ALTERATION OF THE WETTING CHARACTER OF A COMPOSITE ROCK, THROUGH THE USE OF NANOPARTICLES AS AN ENHANCED OIL RECOVERY METHOD, BEN NEVIS FORMATION, HEBRON FIELD, JEANNE D'ARC BASIN, OFFSHORE NEWFOUNDLAND, CANADA.

by © Daniel J. Sivira Ortega, B.Eng.

A Thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of

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ABSTRACT

The Hebron Field is the fourth major offshore development in eastern Canada. Innovative and efficient techniques, such as nano enhanced oil recovery (Nano-EOR) must be applied to the Hebron Field to improve the low oil recovery projections. This research examined the feasibility of adding SiO_2 nanoparticles to seawater for EOR in the Hebron Field, by analyzing the fluid-fluid interactions between nanofluids and oil and determining fluid-fluid-rock interactions between nanofluids, oil and reservoir rocks. The experiments were conducted at Hebron reservoir conditions using standard cores that best represented Ben Nevis Formation facies. Stable SiO_2 nanoparticle dispersed in seawater decrease the interfacial tension (IFT), and have the function of reducing the oil-water contact angle, making the wetting character of rock surfaces more strongly water wet. The scanning electron microscope (SEM) and mineral liberation analysis (MLA) results were not conclusive. They did, however, reveal major alterations on quartz, carbonate and clay minerals. Inductively coupled plasma – optical emission spectrometry (ICP-OES) analyses verified the dissolution of carbonate minerals in the standard cores.

ACKNOWLEDGMENTS

I would like to thank God for giving me the strength to stay focus and deliver a high-quality research. Thank you to my family, who are the most important part of my life. Even though they are physically far away from me, our love and support for each other surpass any barrier.

My supervisors and collaborators in this thesis were a key in developing this research, especially Dr. Lesley James, who believed in me, and my potential to carry out meaningful research. She became more than a supervisor to me, guiding and advising me with research and non-research-related matters as well. She is an excellent example to follow, particularly her admirable management skills.

My friend Jenny, who is my family in St. John's. I owe her my best moments along this journey, and she also built this research with me.

The help and contribution from all Hibernia EOR Research Group can not be forgotten, and special thanks to Edison Sripal who made the hard and tedious experimental work an enjoyable experience.

I would also like to thank Chevron Canada, Hibernia Management and Development Company (HMDC), InnovateNL (Previous Research and Development Corporation of Newfoundland and Labrador (RDC)), Natural Sciences and Engineering Research Council of Canada (NSERC), and the Canadian Foundation for Innovation (CFI) for financial support, and Canada Newfoundland & Labrador Offshore Petroleum Board (C-NLOPB) for suppling Hebron Field samples.

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°API	⟶	American Petroleum Institute Gravity
°C	⟶	Celsius Degree
ADIPEC	⟶	Abu Dhabi International Petroleum Exhibition & Conference
ASP	⟶	Alkaline-Surfactant-Polymer
Ca^{2+}	⟶	Calcium
C-NLOPB	⟶	Canada Newfoundland & Labrador Offshore Petroleum Board
CFI	⟶	Canadian Foundation for Innovation
CO_2	⟶	Carbon Dioxide
EOR	⟶	Enhanced Oil Recovery
HC WAG	⟶	Hydrocarbon Water Alternative Gas
HCl	⟶	Hydrochloric Acid
HDMC	⟶	Hibernia Management and Development Company
ICP - OES	⟶	Inductively Coupled Plasma Optical Emission Spectroscopy
IFT	⟶	Interfacial Tension
km	⟶	Kilometres
m	⟶	Metres
mD	⟶	Millidarcy
Mg^{2+}	⟶	Magnesium
MLA	⟶	Mineral Liberation Analyzer
mm	⟶	Millimetre
MMbbl	⟶	Million Barrels
MMBO	⟶	Million Barrels of Oil
mN/m	⟶	Millinewton per Meter
mol/L	⟶	Moles per Liter
MPa	⟶	Megapascal

NaCl	⟶	Sodium Chloride
N_C	⟶	Capillary Number
nm	⟶	Nanometre
nm^2	⟶	Nanometre Squared
NSERC	⟶	Natural Sciences and Engineering Research Council of Canada
ppm	⟶	Parts per Million
RDC	⟶	Research and Development Corporation of Newfoundland and Labrador
rpm	⟶	Revolutions per Minute
SCAL	⟶	Special Core Analysis
SEM	⟶	Scanning Electron Microscopy
Si	⟶	Silicon
SiO_2	⟶	Silicon Dioxide
SP	⟶	Surfactant-Polymer
USBM	⟶	United State Bureau of Mines
WI	⟶	Wettability Index
wt%	⟶	Percentage by Weight
θ	⟶	Contact Angle
θ_{nf}	⟶	Contact Angle of Nanofluid-Oil-Rock
θ_{sw}	⟶	Contact Angle of Seawater-Oil-Rock
µm	⟶	Micrometres
v	⟶	Darcy Velocity
μ	⟶	Displacing Fluid Viscosity
σ	⟶	Interfacial Tension
σ_{so}	⟶	IFT Between the Solid and Oil
σ_{sw}	⟶	IFT Between the Solid and Water
σ_{wo}	⟶	IFT Between Water and Oil

LIST OF APPENDICES

CHAPTER I - INTRODUCTION AND OVERVIEW

Developing innovative and efficient methods to produce more oil are key factors for Canada to remain one of the top ten oil producers in the world. The most recently discovered reservoirs in Canada are in challenging and harsh environments such as deep formation or deep water. The Hebron Project, offshore Newfoundland and Labrador, is a good example. Due to their inherent high costs to produce, efficient technologies must be deployed to maximize oil recovery.

