservoir depends on the initial wetting conditions. Whereas, the initial wetting conditions are controlled by formation water composition in addition to temperature, oil and rock composition. The pore fluid of carbonate formations often contain some amount of potential scale forming ions like Sr^{2+} and Ba^{2+}. These ions are always removed from the synthetic formation water in lab experiments to avoid precipitation problems. But these ions effect the initial wetting conditions as described by Sohal el al. [75]. In the flotation experiments the chalk powder that was aged with synthetic Ekofisk formation water (EFW) depleted in Sr^{2+} and Ba^{2+} ions produced 5% less oil-wet conditions compared to the chalk that was aged with EFW containing Sr^{2+} and Ba^{2+} ions at 100^oC as shown in Figure 5.3. Therefore, the cores should always have these potential scale forming cations in lab recovery experiments otherwise the results would be different if implemented in a real reservoir system. Suijkerbuijk et al. [125] also observed the same effect in sandstone cores and stated that the depletion of potential scale-forming cations, such as Sr^{2+} and Ba^{2+}, from synthetic formation water may lead to an unrepresentative wettability restoration (overestimating water-wetness). These divalent cations are expected to play a disproportionately large role in the estimation of wetting state of a rock after aging, if the $Mg^{2+} \longrightarrow Ca^{2+}$ trend is extrapolated. The flotation data shows that depletion of these potential scale forming ions from brines will overestimate the water-wetness by as much as 35% at room temperature and 5% at 100^oC. Although this effect is reduced as temperature increased; it will have some effect in low temperature reservoirs.

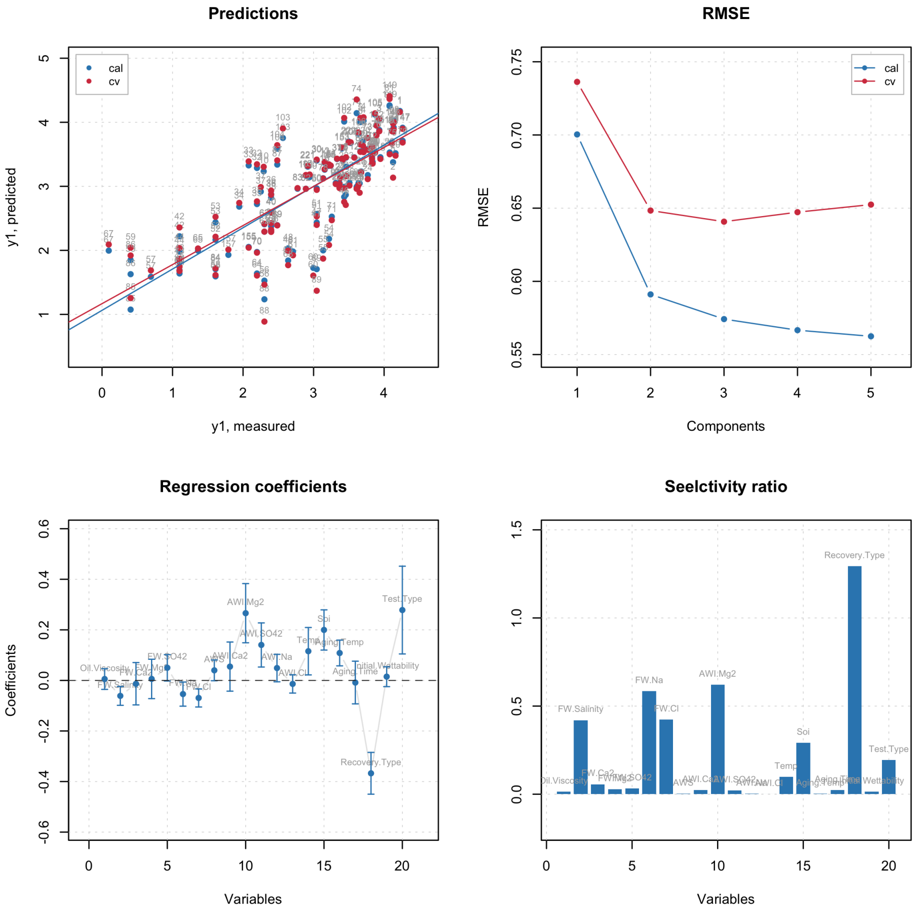


Fig. 5.2: PLS-R model of chalk data with regression coefficient and selectivity ratio plots.

5.3 Effect of Ionic Composition on Wettability

There are two separate effects that improve the oil recovery in carbonates. One of them is related to ionic composition and depends on the concentration of PDIs in injected water (advanced water). PDIs are the ions that can significantly change the surface charge of carbonates and include Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-} and BO_3^{3-}. The mechanism behind the improved oil recovery by injecting/imbibing advanced water enriched with PDIs has been explained in full detail in section 2.2.1.

Buckley [45] described the crude oil brine interface as positively charged at low pH (< 3.5) and negatively charged at high pH (> 3.5) due to dissociation of organic acids and basic compounds. Therefore, the water rock-brine

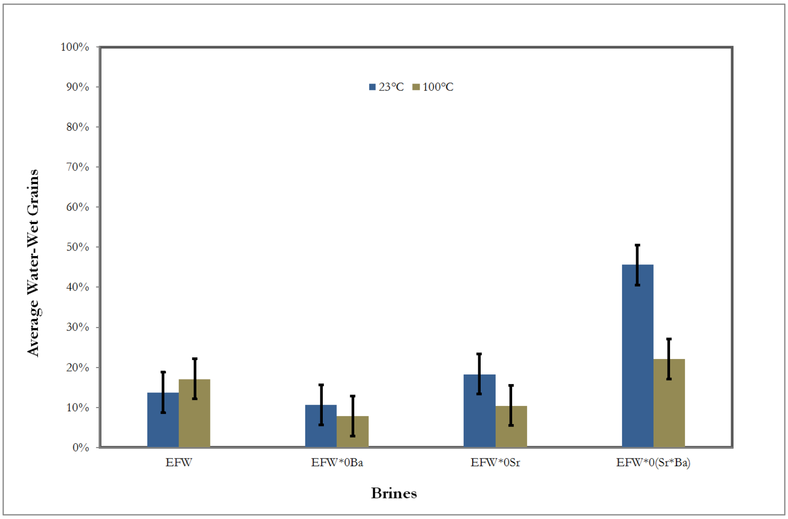


Fig. 5.3: Effect of potential scale forming ions on wetting conditions. Error bars represent ± 5%, the experimental uncertainty associated with the flotation technique. Source: [75]

interface charge is altered through adsorption of PDIs on rock surface and creates a repulsion between two interfaces. In most of the published studies [21, 27, 29, 32–34, 37] sulfate used as a reactive anion for this purpose. The proposed mechanism was the adsorption of $SO_4{}^{2-}$ on chalk surfaces that reduced the positive charge density of carbonate surface and allowed Ca^{2+} & Mg^{2+} to approach the surface to release carboxylic acid groups at temperature higher than 100^oC [33]. In addition to sulfate, phosphate ($PO_4{}^{3-}$) and borate ($BO_3{}^{3-}$) have also been tested as potential determining anions (PDAs) to improve recovery in carbonates by Gupta et al [12]. But there was a lack of systematic study to isolate the effect of low salinity (low salinity is used as a relative term compared to formation water) and PDIs to change the wettability. It becomes even harder in cases where sulfate is produced from an internal source such as anhydrite ($CaSO_4$).

Flotation technique differentiated the contribution of each effect clearly as depicted in Figure 5.4 [75]. The synthetic seawater with sulfate, seawater with borate and seawater without sulfate were used to observe the influence of PDIs and low salinity separately. Lowing salinity by dilution has been evaluated in both mods; with and without potential anions. Seawater was used as a base line and it was observed that dilutions improved water wetness up to 20D in this case. The SW*B*0S and SW*0S brines behaved almost identically but brines without sulfate produced up to 15% less water-wet grains compared to SW at the lower dilution factors. At dilution of 20 and 100X, borate is not as effective as sulfate, but more effective than brine that lacks any PDAs.

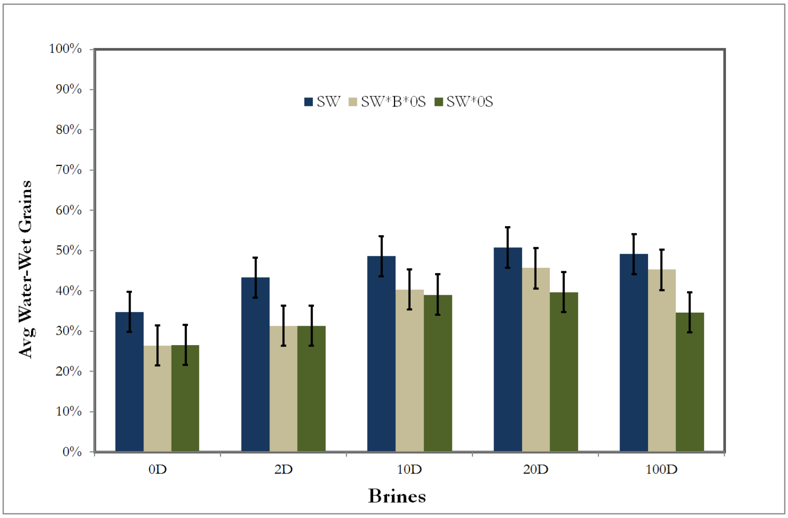


Fig. 5.4: Comparison of wettability alteration caused by SW, SW*B*0S, and SW*0S at 100^oC. Error bars represent ± 5%, the experimental uncertainty associated with the flotation technique. Source: [75]

However, at the experimental pH conditions the dominant (>50%) aqueous species of sulfur is the divalent anion, $SO_4{}^{2-}$, while the dominant aqueous species of boron is boric acid (neutral H_3BO_3 >90%) leaving only 5 to 10% as the borate anion. The effect of calcite surface charge from sulfate adsorption can be described using Equation 5.1 where $>CaOH_2^+$ is the positively charged surface site of calcite. Equation 5.1 [75] shows that the sulfate anion attaches to the positively-charged surface site and renders it negatively charged shifting the overall surface charge. A similar equation could be written for borate, but the amount of available borate in solution is much less than the sulfate. This is consistent with the observations of the smaller effect for borate and it can be clearly seen in Figure 5.5 at 100^{o}C.

$$>CaOH_2^+ + SO_4^{2-} = >CaSO_4^- + H_2O \tag{5.1}$$

5.4 Effect of Ionic Strength on Wettability

In this aspect of ionically modified water the concentration of total dissolved solids as well as water without potential determining anions (SO_4^{2-}, PO_4^{3-} and BO_3^{3-}) was used to improve the water-wetness. Water wetness of chalk particles increased by decreasing the total dissolved solids in this CBR system as observed in flotation experiments and shown in Figure 5.6. The amount

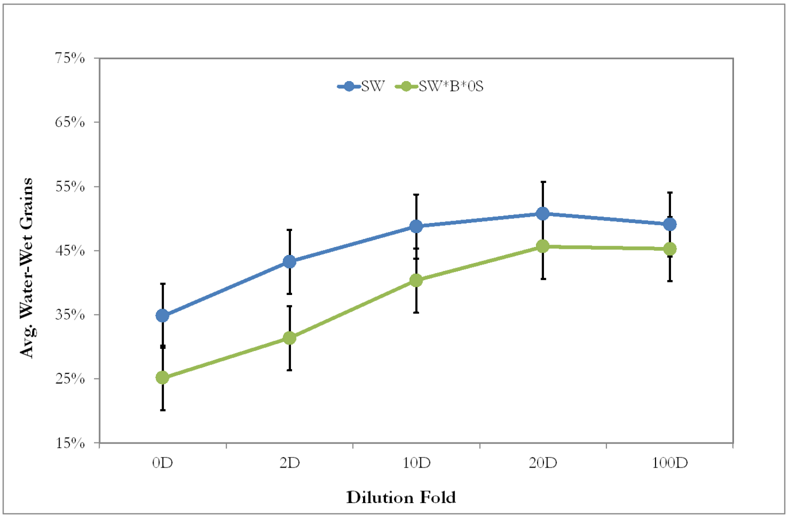


Fig. 5.5: Comparison of wettability alteration potential of SW and SW*B*0S at 100^{o}C. Error bars represent ± 5%, the experimental uncertainty associated with the flotation technique.

of total dissolved solids in the brines was decreased by adding DIW. So, the dilution of original brines (SW, SW*B*0S and SW*0S) improved the water wetness up to 20 times dilution. On further dilution water wetness did not improve instead it started to decrease. The results show that a certain amount of PDIs is needed to optimize the effect. This can be clearly seen in Figure 5.6. The dilution of each individual brine improved the water wetness up to 20X as well as comparison of the three brines showed that dilution of brines containing potential anions improved the water wetness more than the brines that don't contain potential anions. Moreover, the results show that seawater containing sulfate improved the water wetness more than the seawater containing borate in all dilutions.

It can be seen in Figure 5.6 there are 5 to 11% additional water-wet grains in brines saturated with PDIs compared to brines without potential determining ions.