The Hebron project is the fourth major offshore development in Newfoundland and Labrador. It is located in the Jeanne d'Arc Basin 350 kilometers offshore southeast of St. John’s, Newfoundland and Labrador, Canada. The current best estimate of total oil in place for the Hebron asset are 2,620 million barrels of oil, with the Ben Nevis Formation anticipated to produce approximately 70 percent of the Hebron Project's crude oil. Only 30 %, however, is considered to be recoverable without application of enhanced oil recovery (EOR) methods to increase this recovery factor. The results of special core laboratory analysis tests indicate that the Ben Nevis Formation is weakly water-wet as defined by the United State Bureau of Mines (USBM) wettability tests (CNLOPB, 2011).

Understanding formation wettability is crucial for optimizing oil recovery. The oil-versus-water wetting preference influences many aspects of reservoir performance, particularly in enhanced oil recovery techniques.

The wettability modifier has mostly been evaluated under EOR methods such as low salinity, or ASP (Alkaline-Surfactant-Polymer). When considering remote and harsh locations such as the Hebron Field location, however, nanoparticle injection is considered a viable method due to lower costs, the volume and ease of nanoparticle transportation, minimal facility requirements, and environmental concerns. Although nanoparticle injection is an innovative method, it has typically been examined under unrealistic conditions (for example, sodium chloride (NaCl) or synthetic brine as a dispersant and/or conducting the experiments at ambient conditions). The goal of this research is to determine the suitability of SiO_2 nanoparticles as water additives for EOR purposes in Ben Nevis Formation (Hebron Field) under realistic conditions, reducing the gap between laboratory and field conditions.

1.1 Nano-EOR Objectives, Scope, and Organization of Thesis

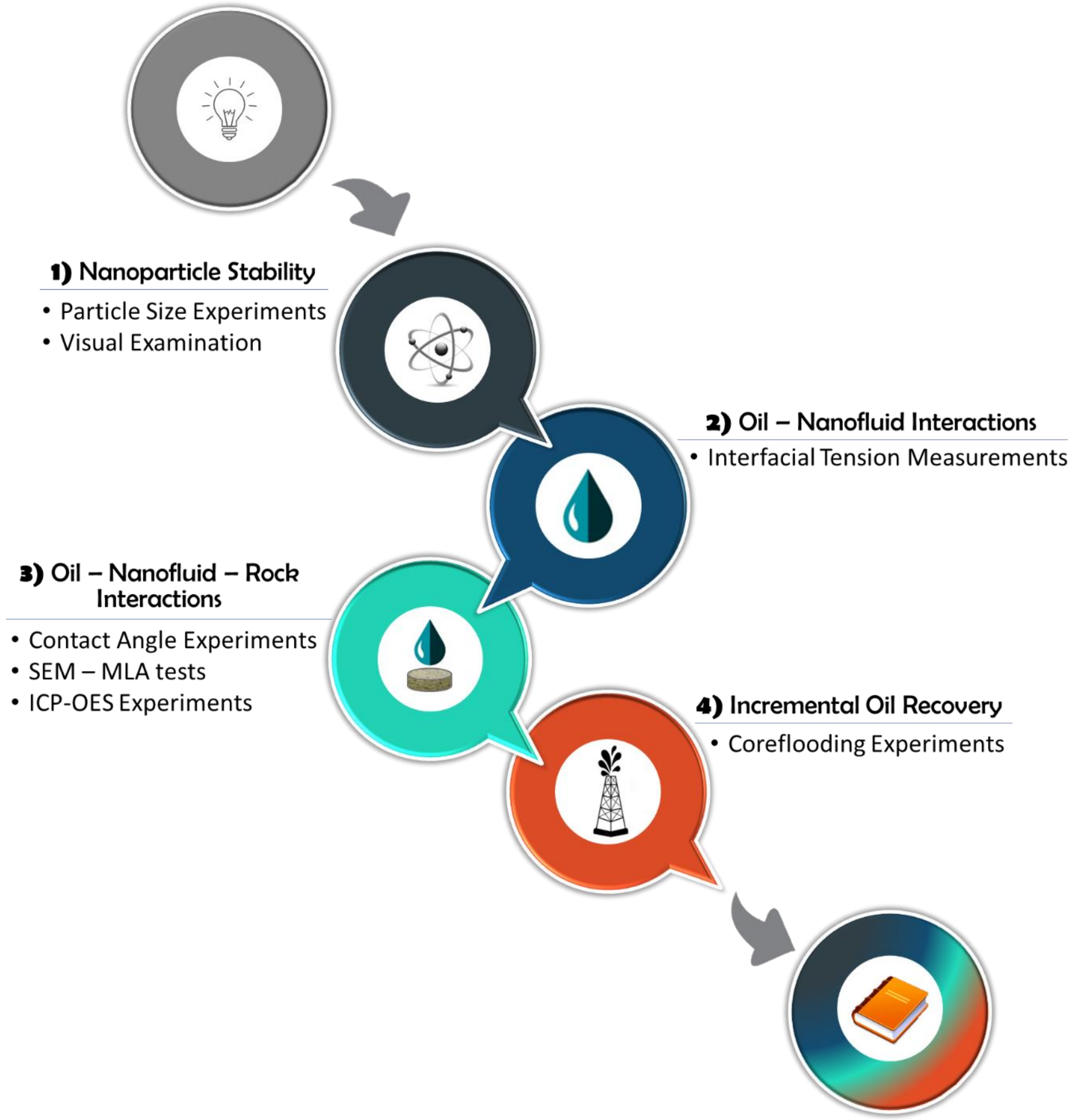

Figure 1.1 *Nano-EOR Objectives Flowchart*

The Nano-EOR project is designed to characterise, understand, and optimise SiO_2 nanoparticles as water additive for EOR purposes in the Hebron Field. The objectives of this project are schematized in Figure 1.1. This project involved four main steps to examine the feasibility of adding nanoparticles to seawater for EOR in the Hebron Field: 1) obtaining a stable SiO_2 nanofluid, 2) analyzing fluid-fluid interactions between nanofluids and oil, 3) determining the fluid-fluid-rock interactions between nanofluids, oil and reservoir rocks, and 4) measuring the incremental oil recovery.

The first step focused on understanding the stability of SiO_2 nanoparticle disperse in seawater at reservoir temperature conditions. Since the Hebron Field is a located offshore, seawater is the main source of water available for nanofluid injection as an EOR method. A major challenge of this method is stabilizing the nanofluid, as salinity and temperature can both directly affect the nanoparticle stability over time. Agglomeration of nanoparticles is undesirable as they can block pores and reduce reservoir permeability.

The second step involved analysis of interfacial tensions between oil and nanofluid, an essential parameter due to the importance of interfacial tension (IFT) reduction in the incremental oil recovery. The third step emphasised the evaluation of the SiO_2 nanofluid as a wettability modifier, testing three different nanofluid concentrations, two types of standard cores, two wettability restoration methods, and aging periods. Finally, the last step involved coreflooding experiments to measure the incremental oil recovery due to the nanoparticle injection.

This dissertation comprises three linked papers (chapters II, III and IV), upon which I am the main author. The objectives of the chapters II, III and IV are described as follows:

- Chapter II: The Effectiveness of Silicon Dioxide (SiO_2) Nanoparticle as an Enhanced Oil Recovery Agent in Ben Nevis Formation, Hebron Field, Offshore Eastern Canada.
    - ✓ Determination of the contribution of 0.0.1, 0.03, and 0.05 wt% SiO_2 nanoparticle dispersed in seawater on the alteration of IFT.
    - ✓ Preliminary analysis of wettability alteration by SiO_2 nanofluid.

- ✓ Published in the Abu Dhabi International Petroleum Exhibition & Conference (ADIPEC), 7-10 November 2016, Abu Dhabi, UAE.

- Chapter III: Wettability Alteration and Interactions Between Silicon Dioxide (SiO_2) Nanoparticles and Reservoir Minerals in Standard Cores Mimicking Hebron Field Conditions for Enhanced Oil Recovery.
  - ✓ Extensive evaluation of a SiO_2 nanofluid as a wettability modifier agent for two types of standard rocks as a function of aging time and nanofluid concentration.
  - ✓ Scanning electron microscopy - mineral liberation analyzer (SEM - MLA) analysis to monitor the mineralogical changes on rock surface before and after the EOR technique.
  - ✓ Evaluation of the nanofluid before and after the aging process by an inductively coupled plasma optical emission spectroscopy (ICP-OES).
  - ✓ Published in the 19th European Symposium on Improved Oil Recovery, 24-27 April 2017, Stavanger, Norway.

- Chapter IV: Optimization of Silicon Dioxide Nanoparticle (SiO_2) as a Wettability Modifier for Enhanced Oil Recovery in Hebron Field, Offshore Eastern Canada.
  - ✓ Application of an optimum wettability restoration procedure to reduce the gap between laboratory and field conditions.
  - ✓ Extensive contact angle experiments to determine the ability of SiO_2 nanofluids to change the wetting character of two types of rock surfaces as a function of aging time and nanofluid concentration.
  - ✓ Comparison between current and previous contact angles analyses to establish the optimum wettability method.
  - ✓ Evaluation of the mineralogical changes in rock before and after aging in nanofluids by mineral liberation analyzer (MLA) tests.

- ✓ Evaluation of a nanofluid before and after the aging process with an inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.
- ✓ To be published in a scientific journal.

The appendices, at the end of the manuscript, contain all data that were not included in the submission of the articles.

1.2 Hebron Asset Overview

1.2.1 Research Project Area

The research project is focused on the Hebron asset, which is located in the Jeanne d'Arc Basin 340 km offshore of St. John's, Newfoundland and Labrador, approximately 9 km north of the Terra Nova, 32 km southeast of Hibernia, and 46 km southwest of White Rose (Figure 1.2) fields. The water depth at Hebron ranges from 88 to 102 m.

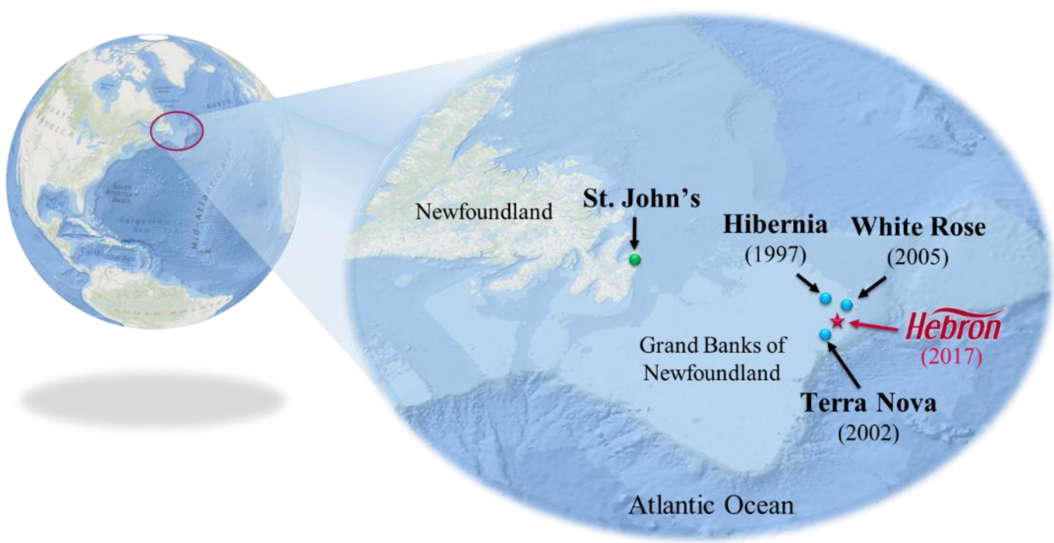

Figure 1.2 *Location of the Hebron Project Area*

The Hebron asset contains three discovered fields (Hebron Field, the West Ben Nevis Field and the Ben Nevis Field), four reservoir formations (Avalon, Ben Nevis, Hibernia, and

Jeanne d'Arc), and five pools. The current best estimation of total oil in place is 2,620 million barrels of oil of which, 30% is considered recoverable. The Hebron Field, specifically the Ben Nevis Formation (Pool 1) is anticipated to produce close to 80% of the Hebron asset's crude oil. The quality of the crude in the Pool 1 is 20 °API (CNLOPB, 2011).