5.5 Effect of Temperature on Wettability

5.5.1 Seawater

The effect of temperature on wettability was evaluated for SW, SW*0S and SW*B*0S and the diluted versions of these brines at 23, 50 and 100^{o}C in same crude-rock system. The influence of temperature on wettability using SW including its dilutions can be seen in Figure 5.7. The system is more water-wet at low temperatures (23 & 50^{o}C) compared to 100^{o}C but the difference in

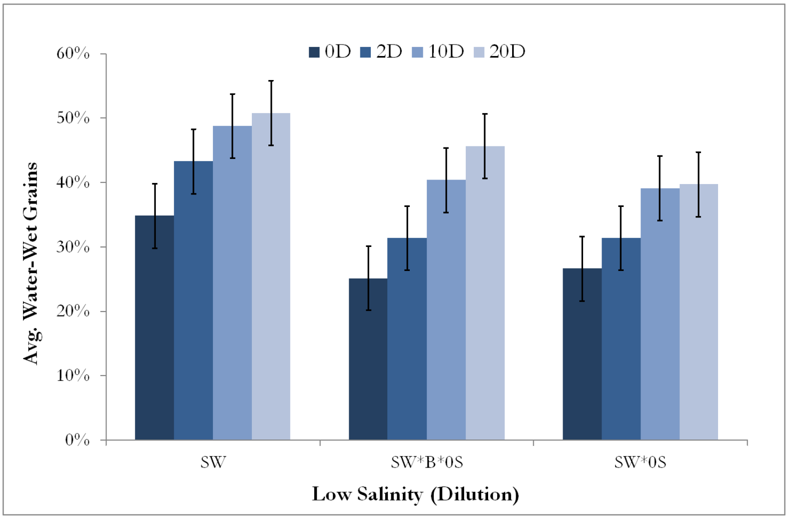


Fig. 5.6: Effect of decreasing ionic strength (dilution) on wettability at 100^oC. Error bars represent ± 5%, the experimental uncertainty associated with the flotation technique.

water-wet fractions among the brines is less with dilution. It may be inferred that temperature sensitivity is more related to the low salinity effect instead of PDIs. Because the difference in wettability shift between the low temperatures (23 & 50^oC) and 100^oC becomes constant after 20D dilution and that may be the temperature effect exclusively. Moreover, magnitude of wettability shift with dilution was small at 23 & 50^oC but it was more pronounced at 100^oC. The maximum shift in wettability was 21% between the lowest and the highest temperature and it was 9 to 16% with dilution at 23 and 100^oC, respectively. Moreover, largest shift in wettability was observed at full strength solution and this effect decreased with dilution. There was no significant shift in wettability with temperature for the most diluted solutions. Sayyouh et al. [126] found higher temperature increased oil wetting for Saudi sandstones. Zhang and Austad [127] determined that the oil wetness increased with increasing temperature for chalk. The seawater flotation experiments showed the same effect, more oil-wet conditions at higher temperatures in this CBR system.

5.5.2 Seawater Without Sulfate

Seawater without sulfate experiments are applicable to the NaCl solutions used for experimental measurements of wettability alteration. Dilution improved the water wetness at a moderate rate up to 10D as shown in Figure 5.8. But further dilution of the brine decreased the water-wet fraction. The shift in wettability with dilution increased with temperature and reached to a max-

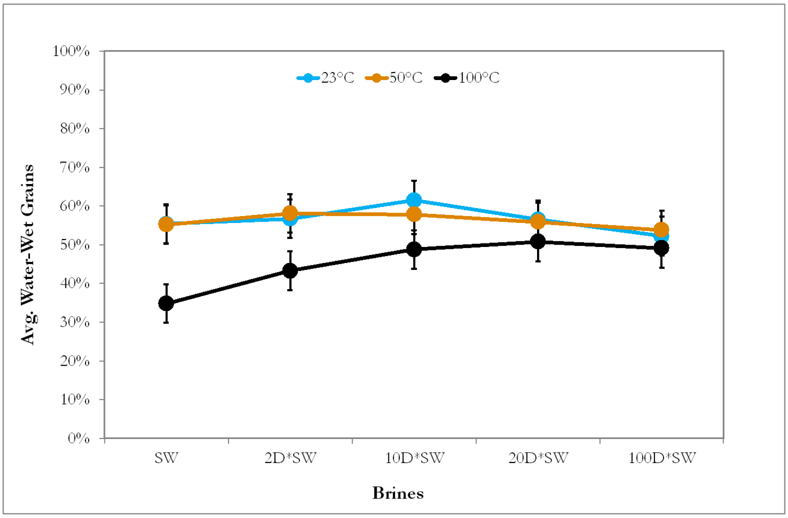


Fig. 5.7: The average amount of water-wet grains at given temperatures using SW. Error bars represent ±5%, the experimental uncertainty associated with the flotation technique.

imum value (13%) at 100^oC. The maximum difference in water-wet fraction is 30% between the temperature limits and it was observed at full strength solution same like SW. Additionally, the shift in wettability within individual temperature range was less than SW and it decreased with dilution. The shift toward water-wetting was much less for the same degree of dilution at 23 and 50^{o}C. But higher temperature (100^oC) turned the grains more oil-wet. However, a systematic change with temperature was seen for the most diluted solutions (100D). Overall the crude-brine-rock system shifted towards oil-wetting as temperature increased. So, it seems that reservoir carbonates are more oil-wet compared to samples measured at surface conditions. The relationship between temperature and wettability for the more saline solutions is not linear, but becomes linear as the salinity decreases. Most important from the practical aspect, dilution can significantly shift the system back towards water-wetness releasing oil from the rock. However, lower temperature systems will be more water-wet initially and have less wettability shift with dilution. The data show experiments < 90^{o}C have almost the same wettability values for seawater and seawater without sulfate, but the 100^{o}C experiments were more water-wet for SW.

5.5.3 Borate Brine

Borate brine is synthetic seawater augmented with 0.0092 mole/l of borate anion instead of sulfate. Borate brine increased the oil wetting of chalk at all the tested temperatures (23, 50 & 100^{o}C) compared to seawater as shown

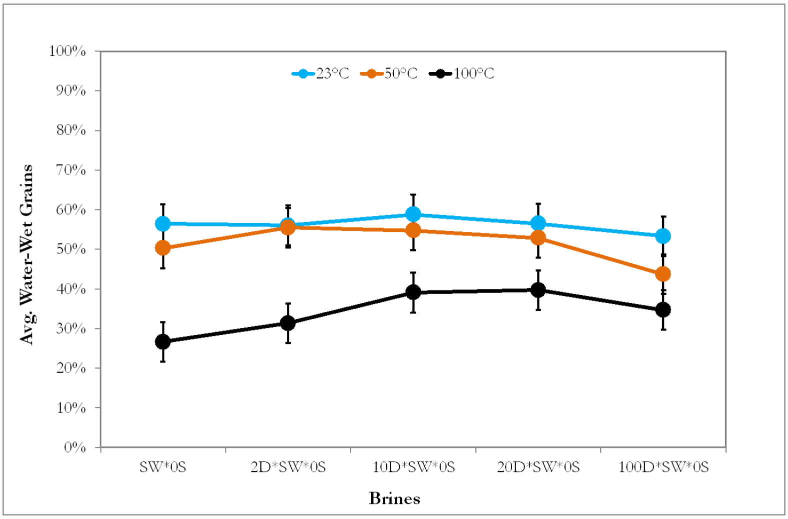


Fig. 5.8: The average amount of water-wet grains at given temperatures using SW*0S. Error bars represent ±5%, the experimental uncertainty associated with the flotation technique.

in Figure 5.9. Dilution of borate brine increased the water wetting up to 20-fold dilution (0.5 mmol/l) at 23 & 50^{o}C, but further dilution did not further improve water wetting. The shift in wettability decreased by increasing temperature from 30% to 20% at 23 and 100^{o}C respectively. The maximum difference in water-wet fraction with full strength solution was only 1% at 23 and 100^{o}C and it increased to 14% as dilution increased to 10D. The 100^{o}C experiments were complicated by observations of precipitate formation. This is assumed to be a borate salt that is relatively insoluble at higher temperatures but that is not yet confirmed. The precipitation was observed up to 4 fold dilutions, and thus may have lowered effective borate concentrations in the brine. So, borate improves oil wetting as did the sulfate with increasing temperature, but may be prone to precipitation at higher temperatures which may limit the effect in field applications.

The comparison of all the three brines at tested temperatures illustrated that dilution of SW shifted the wettability more than SW*0S, and SW*B*0S as it can be seen in Figure 5.10. But the shift in wettability as temperature increased from 23^{o}C to 100^{o}C for SW*0S and SW*B*0S is almost equal (12 to 13%). This fact revealed that seawater is more temperature sensitive than the other brines.

However, data shows that borate brines have less potential to improve the water wetness at 23, 50 and 100^{o}C compared to SW as shown in Figure 5.12. Even the potential of SW*0S is higher than SW*B*0S at low temperatures (23 & 50^{o}C). This difference may be related to fact that the active anionic form of

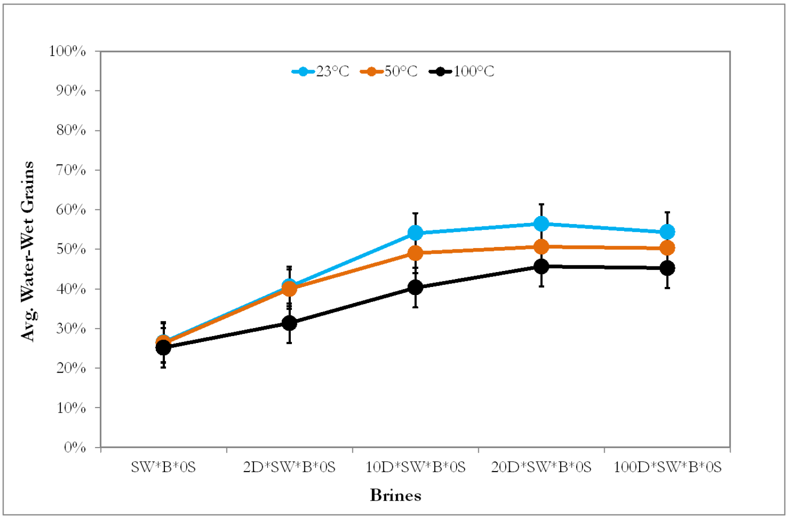


Fig. 5.9: The average amount of water-wet grains at given temperatures using SW*B*0S. Error bars represent ±5%, the experimental uncertainty associated with the flotation technique.

borate brine that attached to carbonate metal ion sites (>Ca^+) was only 5 to 10% at experimental pH values while sulfate was more than 50% reactive as described by Sohal el al. [75].

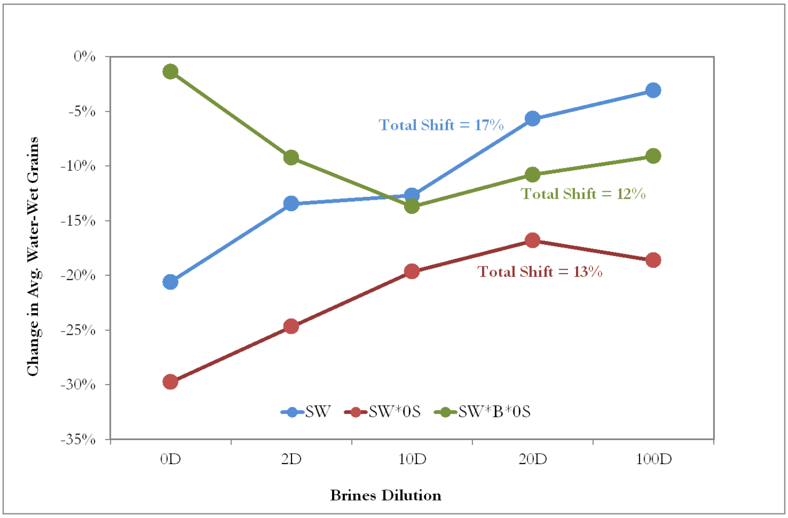


Fig. 5.10: The change in average amount of water-wet grains with increasing temperature from 23^{o}C to 100^{o}C for all the three brines including dilutions.

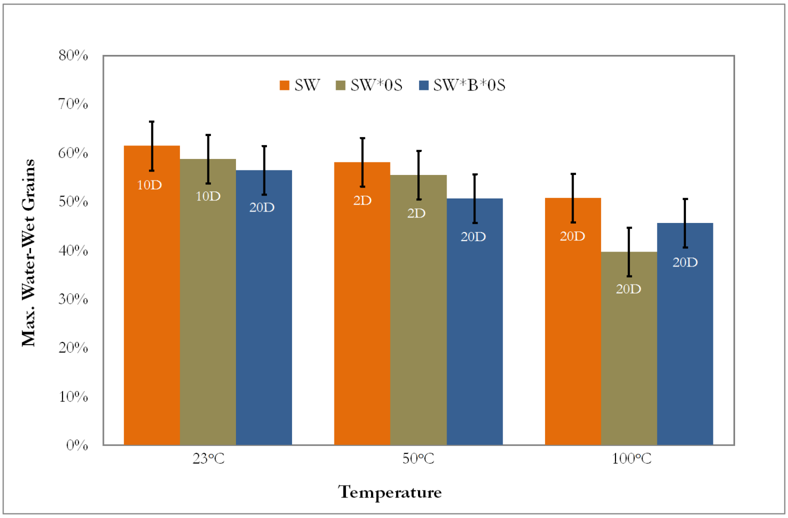


Fig. 5.11: Comparison of maximum water-wet fractions of chalk by SW, SW*0S and SW*B*0S at given temperatures. Error bars represent ±5%, the experimental uncertainty associated with the flotation technique.

5.5.4 Effect of Sulfate Concentration

The potential of synthetic seawater enriched with 2 to 4 times more sulfate than normal SW concentration at given temperatures (23, 50 & 100^{o}C) is shown in Figure 5.12. It can be seen that the potential of sulfate to influence the wettability from 2.4 mmol/l to 96 mmol/l in seawater at low temperatures (23 & 50^{o}C) is trivial. The same effect was observed in chalk at 40 & 80^{o}C by Zhang and Austad [20]. Sulfate improved the water-wet fraction at low concentrations ($\sim$ 0.002 mol/l = 10D*SW) in this CBR system at 23 and 50^{o}C. But on further increasing the concentration of sulfate in SW the system became more oil-wet and the effect increased up to 96 mmol/l at 100^{o}C. It appears that the most important effect of sulfate is that sulfate turned the system more oil-wet if more than 0.002 mol/l used. Exactly, the same results was found by Shariatpanahi et al. [128] in chalk imbibition experiments at room temperature and 50^{o}C. In their experiments oil recovery and water-wetness did not improve when more than 2 mmol/l of sulfate was imbibed. But when they increased the temperature to 100 and 130^{o}C, the water-wetness and oil recovery decreased for the same concentration of sulfate in brine. The flotation results given in Figure 5.12 show the same effect. At 100^{o}C the water-wetness decreased and continued to decrease as amount of sulfate increased in the system. So, increased temperature ($\geqslant$ 90^{o}C) and sulfate concentration (> 0.002 mol/l) decreased the oil recovery and rendered the chalk more oil-wet in imbibition experiments [128]. The same effect on wettability is observed in the flotation experiments. The imbibition study directly correlated the additional oil recovery to improved water-wetness. Thus, improved water wetness in flotation experiments could imply some degree of enhanced oil recovery, but that correlation remains to be determined.

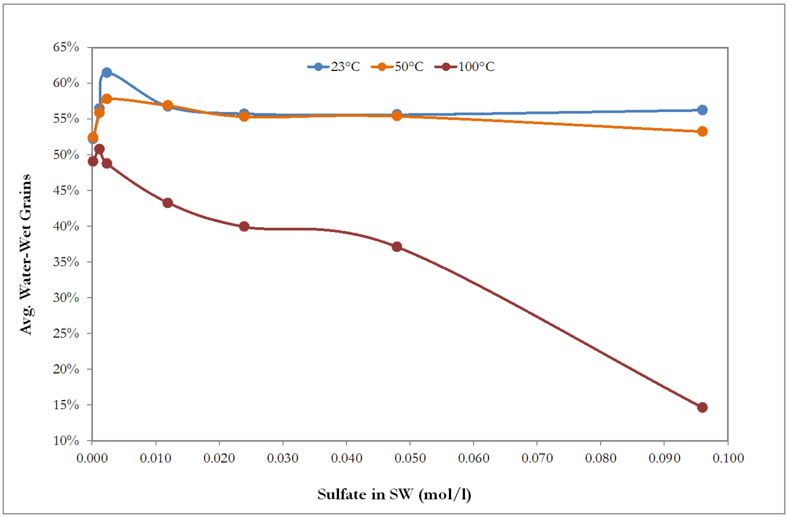


Fig. 5.12: Effect of increasing temperature and concentration of sulfate in SW on wettability.

5.6 Optimum Wettability & Wetting Index

The enhanced oil recovery as a result of wettability alteration by injecting or imbibing ionically modified water has been attributed to improved water wetness [19, 20, 32, 35, 36] but in some results it was linked to neutral-wet state [15, 42, 43, 117]. The residual oil saturation and oil recovery curves based on the results [101, 117, 118, 129] show that maximum recovery and decrease in S_{or} would be achieved at wetting index (WI) of 0 to 0.25 (neutral-wet to weakly water-wet). Further increase in water-wet conditions neither improves the oil recovery nor decreases the residual oil saturation. The explanation of this effect is the trapping of oil as individual droplets at higher water-wet conditions following snap-off. So, it is almost impossible to recover that oil even by increasing the injection pressure. Salathiel [118] stated that if the oil paths are continuous in mixed-wet system, water could displace oil from larger pores and little or no oil would be held by capillary forces in small pores. Jadhunandan and Morrow [117] explained that the maximum oil recovery near neutral wettability is more appealing because it can be argued that the capillary forces are minimized.

Flotation experiments can evaluate the potential of each injected fluid to alter the wettability. The optimum wetting conditions can be easily determined with the help of newly defined flotation wettability index which is based on flotation results. The FWI works in the same fashion as the Amott wettability index and can be easily calculated with the help of Equation 5.2.

$$\mathbf{FWI} = \frac{\textit{(Mass of water-wet fraction)-(Mass of oil-wet fraction)}}{\textit{Total mass}} \tag{5.2}$$

The FWI value varies between -1 and +1 that represents completely oil-wet to completely water-wet conditions respectively and zero indicates the mixed-wet or neutral-wet conditions. The wettability index based on flotation results is plotted in Figure 5.14 for different brines. It can be clearly seen that VB, SW*2S, SW*4S and SW*B*0S brines turn the chalk oil-wet (FWI = -0.85 to -0.35) whereas SW and 20D*SW changed the chalk wettability close to neutral-wet conditions (FWI = -0.25 to +0.25) in this rock-crude system. Therefore, it may be concluded that in this rock crude system 20D*SW provides the optimum results in all tested brines at 100^{o}C. For example, if Valhall brine (VB) is the formation water then by injecting 20D*SW in this CBR system would shift the wettability up to 30% toward water-wet conditions to reach the optimum wetting conditions.

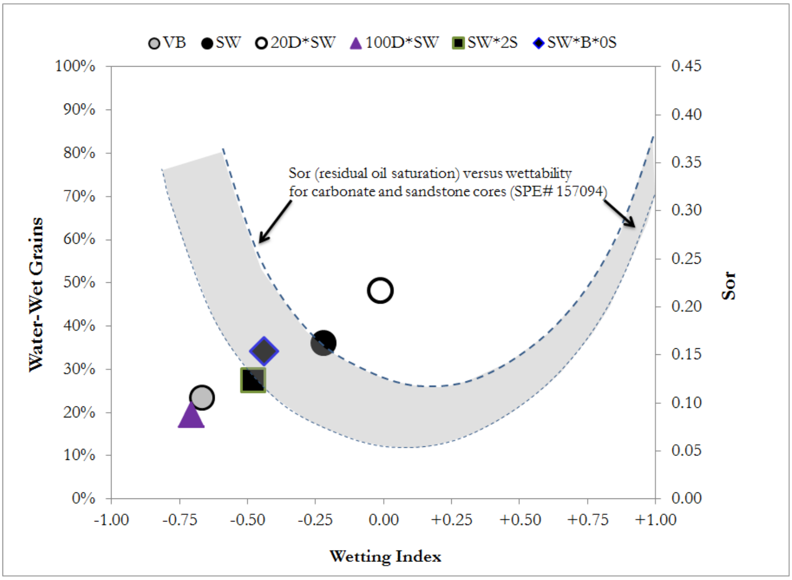


Fig. 5.13: Plotting of data based on wettability index calculated by flotation results at 100^{o}C.

5.6.1 Temperature Effect on Wettability by FWI

Jadhunandan and Morrow [117] calculated the wettability indices as a function of temperature for North Sea and West Texas crude oils. The core samples were taken from Berea sandstone and aged in respective crude oils at temperatures of 20 to 80^{o}C. They plotted wettability indices against aging temperature and observed a decreasing trend of water-wetness with increasing temperature. The flotation results showed the same trend of decreasing water wetness with increasing temperature for Dan chalk as described in the previous sections. The FWI data of seawater was plotted against water-wet fractions at different temperatures as shown in Figure 5.14 and show that oil wetness is increasing with temperature.

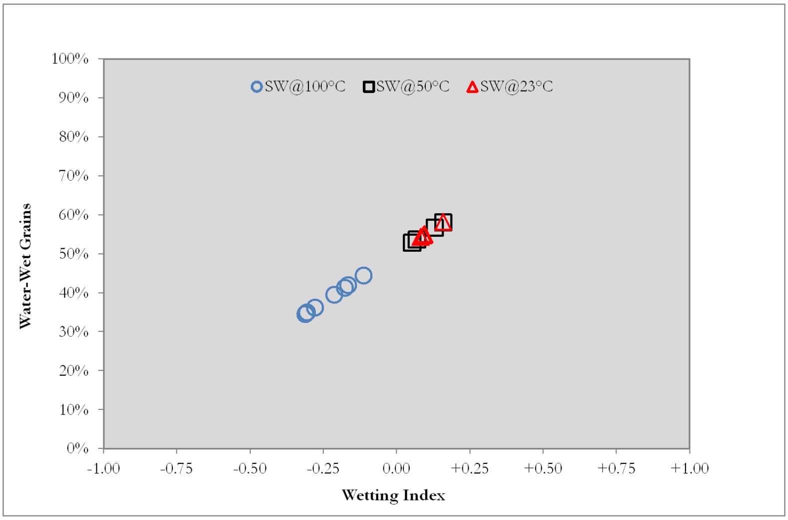


Fig. 5.14: An increasing trend of chalk oil-wetness with increasing temperature.

5.7 Effect of Temperature on IFT

The interfacial tension between crude oil and tested brines at 23 and 100^{o}C are plotted in Figure 5.15. The values vary between 11.5 to 23.5 mN/m at 23^{o}C and 12 to 20.5 mN/m at 100^{o}C. This range of IFT values are much higher that is normally required to develop the miscibility between injected brine and crude oil. Therefore, all the brines that were tested in this study are immisible with crude oil at given conditions. The SW*B*0S decreased the IFT more than SW and SW*0S at 23^{o}C as shown in Figure 5.15. But this trend changed as temperature increased to 90^{o}C, IFT increased for SW*B*0S while it decreased for SW and SW*0S. In this crude brine rock system IFT increased with dilution for all brines at both temperatures. A similar trend of IFT with dilution was observed by Meng et al. [76]. But in many experimental studies [14, 36, 77, 78] IFT between crude oil and brine decreased with dilution. Al-Attar el al. [15] found both trends of IFT change using different brines with same crude oil at 25^{o}C. The IFT changed irregularly in their experiments when the concentration of Ca^{2+} ion in brine increased gradually.

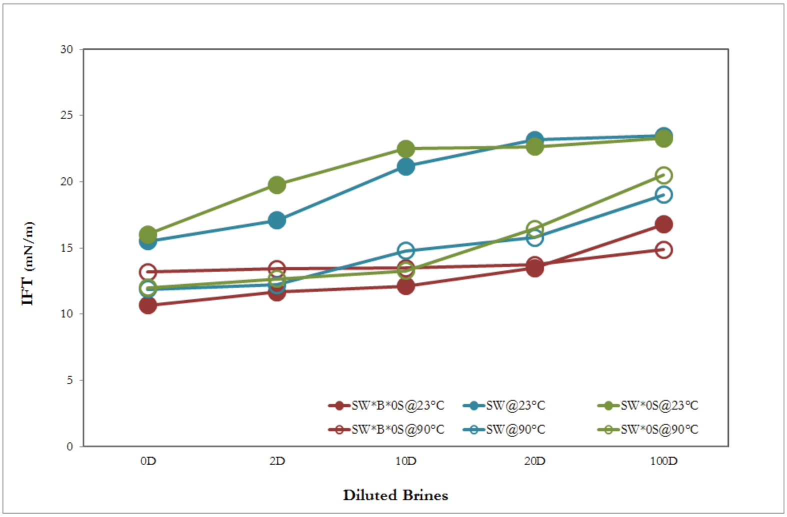


Fig. 5.15: Effect of increasing temperature on IFT of diluted brines. Source: [75]

5.8 Effect of IFT on Wettability

The relative contribution of IFT and wettability to increase the oil recovery is not well understood as described by Sohal et al. [75]. Sheng [1] found in UTCHEM simulation modeling at high IFT values, wettability alteration is important, but recovery can be improved independently by decreasing IFT. Al-Attar et al. [15] performed coreflooding on Abu Dhabi limestone/dolomite cores and found that there was no correlation between enhanced oil recovery and IFT.

Figure 5.16 shows the effect of brine dilution on IFT for SW, SW*B*0S and SW*0S. The results show that dilution increased the both water-wetness and IFT values. According to Sohal et al. [75] there was a positive correlation between wettability alteration & increasing IFT. But the positive correlation between IFT and improved water-wet conditions held only up to 10-20X dilution where the relationship inverted or remained constant.

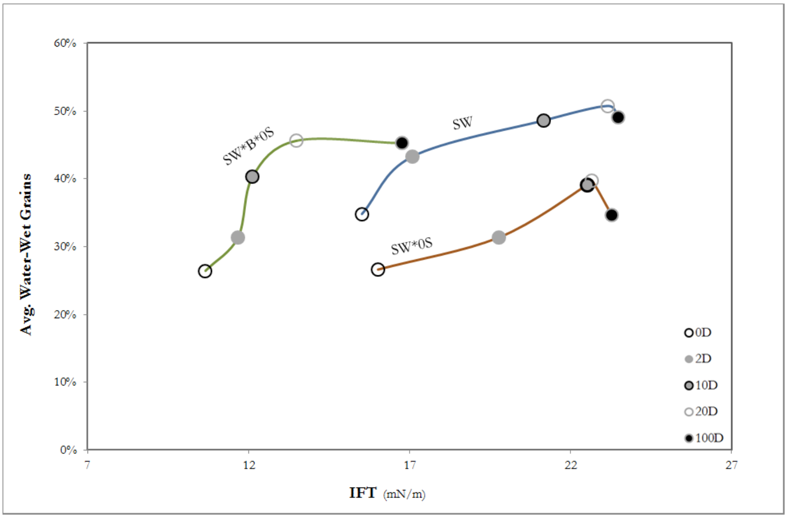


Fig. 5.16: Correlation between IFT at 23°C and average water-wet grains at 100°C. Source: [75]

5.9 Retained Oil

The potential of ionically modified waters to change the wetting conditions is different as it can be seen in Figure 5.6 as the 20D*SW has more potential than SW to improve the water wetness of Dan chalk at same operating conditions. Hence, there would always be potential for more effective fluid (advanced water) to improve the oil recovery by changing wettability until it reaches the optimum wetting conditions. The flotation technique can serve better in screening and identification of most effective advanced water as it provides data by direct observation of the oil adhesion on rock surfaces. This technique also provides information about the amount of oil that is left on the water-wet surfaces after wettability alteration which is hard to measure with any other method. Consistent with flotation results, Thomas et al. [124] also observed that carbonate mineral surfaces were left visibly brown after exposure to organic compounds even if the surfaces remained water-wet. The authors found that organic components of the crude oil such as organic acids adsorbed strongly (chemisorption) on carbonate surfaces, whereas other components such as alcohols and amines adsorbed weakly (physisorped). The weakly-sorbed species could be removed or displaced by most solvents, but strongly adsorbed species could not. The adsorbed species altered the wettability as measured by contact angle. Long-chained organic acids in particular strongly adsorbed [130] and formed mono-layers on the mineral surface. In contrast, the sulfur-containing compounds and nitrogen bases were weakly-adsorbed and the sorption was easily reversed.