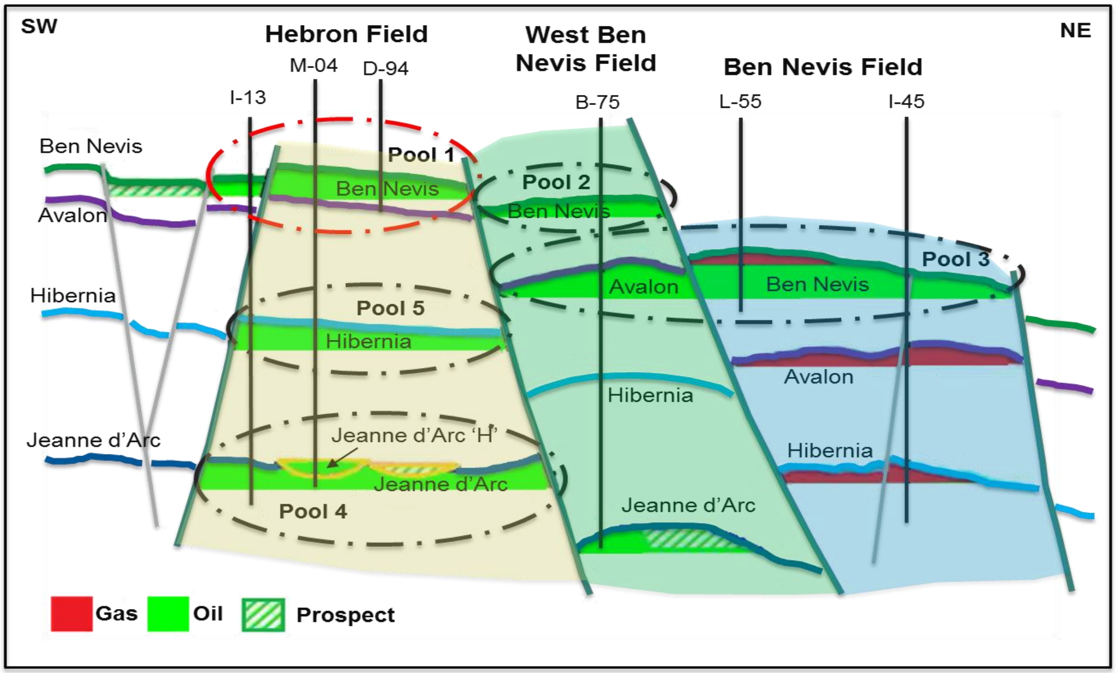

Figure 1.3 *Schematic Cross-Section Across the Hebron Project Area (after CNLOPB, 2011)*

1.2.2 Reservoir Characterization

1.2.2.1 Structural Geology

The Hebron Field is on a horst block in between two grabens at the southwest and northeast. This horst block has two different traps, the first trap is a fault in the Ben Nevis and Hibernia Formation and the second trap is due to combination of structural and stratigraphic configurations in the Jeanne d'Arc Formation. The other two fields (West Ben Nevis and Ben Nevis) are on different fault blocks to the northeast of Hebron Field. The setting of the major faults creates the blocks, and defines the structural traps. The oil-water contacts are determined by spill-points between the fault blocks. The major faults are described as syn-depositional, meaning that deposition occurred at the same as the faulting. These faults had a significant impact on the accommodation and thickness of the preserved reservoirs, and a significant growth in the thickness of the Ben Nevis reservoir across these faults is observed. Unfortunately, the quality of the Ben Nevis reservoir in the thicker sections is lower due to the presence of deeper sedimentary facies. The Avalon, Hibernia, and Jeanne d'Arc Formations were deposited prior to the onset of the third episode of rifting, in which the reservoirs were faulted. Since deposition and faulting occurred as different geological events, these reservoirs do not show a change in thickness or quality across the faults (CNLOPB, 2011).

1.2.2.2 Geology of the Ben Nevis Formation

The Ben Nevis Formation (upper Aptian to Albian) is a 125 to 500 m thick succession of upward fining (fine to very fine grained) calcareous sandstone, with thin interbedded layers of sandy limestone, that grades upward into glauconitic siltstone and shale (CNLOPB, 2011). The depositional environment is primarily lower to upper shoreface environment. The reservoir section is composed predominantly of laminated and bioturbated, medium to fine-grained sandstones. Secondary lithologies include coquinas, shell-rich sandstones, mudstones, and calcite nodules. The reservoir quality is fair to good in Hebron Field (Pool 1) with average permeabilities ranging from 50 to 400 mD and average gross porosities ranging from 10 to 28 percent. The reservoir quality in the Ben Nevis Field (Pool 3) is lower because it is an area dominated by more distal facies. The average permeabilities range from 0.1 to 100 mD, and average gross porosities range from 4 to 24 percent (CNLOPB, 2011).

1.2.2.3 Wetting Character of the Ben Nevis Formation

A special core analysis (SCAL) was conducted on a preserved core from the D-94 well in lower section of the Ben Nevis Formation (Pool 1). The results indicated that the rock is weakly water-wet as defined by the United State Bureau of Mines (USBM) wettability tests (CNLOPB, 2011).

1.3 Enhanced Oil Recovery Overview

The production life of an oil reservoir can be classified base on the recovery method applied. There are three main methods: primary, secondary and tertiary recovery. The first two are termed conventional recovery and they target the mobile oil in the reservoir. Tertiary recovery targets the immobile oil, which can not be produced naturally due to capillary and/or viscous forces. In a conventional oil reservoir, the reservoir rocks are generally pressurized above hydrostatic pressure due to compaction of sedimentary rocks over geologic time. Primary recovery occurs when the fluid in the pressurized layer flow to the surface until the pressure in the reservoir is reduced to hydrostatic pressure. Thereafter, secondary recovery is applied which involves water (water injection) or gas flooding, for pressure maintenance. Waterflooding enhances recovery by sweeping oil to the productions wells, whereas gas injections reduce oil viscosity to improve recovery (Donaldson, Chilingarian, & Yen, 1985).