The amount of oil attached to water-wet grains for SW and diluted SW at

100^{o}C is shown in Figure 5.17. The amount of retained oil can not be directly correlated with the amount of water-wet grains and the amount of refractory oil is similar at about 0.3 grams for SW, 2D*SW and 10D*SW [75]. The 100-fold dilution showed the greatest amount of retained oil on water-wet chalk grains and the 20-fold dilution the least. The details of the retained oil on water-wet grains of Dan chalk for SW*0S and SW*B*0S are given in Sohal et al. [75].

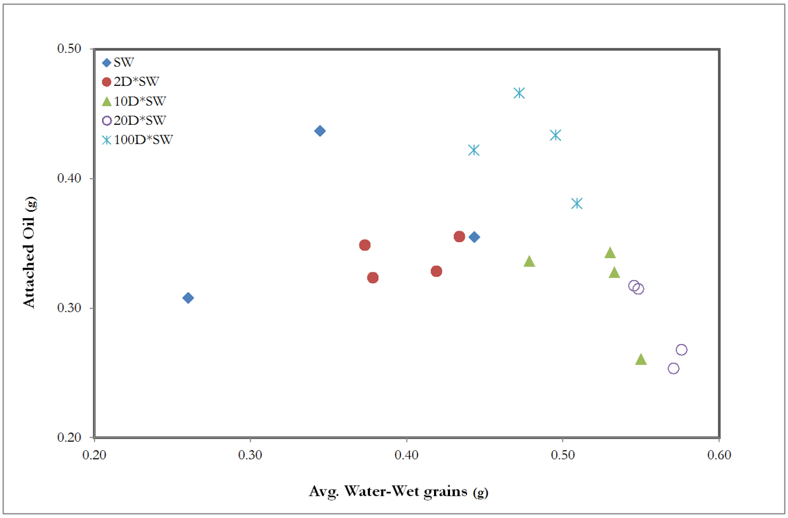


Fig. 5.17: Oil adhesion on water-wet chalk grains in the case of seawater and its different dilutions at 100^{o}C. Source: [75]

6 Conclusions & Further Work

Ionically modified water (advanced water) is an enhanced oil recovery fluid that improves the oil recovery potentially by changing the wettability of a reservoir rock. This work adds the information about fundamental understanding of the wettability alteration mechanisms by changing the fluid composition and strength at different operating conditions. The governing mechanisms behind the wettability alteration were investigated with flotation technique and coherently explained in the respective sections. The overall conclusions of this research work are summarized under the following sections.

Ionic Composition and Wettability

The ionic composition of seawater, seawater without sulfate and seawater enriched with borate instead of sulfate was investigated with flotation technique at three different temperatures (23, 50 & 100^{o}C). Moreover, the effect of potential scale forming ions like Sr^{2+} and Ba^{2+} in formation water was explored with the same technique. Based on the results following conclusions were drawn:

- The Dan chalk that was aged without Sr^{2+} and Ba^{2+} ions in formation water found 30% more water-wet at 23^{o}C and 6% at 100^{o}C compared to the chalk that was aged with these potential scale forming ions.
- Seawater and its diluted versions have more potential to improve the water wetness of Dan chalk than all other used brines at 100^{o}C. The potential of SW*0S and SW*B*0S is almost equal at full strength solution to 2X dilution but on further dilutions borate brines improved the water wetness more than sulfate free brine at 100^{o}C.

Ionic Strength and Wettability

In this aspect of ionically modified water the amount of total dissolved solids in SW, SW*B*0S and SW*0S was gradually decreased by adding DIW and their impact on wettability was explored with flotation the conclusions are as follows:

- The fraction of water-wet surfaces of the Dan chalk increased as dilution increased to 20X at 100^{o}C. Dilution increased the water-wet fraction of Dan chalk for all the tested brines in this CBR system. The brines improved the water wetness in following order SW > SW*B*0S > SW*0S almost for all dilutions.

Temperature Effect

The effect of temperature on potential of all wettability modifying brines was explored with flotation technique. The main conclusions of temperature effect are shortly summarized as:

- Dan chalk was more water-wet at low temperatures (23 & 50^{o}C) in seawater and the water wetness improved up to 10D. But the total shift in wettability was only a few percent. The system was oil-wet at 100^{o}C compared to 23 & 50^{o}C and the oil-wet fraction decreased up to 20D at 100^{o}C. The total shift in wettability was 16% with dilution at 100^{o}C.
- The maximum shift in wettability was 21% between the lowest and the highest temperature in case of SW. It was observed at full strength solution.
- In sulfate free seawater the wettability shift was 5 to 12% at 23 and 50^{o}C respectively. It reached to a maximum value of 13% when temperature was increased to 100^{o}C.
- The maximum difference in water-wet fraction was 30% over the temperature range and was observed at full strength solutions.
- Borate brine turned the Dan chalk oil-wet relative to other brines at full strength solution at all tested temperatures. Hence, Dilution improved the water wetness up to 20D similar to the other brines at 23 & 50^{o}C.
- The shift in wettability was 30%, 24% and 20% at 23, 50 and 100^{o}C respectively for SW*B*0S. The maximum difference in water-wet fraction at full strength solution of borate brine was only 1% between 23 and 100^{o}C and it increased upto 14% as dilution increased to 10D.
- The comparison of all the three brines showed that dilution of SW shifted the wettability more than SW*0S and SW*B*0S as temperature increased from 23 to 100^{o}C.

Sulfate Concentration

The potential of synthetic seawater enriched with 2 to 4 times more sulfate than normal SW was investigated at 23, 50 & 100^{o}C and the following results were obtained.

- Sulfate improved the water-wet fraction at low concentrations (0.002 mol/l = 10DSW) in this crude-brine-rock system at 23 and 50^{o}C. But on further increasing the concentration of sulfate in SW it turned the system oil-wet and constantly increased oil-wetting up to 96 mmol/l at 100^{o}C.

Wettability and IFT

The IFT between crude oil and advanced fluids was measured at 23 and 90^{o}C. An attempt was made to find a relation between wettability and IFT. The following conclusions were drawn:

- By increasing the temperature from 23^{o}C to 90^{o}C the IFT decreased for SW and SW*0S brines. But in case of borate brine it increased when temperature was shifted from 23 to 90^{o}C. Dilution of all the tested brines increased the IFT at all temperatures.

Recommendations for Further Work

The flotation is a simple and easy technique to measure the wetting characteristics of a reservoir rock. The influence of different parameters like brine, temperature, crude oil, rock composition (mineralogy), pH etc., on wettability can be easily determined with good reproducibility and precision in a short period of time. The most important future recommendations are as follows:

- Flotation successfully matched the already published imbibition and coreflood results. But there is a need to investigate the amount of additional oil recovered in corefloods as a result of wettability alteration at the same CBR system and operating conditions. This way a relation could be established between fraction of wettability alteration and recovered amount of additional oil.
- Oil inside the reservoir pores exists at a certain pore pressure and flotation can be upgraded to add the influence of pressure on wettability. This approach is under consideration at the department.
- The role of pH change is very significant in the process of low salinity (diluted brines) waterflooding and could be easily independently explored with flotation.
- Flotation should be tested to identify the role of crude oil with different acid and base numbers on wettability.
- In the current study only 23, 50 and 100^{o}C were used to explore the temperature effect but higher temperatures should also be considered.
- In this work the potential of different brines was investigated using single rock (Dan outcrop chalk) and crude oil. But this work should be extended to other rock types like limestone, dolomite, sandstone etc. Especially, the results of outcrop and reservoir cores of similar lithologies must be compared and studied to evaluate any differences.

- The separate effect of Ca and Mg ions on wettability changes of chalk reservoirs should be investigated.

References

[1] James J Sheng. Comparison of the effects of wettability alteration and ift reduction on oil recovery in carbonate reservoirs. *Asia-Pacific Journal of Chemical Engineering*, 8(1):154–161, 2013.

[2] Kishore. K. Mohanty and Sriram Chandrasekhar. Wettability alteration with brine composition in high temperature carbonate reservoirs. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, New Orleans, Louisiana, USA, September-Oct 30-2, 2013. Paper SPE 166280.

[3] Rod Sloan. Quantification of uncertainty in recovery efficiency predictions: lessons learned from 250 mature carbonate fields. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Denver, Colorado, USA, October 5-8, 2003. Paper SPE 84459.

[4] Joseph John Taber, FD Martin, and RS Seright. Eor screening criteria revisited-part 1: Introduction to screening criteria and enhanced recovery field projects. *SPE Reservoir Engineering*, 12(03):189–198, 1997.

[5] Vladimir Alvarado and Eduardo Manrique. Enhanced oil recovery: an update review. *Energies*, 3(9):1529–1575, 2010.

[6] Robin Gupta, Bhargaw Adibhatla, and Kishore Kumar Mohanty. Parametric study to enhance oil recovery rate from fractured oil wet carbonate reservoirs. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Denver, Colorado, USA, September 21-24, 2008. Paper SPE 116485.

[7] B. Yadali Jamaloei. Chemical flooding in naturally fractured reservoirs: fundamental aspects and field-scale practices. *Oil & Gas Science and Technology-Revue d'IFP Energies nouvelles*, 66(6):991–1004, 2011.

[8] Anwar R Awan, Rune Teigland, and Jon Kleppe. A survey of north sea enhanced-oil-recovery projects initiated during the years 1975 to 2005. *SPE Reservoir Evaluation & Engineering*, 11(03):497–512, 2008.

[9] J. E. Sylte, L. D. Hallenbeck, and L. K. Thomas. Ekofisk formation pilot waterflood. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Houston, TX, USA, October 2-5, 1988. Paper SPE 18276.

[10] LD Hallenbeck, JE Sylte, DJ Ebbs, and LK Thomas. Implementation of the ekofisk field waterflood. *SPE Formation Evaluation*, 6(3):284–290, 1991.

[11] Tor Austad, Skule Strand, Merete Vadla Madland, Tina Puntervold, and Reidar Inge Korsnes. Seawater in chalk: An eor and compaction fluid. *Paper SPE 11370 presented at the SPE International Petroleum Technology Conference, Dubai, U.A.E, 4-6 December.*, 2007.

[12] Robin Gupta, P Griffin, Lu Hu, Thomas W Willingham, Mauro Lo Cascio, J Jane Shyeh, and CR. Harries. Enhanced waterflood for middle east carbonate cores-impact of injection water composition. In *Proceedings of the SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, September 25-28, 2011. Paper SPE 142668.

[13] T Austad, SF Shariatpanahi, S Strand, CJJ Black, and KJ Webb. Conditions for a low-salinity enhanced oil recovery (eor) effect in carbonate oil reservoirs. *Energy & fuels*, 26(1):569–575, 2011.

[14] Amira Al Harrasi, Rashid Salim Al-maamari, and Shehadeh K Masalmeh. Laboratory investigation of low salinity waterflooding for carbonate reservoirs. In *Proceedings of the SPE International Petroleum Conference and Exhibition*, Abu Dhabi, UAE, November 11-14, 2012. Paper SPE 161468.

[15] Hazim H Al-Attar, Mohamed Y Mahmoud, Abdulrazag Y Zekri, Reyadh Almehaideb, and Mamdouh Ghannam. Low-salinity flooding in a selected carbonate reservoir: experimental approach. *Journal of Petroleum Exploration and Production Technology*, 3(2):139–149, 2013.

[16] A Kafili Kasmaei and DN Rao. Is wettability alteration the main cause for enhanced recovery in low-salinity waterflooding? In *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, April 12-16, 2014. Paper SPE 169120.

[17] Dag C Standnes and Tor Austad. Wettability alteration in chalk: 2. mechanism for wettability alteration from oil-wet to water-wet using surfactants. *Journal of Petroleum Science and Engineering*, 28(3):123–143, 2000.

[18] Skule Strand, Dag C Standnes, and Tor Austad. Spontaneous imbibition of aqueous surfactant solutions into neutral to oil-wet carbonate cores: Effects of brine salinity and composition. *Energy & fuels*, 17(5):1133–1144, 2003.

[19] S Strand, DC Standnes, and T Austad. New wettability test for chalk based on chromatographic separation of scn- and so_4^{2-}. *Journal of Petroleum Science and Engineering*, 52(1):187–197, 2006.

[20] Peimao Zhang, Medad T Tweheyo, and Tor Austad. Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. *Energy & fuels*, 20(5):2056–2062, 2006.

[21] Peimao Zhang, Medad T Tweheyo, and Tor Austad. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions ca^{2+}, mg^{2+}, and so_4^{2-}. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301(1):199–208, 2007.

[22] Tina Puntervold, Skule Strand, Raed Ellouz, and Tor Austad. Modified seawater as a smart eor fluid in chalk. *Journal of Petroleum Science and Engineering*, 133:440–443, 2015.

[23] Sunil Kokal and Abdulaziz Al-Kaabi. Enhanced oil recovery: challenges & opportunities. *World Petroleum Council: Official Publication*, 64, 2010.

[24] M Adeel Sohal, Geoffrey Thyne, and Erik G Søgaard. Review of recovery mechanisms of ionically modified waterflood in carbonate reservoirs. *Energy & Fuels*, 30(3):1904–1914, 2016.

[25] L.W. Lake. *Enhanced oil recovery*. Prentice Hall, 1989.

[26] T Austad, S Strand, EJ Høgnesen, and P. Zhang. Seawater as ior fluid in fractured chalk. In *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Woodlands, Texas, USA, February 2-4, 2005. Paper SPE 93000.

[27] Tor Austad, Skule Strand, and Tina Puntervold. Is wettability alteration of carbonates by seawater caused by rock dissolution. In *Proceedings of the SCA International Symposium*, Noordwijk, Netherlands, September 27-30, 2009. Paper SCA 2009-43.

[28] Tor Austad, Seyed Farzad Shariatpanahi, Skule Strand, Hakan Aksulu, and Tina Puntervold. Low salinity eor-effects in limestone reservoir cores containing anhydrite: a discussion of the chemical mechanism. *Energy & Fuels*, 2015.

[29] Skule Strand, Eli J Høgnesen, and Tor Austad. Wettability alteration of carbonates-effects of potential determining ions (ca^{2+} and so_4^{2-}) and temperature. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 275(1):1–10, 2005.

[30] Eli Jens Hognesen, Skule Strand, and Tor Austad. Waterflooding of preferential oil-wet carbonates: Oil recovery related to reservoir temperature and brine composition. *Paper SPE 94166 presented at the SPE Europec/EAGE Annual Conference, Madrid, Spain, 13-16 June*, 2005.

[31] Tina Puntervold, Skule Strand, and Tor Austad. Water flooding of carbonate reservoirs: Effects of a model base and natural crude oil bases on chalk wettability. *Energy & fuels*, 21(3):1606–1616, 2007.

[32] S Jafar Fathi, Tor Austad, and Skule Strand. Smart water as a wettability modifier in chalk: The effect of salinity and ionic composition. *Energy & fuels*, 24(4):2514–2519, 2010.

[33] S Jafar Fathi, Tor Austad, and Skule Strand. Water-based enhanced oil recovery (eor) by smart water: Optimal ionic composition for eor in carbonates. *Energy & fuels*, 25(11):5173–5179, 2011.

[34] Seyed Jafar Fathi, Tor Austad, and Skule Strand. Water-based enhanced oil recovery (eor) by smart water in carbonate reservoirs. In *Proceedings of the SPE EOR Conference at Oil and Gas West Asia*, Muscat, Oman, April 16-18, 2012. Paper SPE 154570.

[35] Ali A Yousef, Salah Al-Saleh, Abdulaziz Al-Kaabi, and Mohammed Al-Jawfi. Laboratory investigation of novel oil recovery method for carbonate reservoirs. In *Proceedings of the CSUG/SPE Canadian Unconventional Resources and International Petroleum Conference*, Calgary, Alberta, Canada, October 19-21, 2010. Paper SPE 137634.

[36] Ali A Yousef, SH Al-Saleh, and Mohammed Saleh Al-Jawfi. New recovery method for carbonate reservoirs through tuning the injection water salinity: Smartwater flooding. In *Proceedings of the SPE EUROPEC/EAGE Annual Conference and Exhibition*, Vienna, Austria, May 23-26, 2011. Paper SPE 143550.

[37] Julija Romanuka, Jan Hofman, Dick Jacob Ligthelm, Bart Suijkerbuijk, Fons Marcelis, Sjaam Oedai, Niels Brussee, Hilbert van der Linde, Hakan Aksulu, and Tor Austad. Low salinity eor in carbonates. In *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, April 14-18, 2012. Paper SPE 153869.

[38] Yi Zhang and Hemanta Sarma. Improving waterflood recovery efficiency in carbonate reservoirs through salinity variations and ionic exchanges: A promising low-cost smart waterflood approach. In *Proceedings of the SPE International Petroleum Conference and Exhibition*, Abu Dhabi, UAE, November 11-14, 2012. Paper SPE 161631.

[39] Philip C Myint and Abbas Firoozabadi. Thin liquid films in improved oil recovery from low-salinity brine. *Current Opinion in Colloid & Interface Science*, 20(2):105–114, 2015.

[40] NR Morrow, S Ma, X Zhou, and X Zhang. Characterization of wettability from spontaneous imbibition measurements. *Paper PETSOC-94-47 presented at the Annual Technical Meeting, Calgary, Alberta, 12-15 June.*, 1994.

[41] SK Masalmeh. Impact of capillary forces on residual oil saturation and flooding experiments for mixed to oil-wet carbonate reservoirs. In *Proceedings of SCA International Symposium of the Society of Core Analysts*, berdeen, Scotland, UK, August 27-30, 2012. Paper SCA2012-11.

[42] MM Sharma and PR Filoco. Effect of brine salinity and crude-oil properties on oil recovery and residual saturations. *SPE Journal*, 5(03):293–300, 2000.

[43] Chinedu Christian Agbalaka, Abhijit Yeshwant Dandekar, Shirish Liladhar Patil, Santanu Khataniar, and James Hemsath. The effect of wettability on oil recovery: a review. In *Proceedings of the SPE Asia Pacific Oil and Gas Conference and Exhibition*, Perth, Australia, October 20-22, 2008. Paper SPE 114496.

[44] William Anderson. Wettability literature survey-part 2: Wettability measurement. *Journal of Petroleum Technology*, 38(11):1–246, 1986.

[45] Jill S Buckley. Chemistry of the crude oil/brine interface. In *Proceedings of the SPE 3rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery*, September 21-23, 1994.

[46] George Hirasaki and Danhua Leslie Zhang. Surface chemistry of oil recovery from fractured, oil-wet, carbonate formations. *SPE Journal*, 9(2):151–162, 2004.

[47] Hassan Mahani, Arsene Levy Keya, Steffen Berg, Willem-Bart Bartels, Ramez Nasralla, and William R Rossen. Insights into the mechanism of wettability alteration by low-salinity flooding (lsf) in carbonates. *Energy & Fuels*, 29(3):1352–1367, 2015.

[48] MA Fernø, R Grønsdal, J Åsheim, A Nyheim, M Berge, and A Graue. Use of sulfate for water based enhanced oil recovery during spontaneous imbibition in chalk. *Energy & fuels*, 25(4):1697–1706, 2011.

[49] Ahmed M Shehata, Mohammed B Alotaibi, and Hisham A Nasr-El-Din. Waterflooding in carbonate reservoirs: Does the salinity matter? *SPE Reservoir Evaluation & Engineering*, 17(3):304–313, 2014.

[50] John C Crittenden, R Rhodes Trussell, David W Hand, Kerry J Howe, and George Tchobanoglous. *MWH's water treatment: principles and design*. John Wiley & Sons, 2012.

[51] Ali A Yousef, Salah Al-Saleh, Abdulaziz Al-Kaabi, and Mohammed Al-Jawfi. Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs. *SPE Reservoir Evaluation & Engineering*, 14(5):578–593, 2011.

[52] Ali A Yousef, Salah Al-Saleh, and Mohammed Al-Jawfi. Improved/enhanced oil recovery from carbonate reservoirs by tuning injection water salinity and ionic content. In *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, April 14-18, 2012. Paper SPE 154076.

[53] Hassan Mahani, Arsene Levy Keya, Steffen Berg, and Ramez Nasralla. The effect of salinity, rock type and ph on the electrokinetics of carbonate-brine interface and surface complexation modeling. In *Proceedings of the SPE Reservoir Characterisation and Simulation Conference and Exhibition*, Abu Dhabi, UAE, September 14-16, 2015. Paper SPE 175568.

[54] Robert J Hunter. *Foundations of colloid science*. Oxford University Press, 2001.

[55] Pallab Ghosh. *Colloid and interface science*. PHI Learning Pvt. Ltd., 2009.

[56] RJ Hunter. *Colloid science: zeta potential in colloid science: principles and applications*. London: Academic Press, 1981.

[57] Karlheinz Graf and Michael Kappl. *Physics and chemistry of interfaces*. John Wiley & Sons, 2006.

[58] Victor M Starov, Manuel G Velarde, and Clayton J Radke. *Wetting and spreading dynamics*, volume 138. CRC press, 2007.

[59] GJ Hirasaki. Wettability: fundamentals and surface forces. *SPE Formation Evaluation*, 6(2):217–226, 1991.

[60] Berrin Tansel, John Sager, Tony Rector, Jay Garland, Richard F Strayer, Lanfang Levine, Michael Roberts, Mary Hummerick, and Jan Bauer. Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. *Separation and Purification Technology*, 51(1):40–47, 2005.

[61] Jacob N Israelachvili. *Intermolecular and surface forces: revised third edition*. Academic press, 2011.

[62] Marziyeh Rahbar, Ali Roosta, Shahab Ayatollahi, and Mohammad H Ghatee. Prediction of three-dimensional (3-d) adhesion maps, using the stability of the thin wetting film during the wettability alteration process. *Energy & Fuels*, 26(4):2182–2190, 2012.

[63] Zohreh Jalili and Vahid Alipour Tabrizy. Mechanistic study of the wettability modification in carbonate and sandstone reservoirs during water/low salinity water flooding. *Energy and Environment Research*, 4(3):78, 2014.

[64] Quan Xie, Ali Saeedi, and Ehsan Pooryousefy. Extended dlvo-based estimates of surface force in low salinity water flooding. *Journal of Molecular Liquids*, 2016.

[65] Joseph Keddie and Alexander F Routh. *Fundamentals of latex film formation: processes and properties*. Springer Science & Business Media, 2010.

[66] Nora Kristen and Regine von Klitzing. Effect of polyelectrolyte/surfactant combinations on the stability of foam films. *Soft Matter*, 6(5):849–861, 2010.

[67] ZI Khatib and JR Salanitro. Reservoir souring: analysis of surveys and experience in sour waterfloods. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, San Antonio, Texas, USA, October 5-8, 1997. Paper SPE 38795.

[68] Ahmed Kasha, Hasan Al-Hashim, Wael Abdallah, Reza Taherian, and Bastian Sauerer. Effect of ca^{2+}, mg^{2+} and so_4^{2-} ions on the zeta potential of calcite and dolomite particles aged with stearic acid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 482:290–299, 2015.

[69] Asghar Gandomkar and Mohammad Reza Rahimpour. Investigation of low-salinity waterflooding in secondary and tertiary enhanced oil recovery in limestone reservoirs. *Energy & Fuels*, 29(12):7781–7792, 2015.

[70] Adeel Zahid, Erling Halfdan Stenby, and Alexander A. Shapiro. Smart waterflooding (high sal/low sal) in carbonate reservoirs. In *Proceedings of the SPE Europec/EAGE Annual Conference*, Copenhagen, Denmark, June 4-7, 2012. Paper SPE 154508.

[71] A Hiorth, LM Cathles, and MV Madland. The impact of pore water chemistry on carbonate surface charge and oil wettability. *Transport in porous media*, 85(1):1–21, 2010.

[72] ST Dubey and PH Doe. Base number and wetting properties of crude oils. *SPE Reservoir Engineering*, 8(3):195–200, 1993.

[73] Koichi Takamura and Ross S Chow. The electric properties of the bitumen/water interface part ii. application of the ionizable surface-group model. *Colloids and Surfaces*, 15(1):35–48, 1985.

[74] Eli J Høgnesen, Martin Olsen, and Tor Austad. Capillary and gravity dominated flow regimes in displacement of oil from an oil-wet chalk using cationic surfactant. *Energy & fuels*, 20(3):1118–1122, 2006.

[75] M Adeel Sohal, Geoffrey Thyne, and Erik G Søgaard. Novel application of the flotation technique to measure the wettability changes by ionically modified water for improved oil recovery in carbonates. *Energy & Fuels*, 30(8):6306–6320, 2016.

[76] W Meng, MR Haroun, HK Sarma, JT Adeoye, P Aras, S Punjabi, MM Rahman, and M Al Kobaisi. A novel approach of using phosphate-spiked smart brines to alter wettability in mixed oil-wet carbonate reservoirs. In *Proceedings of the SPE International Petroleum Exhibition and Conference*, Abu Dhabi, UAE, November 9-12, 2015. Paper SPE 177551.

[77] Taha Moustafa Okasha and Abduljalil Alshiwaish. Effect of brine salinity on interfacial tension in arab-d carbonate reservoir, saudi arabia. In *Proceedings of the SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, March 15-18, 2009. Paper SPE 119600.

[78] Murtdha AlShaikh and Jagannathan Mahadevan. Impact of brine composition on carbonate wettability: a sensitivity study. In *Proceedings of the SPE Saudi Arabia Section Technical Symposium and Exhibition*, Al-Khobar, Saudi Arabia, April 21-24, 2014. Paper SPE 172187.

[79] Chandra S Vijapurapu and Dandina N Rao. Effect of brine dilution and surfactant concentration on spreading and wettability. In *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Houston, Texas, USA, February 5-7, 2003. Paper SPE 80273.

[80] Mohammed B Alotaibi and Hisham A. Nasr-El-Din. Salinity of injection water and its impact on oil recovery. *Paper SPE 121569 presented at the SPE EUROPEC/EAGE Conference and Exhibition, Amsterdam, The Netherlands, 8-11 June*, 2009.

[81] Matteo Gennaro. The chalk depositional system in the central graben-concepts of regional geology, sedimentology and stratigraphy. *3D seismic stratigraphy and reservoir characterization of the Chalk Group in the Norwegian Central Graben, North Sea*, 2011.