During the mature phase of field life, tertiary recovery methods, also known as enhanced oil recovery (EOR) are considered. These methods change the fundamental physics or chemistry of the reservoir conditions to improve the oil recovery (Morrow & Heller, 1985). They are generally classified into thermal techniques, gas injections and chemical methods (Figure 1.4). Each EOR technique has a unique mechanism, and the method applied will depend on the reservoir properties and conditions.

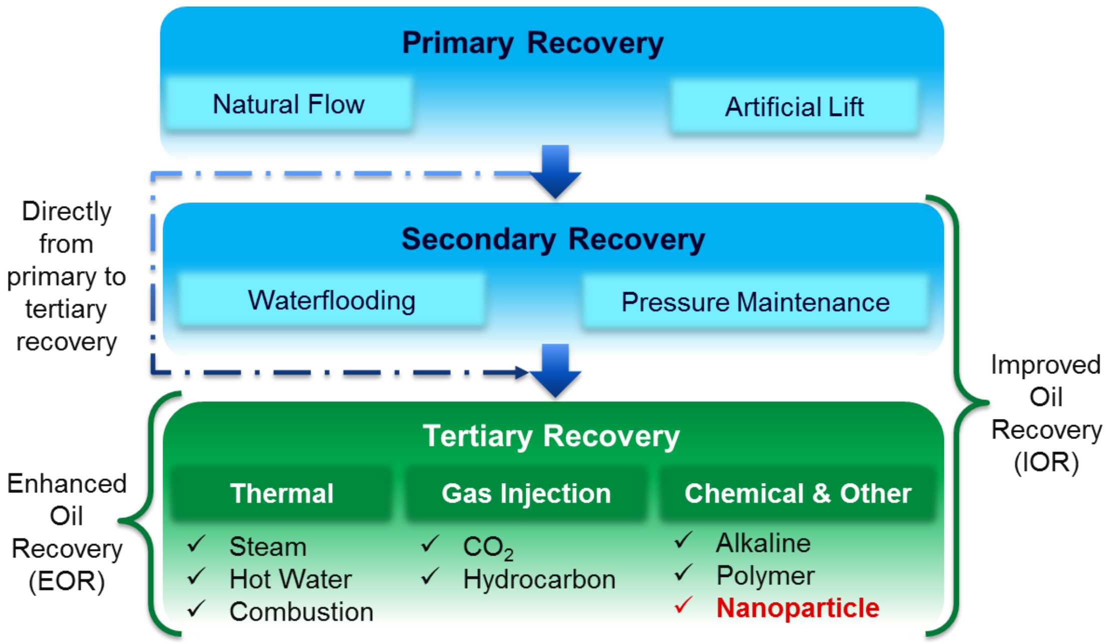

Figure 1.4 *Three Phases of Oil Recovery*

1.3.1 Enhanced Oil Recovery Considerations for Hebron Field

The Hebron development plan outlines a preliminary high-level screening of EOR methods. The initial screening of the Ben Nevis Formation (Pool 1) suggests favorable EOR techniques such as gas injection, polymer flooding, and chemical flooding, and discarded thermal EOR method (CNLOPB, 2011).

Valencia, et al. (2017), considering the following variables for EOR: oil gravity, oil viscosity, rock type, porosity, permeability, net reservoir, depth, and reservoir temperature. They evaluated diverse EOR methods such as: miscible gas (CO_2 and hydrocarbon water alternative gas or HC WAG) injection, immiscible gas (nitrogen, CO_2, and HC WAG) injection, chemical flooding (polymer, and alkali-surfactant-polymer or ASP), and thermal methods (combustion and steam). From their evaluation, it was concluded that the best techniques would be CO_2 and HC WAG as immiscible gas injections, and chemical flooding using polymer.

The EOR screening criteria for this research was based on the oil characteristics and reservoir properties of the Ben Nevis Formation and targeting the fluid-fluid interactions and fluid-rock interactions. Four chemical flooding were evaluated low-salinity, surfactant-polymer (SP), alkali-surfactant-polymer (ASP), and nanofluid. The first three methods were not considered further because either the Ben Nevis Formation features, or oil properties did not meet the criteria to apply the technique.

One of the requirements for the successful application of low-salinity injection is a high percentage of clay minerals. The effect of low-salinity is related to the presence of clay minerals, and consequently, it is generally accepted that the effect is caused by wettability alteration of clay minerals (Yousef, et al., 2011). The amount of clay minerals presents in the Ben Nevis Formation, however, is only 0.3% to 3%, making this technique unviable.

Surfactant-Polymer (SP) EOR methods improve the displacement and sweep efficiencies. The surfactant reduces interfacial tension (IFT) between the displacing and displaced phases and the polymer improve the mobility ration. Previous research indicated the importance of the oil gravity to the effectiveness of this technique, hence it was recommended that the oil gravity should be greater than 25 °API (Gao, et al., 2010). The oil gravity in the Hebron Field is lower than the recommended values and the application of this technique would not be effective.

The third method considered was alkali-surfactant-polymer (ASP) flooding, which is a technique in which alkaline solutions are injected into the reservoir. This chemical solution reacts with the natural acids (naphthenic acids) present in crude oil to form surfactants in-situ (sodium naphthenate) that operate in the same way as injected synthetic surfactants to reduce interfacial tension between oil and water. The polymer solution is then injected into the reservoir to enhance the mobility ratio. The role of the alkali in the ASP process is to reduce the adsorption of the surfactant during displacement through the formation of sequestering divalent ions. The presence of alkali can also alter formation wettability to reach a desire wetting character (Olajire, 2014). To successfully implement this technique, it is suggested that the formation-water chlorides should be lower than 20,000 ppm and divalent ions (Ca^{2+} and Mg^{2+}) lower than 500 ppm (Taber, et al., 1997). The chloride concentrations in formation waters from the Ben Nevis Formation are approximately 34,925 ppm, and the divalent ions are higher than 500 ppm.

In summary, nanoparticle injection was considered as the most suitable chemical flooding alternative for the Ben Nevis Formation. It is a new and an innovative method, and the amount of research available has grown in the past few years (Aurand, et al., 2014; Hendraningrat, et al., 2012; Hendraningrat, et al., 2013; Hendraningrat & Torsæter, 2014; Li, et al., 2013). Most these researchers conclude that if a specific nanoparticle at the right concentration is injected into a reservoir, it can alter the wetting character, reduce the interfacial tension, and increase oil recovery.

1.3.2 Nanoparticles as a Water Additive for Enhanced Oil Recovery

Nanotechnology as an EOR technique has become more popular during the last few years due to its promising results at the laboratory scale (Hendraningrat et al., 2012). The trends of some top successful industries around the world are based on miniaturization and nanotechnology. Nanoparticles are materials ranging in size between 1nm to 100 nm, similar to the size of proteins or viruses (Figure 1.5). The specific physical and chemical properties of a nanoparticle stem from the core, which is surrounded by the shell that provides a protective layer (Das, et al., 2008).

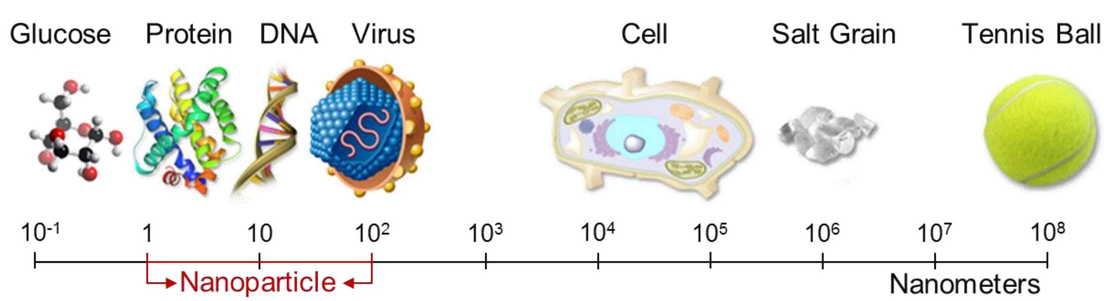

Figure 1.5 *Nanoparticles Sizes Relatives to Other Materials*

(Modified Image from /www.wichlab.com)

EOR is designed to either generate fluid-fluid interaction between injected fluid and the fluid in the reservoir, such as oil, formation water and/or gas, or fluid-rock interaction between the fluid injected and the rock. Nanoparticles as a water additive for EOR are targeted to generate both fluid-fluid and fluid-rock interactions.

1.3.2.1 Targeted Properties

The two main targets of silicon dioxide nanoparticles (SiO_2) as EOR agents are interfacial tension and wettability alteration. The interfacial tension is the well-defined interface that appears along the contact of two immiscible fluids such as gas-liquid or liquid-liquid (Figure 1.6). The IFT represents only a few molecular diameters in thickness, and it is measured in force per unit length (mN/m) (Donaldson et al., 1985). When this force is low enough, it can increase the capillary number, which affects the microscopic pore-level oil displacement (Lake, et al., 2014).

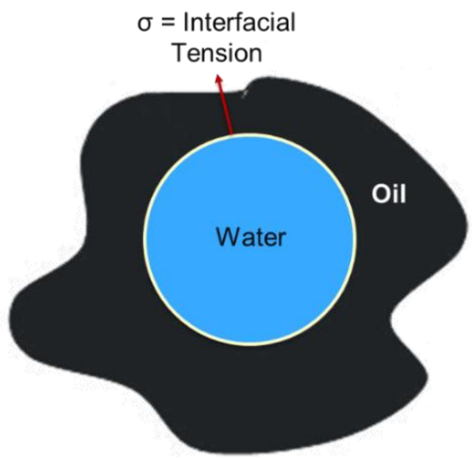

Figure 1.6 *Interfacial Tension*

Wettability is an essential rock property for enhancing oil recovery because it describes the preference of a solid to be in contact with one liquid rather than another in a three-phase system. A three-phase system is shown in Figure 1.7, where a drop of oil is surrounded by water on a rock surface. There are three cases that represent the principal types of wettability (Morrow & Heller, 1985). In water wet condition, the contact angle resulting from an oil-water-solid equilibrium is usually low. In an oil wet system, the drop of oil spreads along the rock surface and the contact angle is relatively high. Finally, in an intermediate wet condition, the resulting contact angle is between 75° to 105° (Treiber & Owens, 1972).

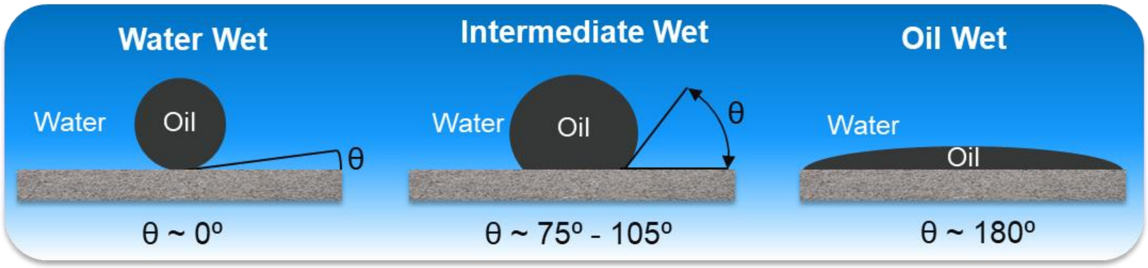

Figure 1.7 *Types of Formation Wettability*

(after Abdallah et al., 2007)

In a porous media scale, if the rock is preferentially water-wet and the rock is saturated with oil, water will imbibe the smaller pores and surrounding grains. In oil wet conditions, the oil imbibes into smaller pores, having a preference to be in touch with the grains (Figure 1.8). If no preference is shown by the rock to either fluid, the system is said to exhibit neutral wettability or intermediate wettability, a condition that one might visualize as being equally wet by both fluids (Tiab & Donaldson, 2004).