[82] JA Cartwright. The kinematics of inversion in the danish central graben. *Geological Society, London, Special Publications*, 44(1):153–175, 1989.

[83] RFP Hardman. Chalk reservoirs of the north sea. *Bulletin of the Geological Society of Denmark*, 30(3-4):119–137, 1982.

[84] M.A. Andersen. *Petroleum Research in North Sea Chalk*. RF-Rogaland Research, 1995.

[85] Jake M Hancock. The petrology of the chalk. *Proceedings of the Geologists' Association*, 86(4):499–535, 1975.

[86] William Lawrence Bragg. The structure of some crystals as indicated by their diffraction of x-rays. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, volume 89, pages 248–277, 1913.

[87] William Alexander Deer, Robert Andrew Howie, and Jack Zussman. *An introduction to the rock-forming minerals*, volume 696. Longman London, 1992.

[88] Nora H. de Leeuw and Stephen C. Parker. Surface structure and morphology of calcium carbonate polymorphs calcite, aragonite, and vaterite: an atomistic approach. *The Journal of Physical Chemistry B*, 102(16):2914–2922, 1998.

[89] Mariëtte Wolthers, Laurent Charlet, and Philippe Van Cappellen. The surface chemistry of divalent metal carbonate minerals; a critical assessment of surface charge and potential data using the charge distribution multi-site ion complexation model. *American Journal of Science*, 308(8):905–941, 2008.

[90] Frank Heberling, Thomas P Trainor, Johannes Lützenkirchen, Peter Eng, Melissa A Denecke, and Dirk Bosbach. Structure and reactivity of the calcite–water interface. *Journal of colloid and interface science*, 354(2):843–857, 2011.

[91] Promorphology of Crystals 3d crystals. `http://www.metafysica.nl/turing/preparation_3dim_4.html`. Accessed: 2016-09-21.

[92] Dudley William Thompson and Pamela Gillian Pownall. Surface electrical properties of calcite. *Journal of colloid and interface science*, 131(1):74–82, 1989.

[93] Susan L Stipp and Michael F Hochella. Structure and bonding environments at the calcite surface as observed with x-ray photoelectron spectroscopy (xps) and low energy electron diffraction (leed). *Geochimica et Cosmochimica Acta*, 55(6):1723–1736, 1991.

[94] William M White. *Geochemistry*. John Wiley & Sons, 2013.

[95] Philippe Van Cappellen, Laurent Charlet, Werner Stumm, and Paul Wersin. A surface complexation model of the carbonate mineral-aqueous solution interface. *Geochimica et Cosmochimica Acta*, 57(15):3505–3518, 1993.

[96] Y Liang, AS Lea, DR Baer, and MH Engelhard. Structure of the cleaved $caco_3$ (1014) surface in an aqueous environment. *Surface Science*, 351(1):172–182, 1996.

[97] Patrick V Brady and Geoffrey Thyne. Functional wettability in carbonate reservoirs. *Energy & Fuels*, 2016.

[98] Jill S Buckley. Evaluation of reservoir wettability and its effect on oil recovery. *Final Report*, 1997.

[99] James G Speight. *The chemistry and technology of petroleum*. CRC press, 2014.

[100] Simon I Andersen, Mahavadi Sharath Chandra, John Chen, Ben Yanbin Zeng, Fenglou Zou, Mmilili M Mapolelo, Wael A Abdallah, and Johannes Jan Buiting. Detection and impact of carboxylic acids at the crude oil-water interface. *Energy & Fuels*, 2016.

[101] Abhijit Y Dandekar. *Petroleum reservoir rock and fluid properties*. CRC press, 2013.

[102] Elaine G Shafrin and William A Zisman. Constitutive relations in the wetting of low energy surfaces and the theory of the retraction method of preparing monolayers1. *The Journal of Physical Chemistry*, 64(5):519–524, 1960.

[103] Contact angles and Wettability rame'-hart, glossary of surface science terms. `http://www.ramehart.com/`. Accessed: 2016-09-27.

[104] Derrick O Njobuenwu, Esio O Oboho, and Rhoda H Gumus. Determination of contact angle from contact area of liquid droplet spreading on solid substrate. *Leonardo Electronic Journal of Practices and Technologies*, 10:29–38, 2007.

[105] FC Benner and FE Bartel. The effect of polar impurities upon capillary and surface phenomena in petroleum production. In *Proceedings of the API Drilling and Production Practice*, pages 341–348, 1941.

[106] CJ Radke, AR Kovscek, and H Wong. A pore-level scenario for the development of mixed wettability in oil reservoirs. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Washington, D.C., USA, October 4-7, 1992. Paper SPE 24880.

[107] Forrest F Craig. *The reservoir engineering aspects of waterflooding*, volume 3. Society of Petroleum Engineers, 1971.

[108] Faruk Civan. *Reservoir formation damage*, volume 2. Gulf Professional Publishing, 2015.

[109] JE Bobek, CC Mattax, and MO Denekas. Reservoir rock wettability its significance and evaluation. *Trans. AIME*, 213:155–160, 1958.

[110] William G Anderson. Wettability literature survey-part 4: Effects of wettability on capillary pressure. *Journal of Petroleum Technology*, 39(10):1–283, 1987.

[111] William G Anderson. Wettability literature survey part 5: The effects of wettability on relative permeability. *Journal of Petroleum Technology*, 39(11):1–453, 1987.

[112] Irving Fatt and Waldemar A Klikoff Jr. Effect of fractional wettability on multiphase flow through porous media. *Journal of Petroleum Technology*, 11(10):71–76, 1959.

[113] Jack Newcombe, John McGhee, and MJ Rzasa. Wettability versus displacement in water flooding in unconsolidated sand columns. *Trans. AIME*, 204(1955):227–232, 1955.

[114] HY Jennings Jr. Surface properties of natural and synthetic porous media. *Prod. Monthly*, 21(5):20–24, 1957.

[115] Harvey T Kennedy, Edward O Burja, and Robert S Boykin. An investigation of the effects of wettability on oil recovery by water flooding. *The Journal of Physical Chemistry*, 59(9):867–869, 1955.

[116] TF Moore and RL Slobod. The effect of viscosity and capillarity on the displacement of oil by water. *Producers Monthly*, 20(10):20–30, 1956.

[117] P. P. Jadhunandan and N. R. Morrow. Effect of wettability on waterflood recovery for crude-oil/brine/rock systems. *SPE Reservoir Engineering*, 10(01):40–46, 1995.

[118] RA Salathiel. Oil recovery by surface film drainage in mixed-wettability rocks. *Journal of Petroleum Technology*, 25(10):1–216, 1973.

[119] James Sheng. *Enhanced oil recovery field case studies*. Gulf Professional Publishing, 2013.

[120] Tianguang Fan and Jill S Buckley. Acid number measurements revisited. In *Proceedings of the SPE/DOE Symposium on Improved Oil Recovery*, Tulsa, Oklahoma, USA, April 22-26, 2006. Paper SPE 99884.

[121] Earl Amott. Observations relating to the wettability of porous rock. In *Proceedings of the SPE Fall Meeting of Basin Section*, Los Angeles, California, USA, October 16-17, 1958. Paper SPE 1167.

[122] Erle C Donaldson, Rex D Thomas, and Philip B Lorenz. Wettability determination and its effect on recovery efficiency. *Society of Petroleum Engineers Journal*, 9(01):13–20, 1969.

[123] Norman R Morrow. Wettability and its effect on oil recovery. *Journal of Petroleum Technology*, 42(12):1–476, 1990.

[124] Michele Moisio Thomas, Jamie A Clouse, and John M Longo. Adsorption of organic compounds on carbonate minerals: 1. model compounds and their influence on mineral wettability. *Chemical Geology, Elsevier*, 109(1):201–213, 1993.

[125] BMJM Suijkerbuijk, JP Hofman, Dick Jacob Ligthelm, Julija Romanuka, Niels Brussee, HA Van der Linde, and AHM Marcelis. Fundamental investigations into wettability and low salinity flooding by parameter isolation. In *Proceedings of the SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, April 14-18, 2012. Paper SPE 154204.

[126] MH Sayyouh, AM Hemeida, MS Al-Blehed, and SM Desouky. Role of polar compounds in crude oils on rock wettability. *Journal of Petroleum science and Engineering*, 6(3):225–233, 1991.

[127] P Zhang and Tor Austad. The relative effects of acid number and temperature on chalk wettability. In *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Woodlands, Texas, USA, February 2-4, 2005. Paper SPE 92999.

[128] Seyed Farzad Shariatpanahi, Skule Strand, and Tor Austad. Initial wetting properties of carbonate oil reservoirs: effect of the temperature and presence of sulfate in formation water. *Energy & Fuels*, 25(7):3021–3028, 2011.

[129] Shahab Ayatollahi and Mohammad M Zerafat. Nanotechnology-assisted eor techniques: New solutions to old challenges. In *Proceedings of the SPE Oilfield Nanotechnology Conference and Exhibition*, Noordwijk, Netherlands, June 12-14, 2012. Paper SPE 157094.

[130] Paulina Mwangi, Geoffrey Thyne, and Dandina Rao. Extensive experimental wettability study in sandstone and carbonate-oil-brine systems: Part 1 screening tool development. In *Proceedings of the SCA International Symposium*, Napa Valley, California, USA, September 16-19, 2013. Paper SCA 3013-84.

Appendices

Appendix A

Flotation Technique Refinement

A couple of experiment results that were performed to improve the flotation technique are presented here as it has been mentioned in flotation technique description, section 4. The effect of major influencing factors is explained with the help of pictures, diagrams and charts. It was hard to add all the experiment results due to space limits so only a few of them are selected to present here.

Shaking and Mixing Effect

Oil shaking affects the overall percentage of oil-wet and water-wet chalk grains. On frequent shaking oil is forced to attach to chalk grains and consequently larger amount of oil attached to the water-wet grains as it can be seen in the right hand side test tube of Figure A1. In solvent cleaning step of flotation process a large amount of oil was recovered from water-wet grains that were frequently shaken. A comparison of different shaking times of crude oil is depicted in Figure A1.

Oil Aging Effect

It was measured by aging the chalk powder at room temperature and 100^oC with different brines from 2 hours to 2 week. The results showed that grains were more water-wet if aged less than 15 hours after that aging did not influence the results significantly as it can be seen in Figure A2. Especially, at high temperature (100^oC) 15 hours aging was enough but in this experimental study all the samples were aged at least for 24 hours.

Oil and Brine Volume Effect

In this experimental study different volumes of brine from 5 to 15 ml were used and results were quite similar for all values. But it was more convenient to separate the oil-wet and water-wet chalk grains when 15 ml of brine

Fig. A1: The right hand side test tube showing the frequent shaking while the left hand side test tube showing the appropriate shaking (twice a day for few seconds) results.

were used. It also depends on the volume of the test tube so in these experiments the total volume of the test tube was 20 ml. Therefore, 10 ml of the brine selected so that during mixture shaking and aging all the grains get equal chance to mix with aqueous and oleic phases. But different oil volumes influenced the results a lot as it can be seen in Figure A3. In this testing procedure the brine volume (10 ml) was kept constant whereas oil volumes changed from 3 ml to 8 ml. The bottom right test tubes are showing 5 ml brine and 8 ml of crude oil and mixture turned into emulsion. So, oil should not be more than 50 % in ratio to perform the experiments.

Effect of Grains Mass

The best mass of the grains depends on the volume of oil, brine and test tube in this study 10 ml of brine and 5 ml of crude oil were used. But different masses of chalk grains were tested with 3 ml of decane 10 ml of brine and only three of them are presented in Figure A4. Higher mass of chalk grains produced more repeatable results but the selection of right mass also depends on the other factors as described above. But the average results of 1.0 g of chalk sample were almost equal to higher masses therefore it was selected to continue the experiments.

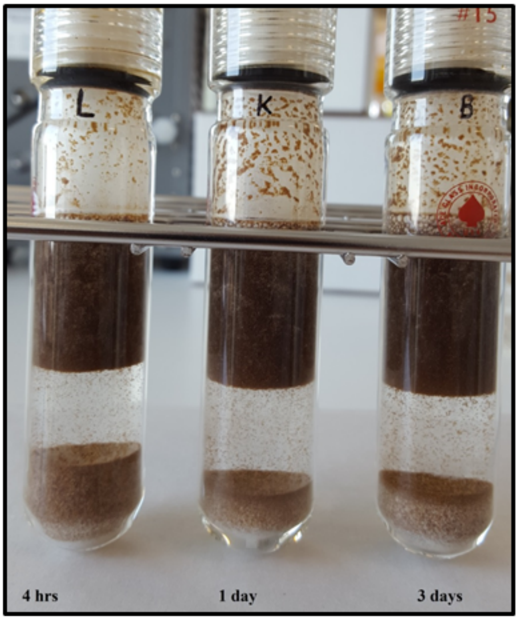


Fig. A2: The effect of different aging time on wetting conditions.

Effect of Grains Size

Three different types of grain sizes $\leqslant 30$ μm, $\leqslant 50$ μm and 50-100 μm were tested and it has been observed that the grain sizes did not influence the average results significantly. But the grain size between 50 to 100 μm provided the best results and selected in this experimental study as shown in Figure A5. The real pictures of the test tubes for right grain size selection are not available.

Calculations

The details of the modified flotation technique has been explained in section 4. But the process to complete one set of experimental study with necessary calculation steps is explained in Table A1. The calculation of each single test tube was performed by following the steps given in table. Then the test results of all the tubes for every individual brine were averaged to get a single confident value of oil-wet and water-wet fractions.