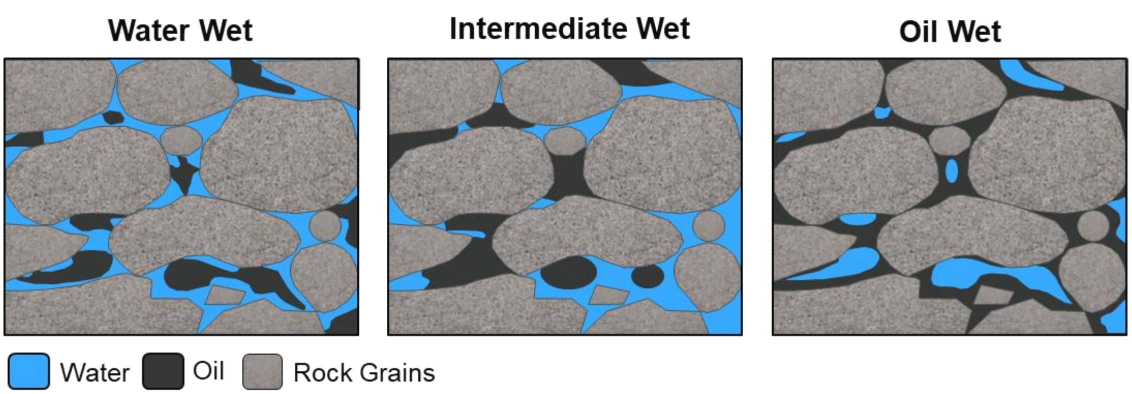

Figure 1.8 *Types of Formation Wettability in a Porous Media Scale*

(after Abdallah et al., 2007)

Relative permeability curves are used for the quantitative evaluation of water flooding performance, and the relative permeability curves are affected by the changes in the wetting character of the rock. As a result, changes in water flooding behavior are seen as the system wettability is altered, and it is clearly shown in Figure 1.9. The curves show that as the system becomes more oil-wet, less oil is recovered at any given amount of injected water.

In the water-wet system, the oil displacement will finish earlier in comparison with an oil wet system (Tiab & Donaldson, 2004).

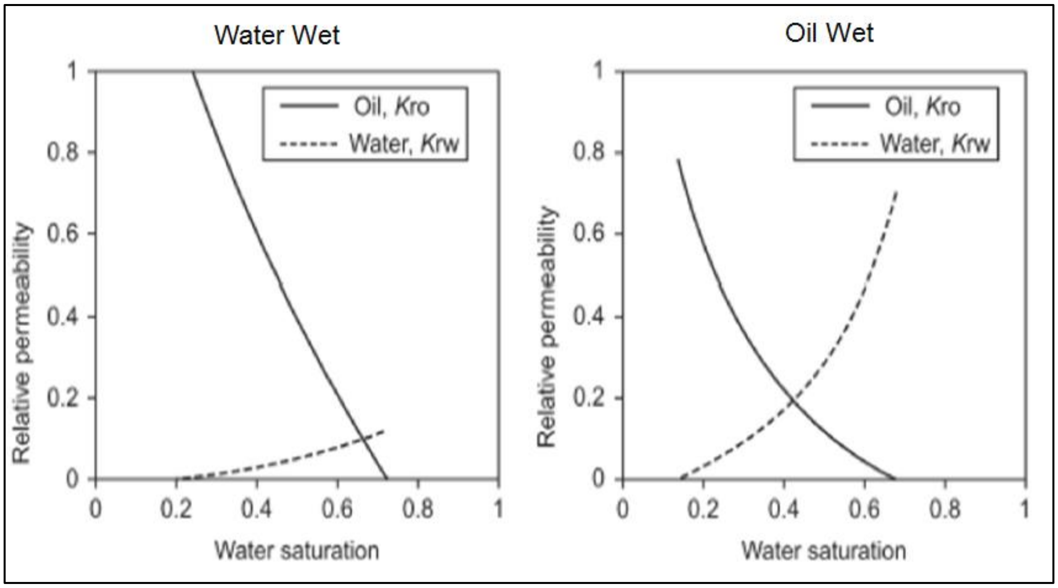

Figure 1.9 *Relative Permeability in Water-Wet Reservoirs Versus Oil-Wet Reservoirs (after Tiab & Donaldson, 2004)*

1.4 Co-Authorship Statement

The chapters presented in manuscript format have been, or will be, published. The following information describes the work completed by the main author and co-authors. The research was predominantly completed by the main author with collaboration, guidance and editorial advice from the main supervisor, co-supervisors and other collaborators.

Daniel J. Sivira (main author) designed and performed fluid-fluid interaction (interfacial tension tests) and fluid-rock interaction (contact angle experiment, MLA-SEM analysis, and ICP-OES study) experiments. He also prepared the core samples before the analysis (wettability restoration and aging in nanofluid technique), and the preparation and collection of the fluids to be analysed. Finally, the main author analysed data and wrote the articles and this manuscript.

Dr. Lesley James (main supervisor) was strongly involved at every single stage of the research. She and the main author structured the project. Her expert guidance was essential in developing the project. She carefully reviewed the design of the experiments and monitored the performance. Dr. James provided her expertise analysing the data and collaborated with productive editorial comments after a long review of the articles and manuscript.

Jenny Kim was one of the main collaborators of this research. She helped with the preparation of the nanofluid and core samples. She also assisted in designing and conducting the experiments. Jenny was involved with the analysis of the result providing explanations from a chemist’s point of view, and lastly, reviewed the articles and manuscript.

Dr. Johansen Thormod (co-supervisor) assisted in the early stages of the project, specifically in the first article (Chapter II), providing positive guidance to design the experiments. He also revised Chapter II and suggested constructive editorial comments.

Dr. Yahui Zhang (co-supervisor) joined the project at the beginning of the second article because of his expertise in chemistry. He was strongly involved in the project from then, and provided key suggestions in one of the most challenging aspect of the project, which was the stability of the nanofluid. He provided helpful advises in the analysis of the results, and reviewed the second (Chapter III) and third articles (Chapter IV) and the manuscript suggesting beneficial comments.