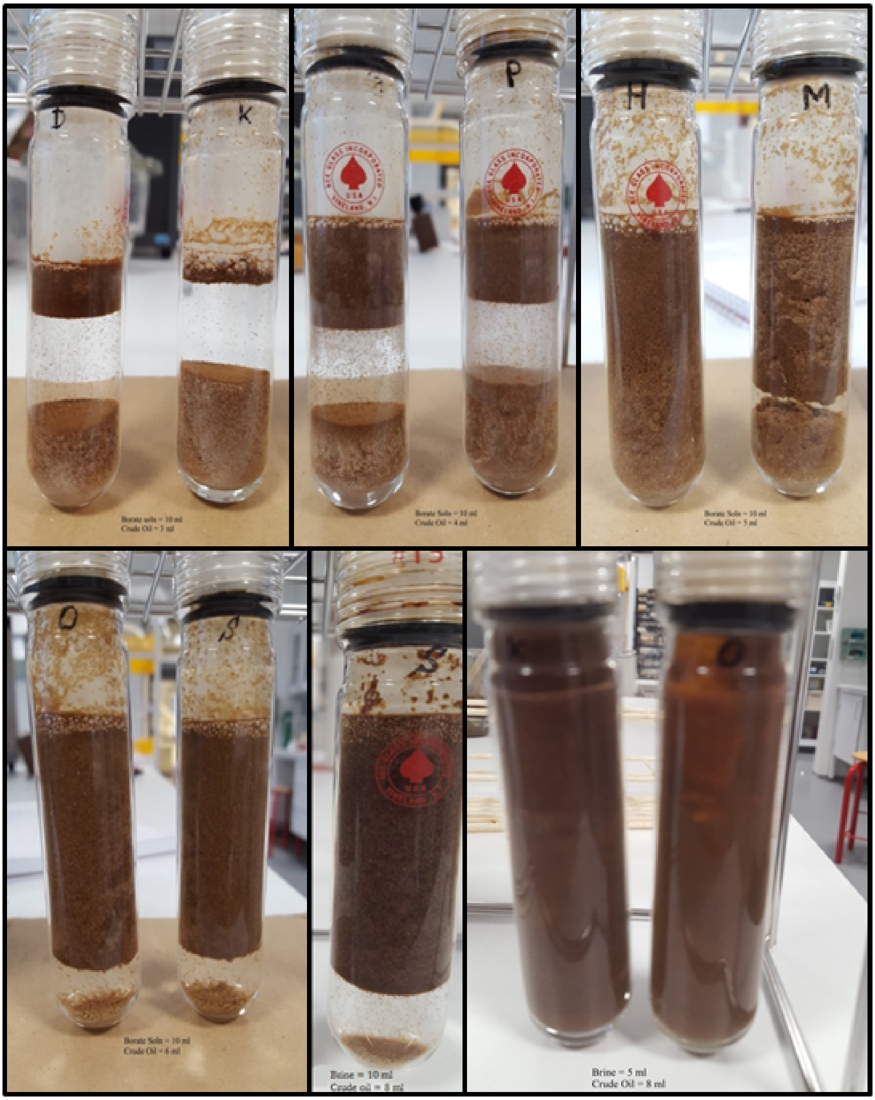


Fig. A3: The effect of different Oil and brine volumes on oil-wet and water-wet conditions.

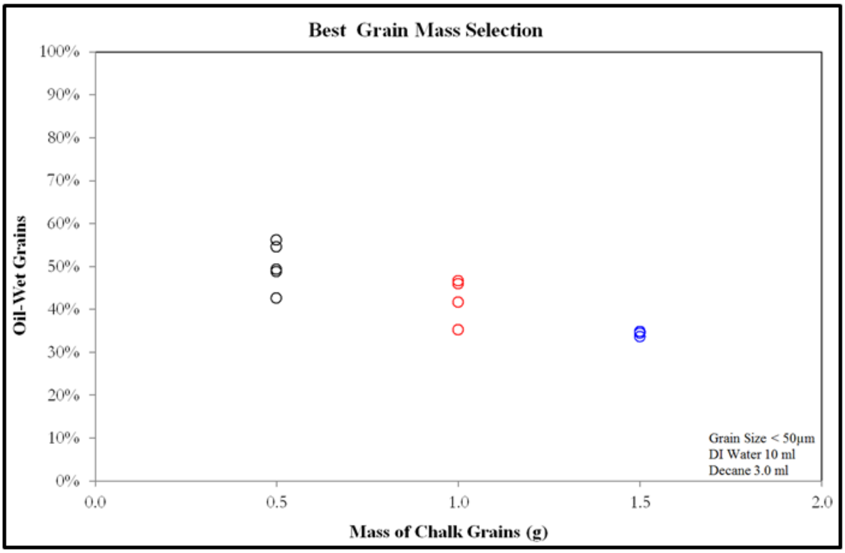


Fig. A4: The effect of different mass of chalk grains on water-wet and oil-wet percentages.

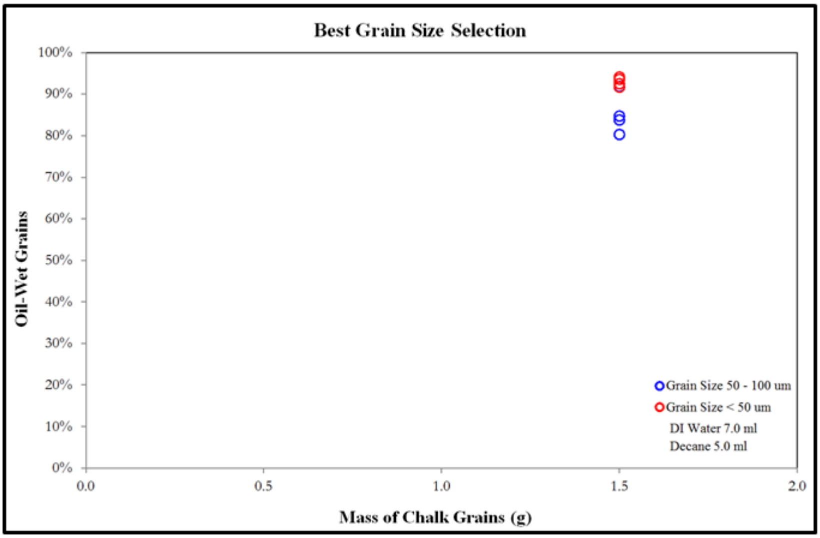
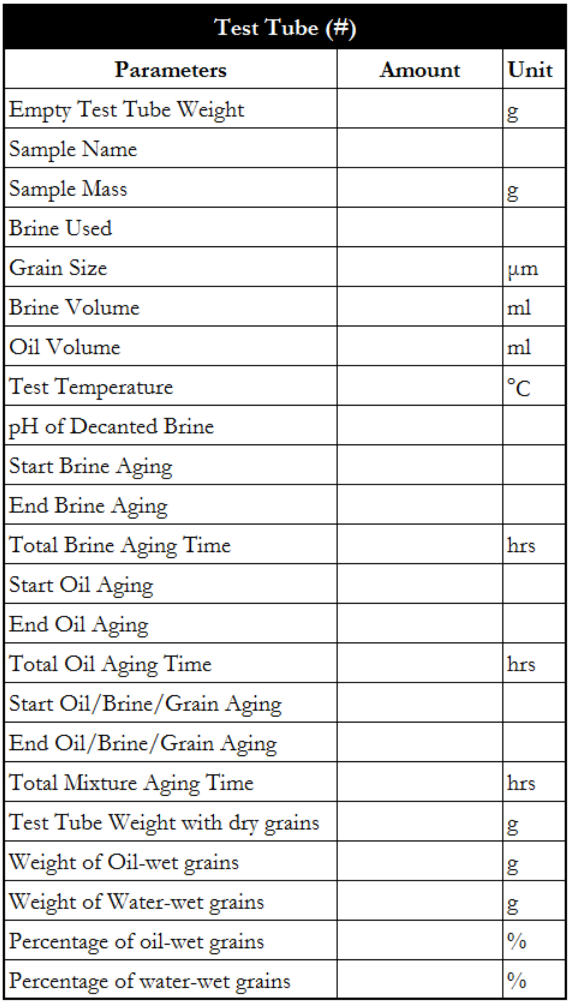


Fig. A5: The effect of different grain sizes of chalk on water-wet and oil-wet percentages.

Table A1: Floation experiment calculations.



Test Tube (#)		
Parameters	**Amount**	**Unit**
Empty Test Tube Weight		g
Sample Name		
Sample Mass		g
Brine Used		
Grain Size		µm
Brine Volume		ml
Oil Volume		ml
Test Temperature		°C
pH of Decanted Brine		
Start Brine Aging		
End Brine Aging		
Total Brine Aging Time		hrs
Start Oil Aging		
End Oil Aging		
Total Oil Aging Time		hrs
Start Oil/Brine/Grain Aging		
End Oil/Brine/Grain Aging		
Total Mixture Aging Time		hrs
Test Tube Weight with dry grains		g
Weight of Oil-wet grains		g
Weight of Water-wet grains		g
Percentage of oil-wet grains		%
Percentage of water-wet grains		%

Appendix B

Additional Plots of Statistical Analysis

Preliminary Analysis

Statistical analysis of the carbonate dataset refined at several stages before reaching to the final outcome. There were many outliers and missing values that were excluded at different steps of the analysis to get a reliable, statistically significant and consistent end result. The response variable, AOR, was found heavily skewed with most of the values between 0 and 10 in the initial distribution plots as shown in Figure B1. Then the data was logarithmically transformed and all the records with AOR = 0 were removed.

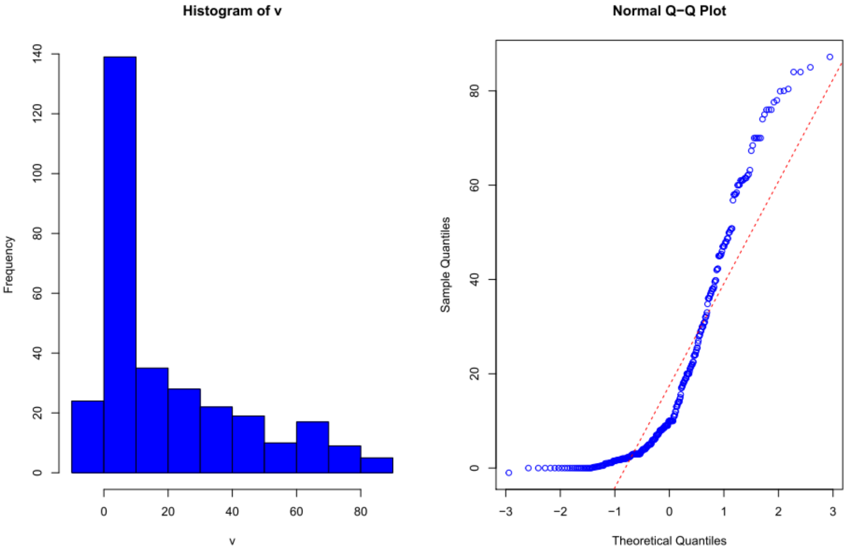


Fig. B1: A histogram and distribution plot of original data.

The association between rock type and recovery type with AOR is shown in box plot given in Figure B2. It can be seen that secondary recovery was preferred for Chalk while tertiary was favored for the limestone.

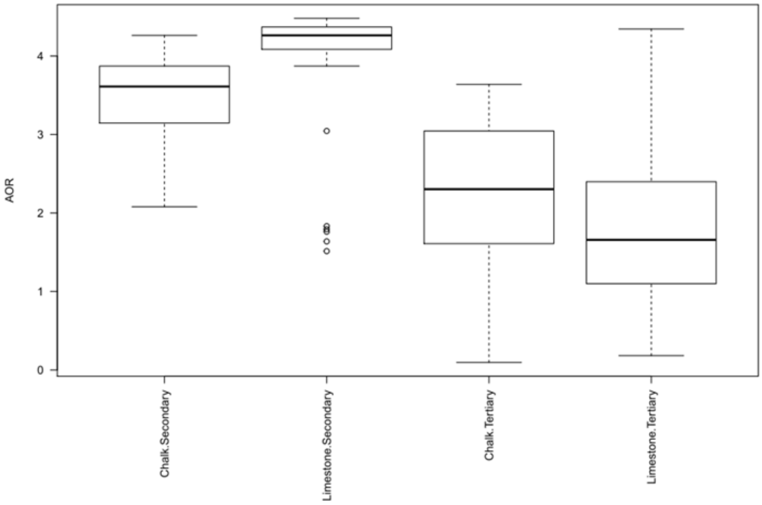


Fig. B2: Boxplot of additional oil recovery versus rock and recovery types.

The boxplots for rock and test types were created to see the association between these parameters and AOR. It has been observed that there were not enough test results available for chalk secondary & tertiary coreflood as well as limestone secondary imbibition as shown in Figure B3. The results were consistent with higher AOR in secondary recovery mode but it was hard to conclude anything about test types as they were strongly associated with rock types.

For quantitative analysis of the categorical variables data was split into following different groups to analyze the each group separately.

- Secondary vs tertiary recovery in limestone core flooding
- Secondary vs tertiary recovery in chalk imbibition
- Limestone vs chalk in tertiary imbibition
- Limestone core flooding vs imbibition in tertiary recovery

The results of all the groups are depicted in the plots given in Figure B4, B5, B6 & B7.

Principle Component Analysis

The principle component analysis of whole dataset without oil acid number is depicted in Figure B8.

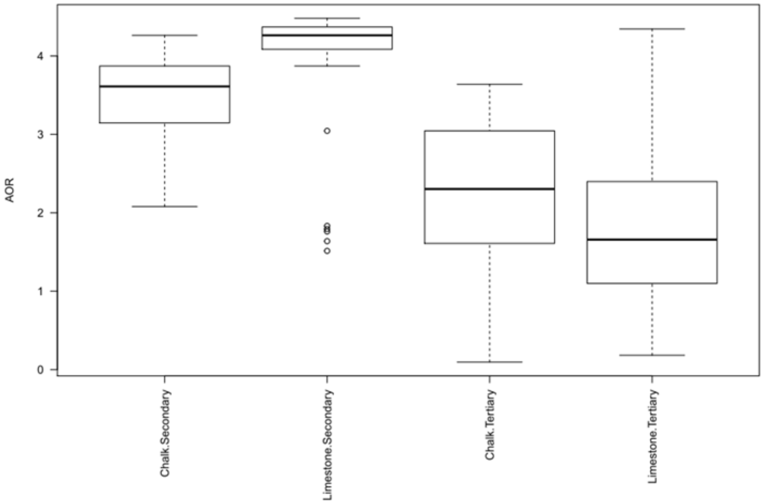


Fig. B3: Boxplot of additional oil recovery versus rock & test types.

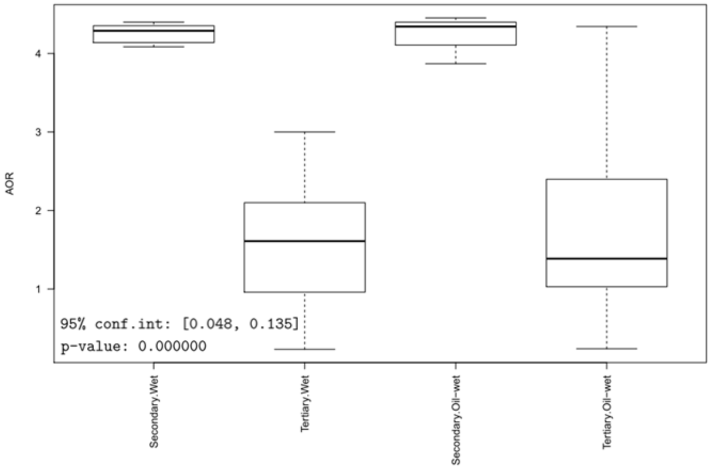


Fig. B4: Boxplot of AOR and recovery type in limestone core flooding.

A Partial Least Squared Regression model with variables having relatively higher selectivity ratio for chalk data is depicted in Figure B9.

The principle component analysis of first three components of limestone data is illustrated in Figure B10.

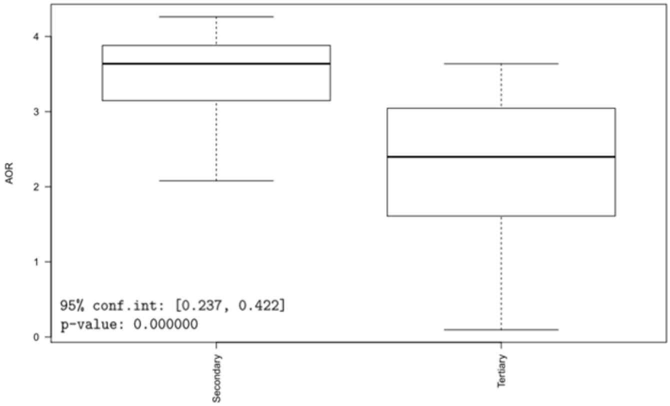


Fig. B5: Boxplot of AOR and recovery types in chalk imbibition.

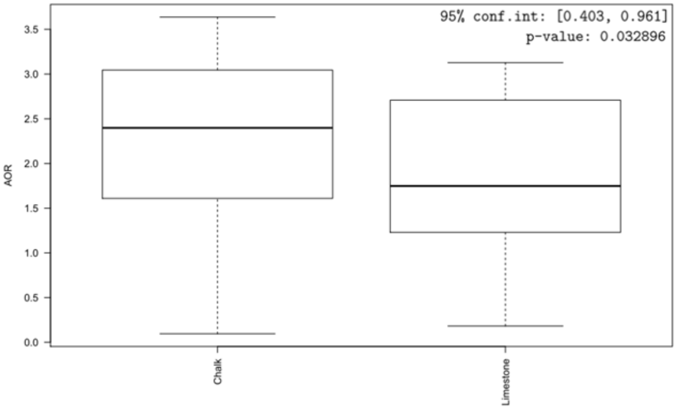


Fig. B6: Boxplot of AOR and rock types in chalk tertiary imbibition.

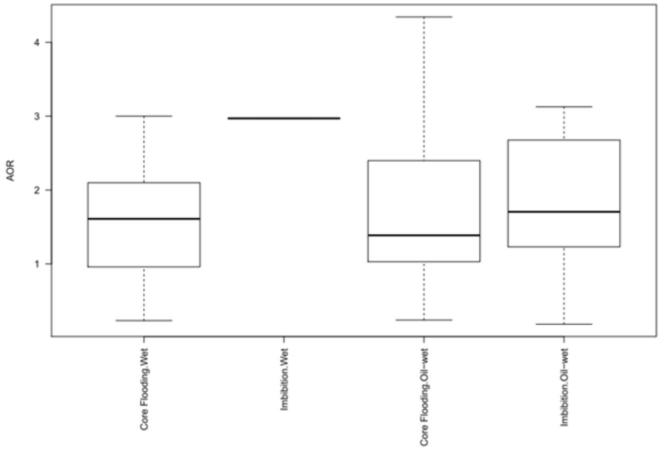


Fig. B7: Boxplot of AOR and limestone different recovery types at tertiary stage.

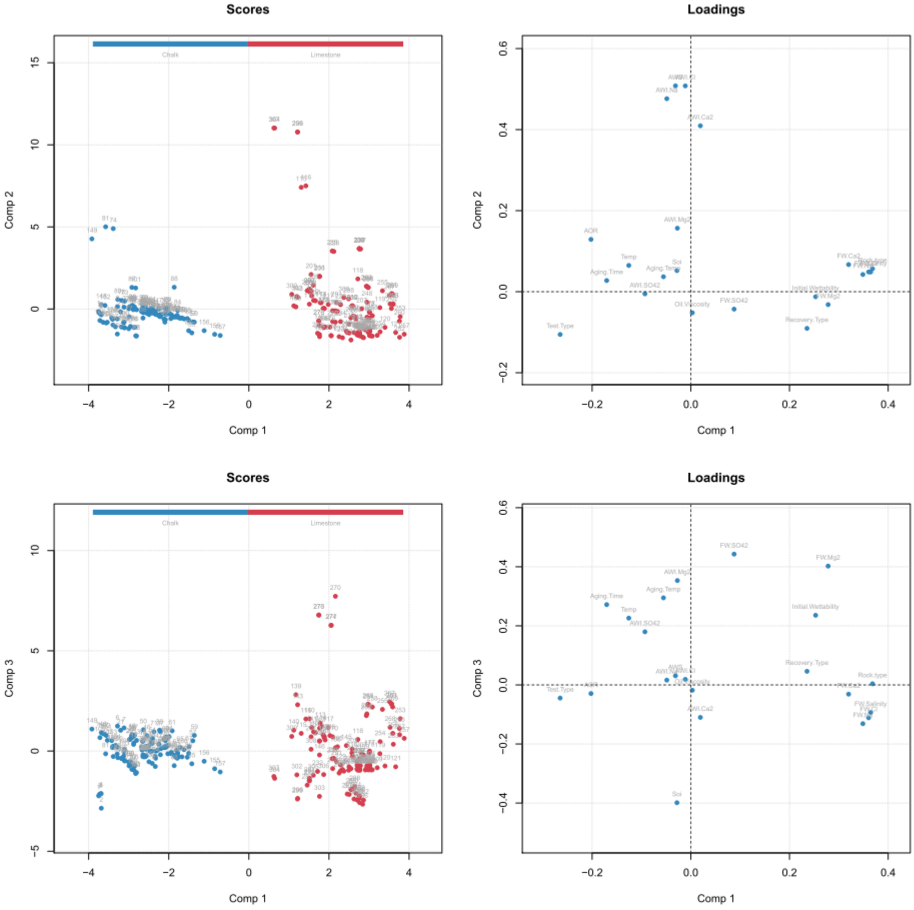


Fig. B8: Scores and loadings plot of first two PCs of whole data wihtout oil acind number.

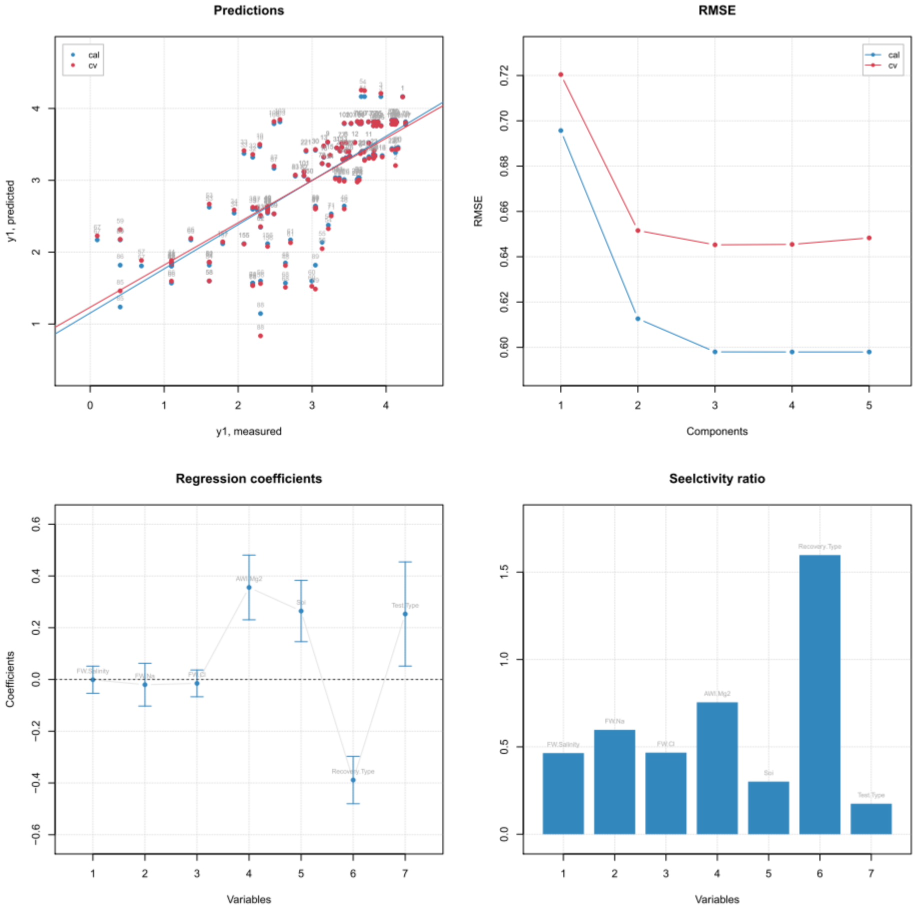


Fig. B9: PLS-R model of chak data with regression coefficient and higher selectivity ratio plots.

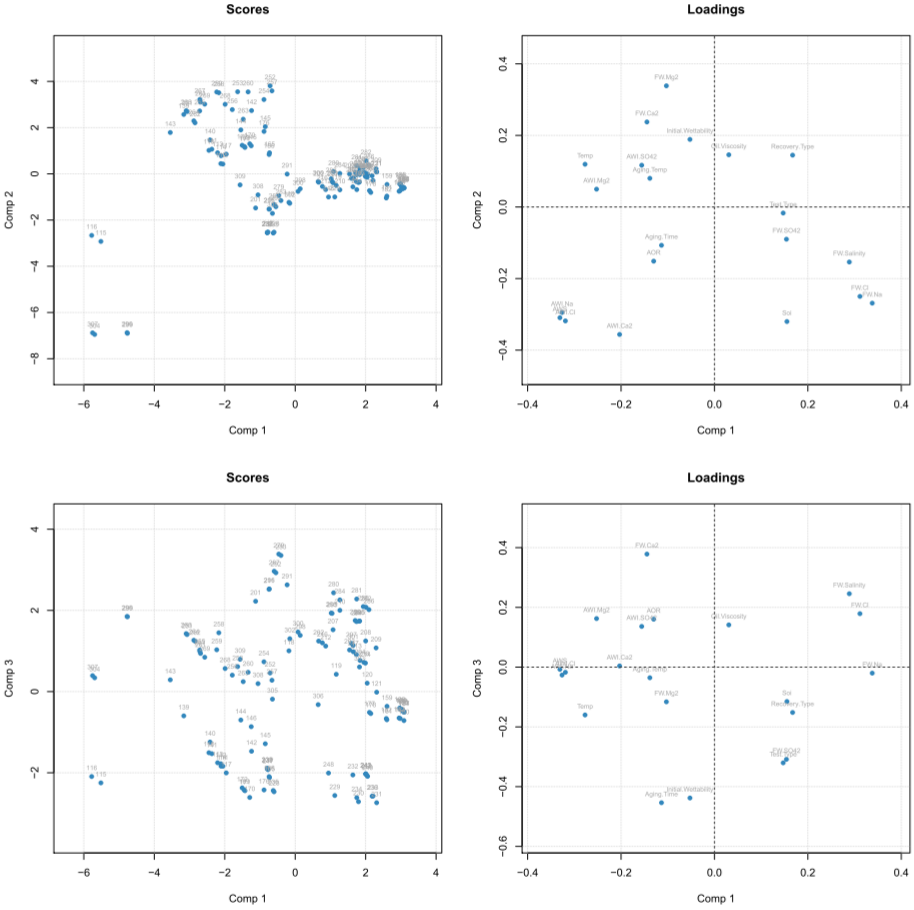


Fig. B10: Scores and loadings plot of first three PCs of limestone data.

ISSN (online): 2246-1248
ISBN (online): 978-87-7112-831-4

AALBORG **UNIVERSITY PRESS**