Dr. Derek Wilton (co-supervisor) joined the research to provide his expertise in geology, and specifically in MLA-SEM analysis. Dr. Wilton assisted in the interpretation of the MLA-SEM results providing a high-quality analysis. He also revised two of the article (Chapter III and Chapter IV) and the manuscript, providing comments and suggestion for improvements.

Edison Sripal collaborated in the Chapter IV (third paper) of this research. He conducted an effective and innovative wettability restoration technique to the core samples prior to the experiments conducted on them.

CHAPTER II - THE EFFECTIVENESS OF SILICON DIOXIDE (SiO_2) NANOPARTICLE AS AN ENHANCED OIL RECOVERY AGENT IN BEN NEVIS FORMATION, HEBRON FIELD, OFFSHORE EASTERN CANADA

D. J. Sivira, H. Kim, L.A. James, T. E. Johansen, and Y. Zhang

Memorial University of Newfoundland, St. John’s, Newfoundland and Labrador, Canada.

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2.1 Abstract

The Hebron Project is the fourth major development offshore Newfoundland and Labrador, Canada, with an estimated 2620 million barrels of oil and a target first oil in 2017. The Ben Nevis reservoir accounts for approximately 80% of the crude oil with an estimated 30% recoverable. Hence, enhanced oil recovery (EOR) requires attention now even before production starts. This research evaluates the effectiveness of silicon dioxide (SiO_2) nanoparticles as a water additive to enhance oil recovery in the Ben Nevis Formation, Hebron Field. The experiments involved two main steps: measuring interfacial tension, and determining the wetting character of the rock surfaces. Unlike previous research using SiO_2 nanoparticles, in this work, the SiO_2 nanoparticles are dispersed in seawater instead of deionized water or simple synthetic brine; experiments are conducted at reservoir conditions (Hebron Field: 62°C and 19.00 MPa); and synthetic cores were used that best represented facies of Ben Nevis Formation. A major challenge was forming a stable SiO_2 nanofluid in North Atlantic seawater. Since salinity directly affected the stability of the nanofluid, hydrochloric acid was used as a stabilizer. Interfacial tension (IFT) was

measured for SiO_2 dispersed in deionized water, as well as stable nanofluids with SiO_2 concentrations of 0.01, 0.03, and 0.05 wt% dispersed in seawater, to determine the contribution of SiO_2 nanoparticle on the alteration of IFT. The contact angles were measured on core plugs before and after aging in 0.01, 0.03, and 0.05 wt% SiO_2 nanofluids, to determine whether SiO_2 nanoparticles can alter the wettability of the core. The results show that hydrophilic SiO_2 nanoparticles are effective water additive for EOR. When comparing IFT experiments with deionized water and SiO_2 nanoparticles dispersed in deionized water, the nanoparticles reduced the IFT from 39.70 mN/m to 21.54 mN/m. IFT is also reduced from 21.80 mN/m to 16.61 mN/m in case of experiments in seawater and a 0.05 wt% stable SiO_2 nanoparticles dispersed in seawater. The contact angle experiments demonstrate that SiO_2 can decrease the contact angle, and therefore make the rock surface more water wet under reservoir conditions. Finally, it is also found that the higher the SiO_2 nanoparticle concentration, the higher the wettability alteration.

2.2 Introduction

Due to the increasing demand for oil, it is necessary to research innovative and effective enhanced oil recovery (EOR) techniques, and optimize oil production from either currently producing fields or future fields. This research project focused on the EOR method for Hebron asset, which is the fourth major development (with first oil targeted for 2017) offshore Newfoundland and Labrador, Canada. The Hebron Field is located in the Jeanne d'Arc Basin, 340 km offshore of St. John's, Newfoundland and Labrador. It is approximately 9 km north of Terra Nova, 32 km southeast of Hibernia, and 46 km southwest of White Rose, as shown in Figure 2.1. The water depth in this area ranges from 88 to 102 m (CNLOPB, 2011). The Hebron asset is estimated to have 2620 million barrels (MMbbl) of total oil in place, of which only 800 MMbbl are considered recoverable.

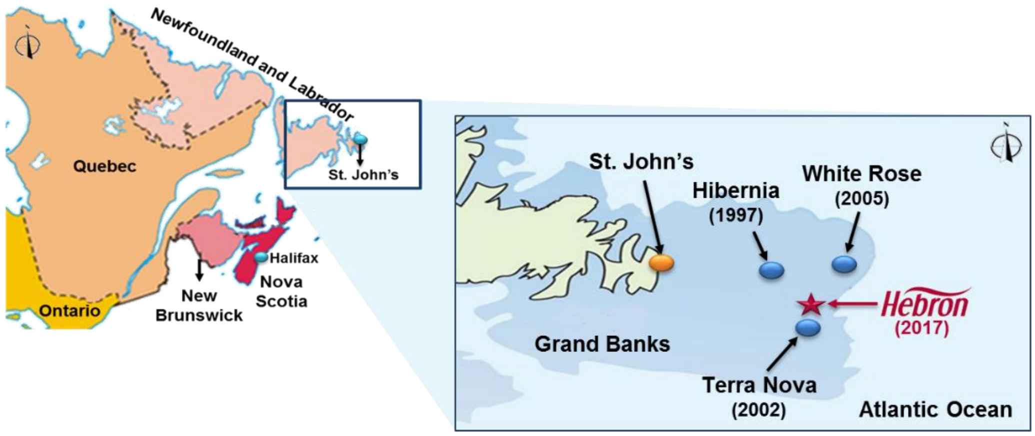

Figure 2.1 *Hebron Project Area Location*
(after CNLOPB, 2011)

The Hebron asset is divided into three fields: Hebron Field, West Ben Nevis Field, and Ben Nevis Field, as shown in Figure 2.2. The Hebron asset presents a total of four reservoirs – Avalon, Hibernia, Jeanne d'Arc, and Ben Nevis Formation – and five pools. This research specifically focuses on the Ben Nevis Formation because this formation is anticipated to produce approximately 80% of the Hebron asset's crude oil. The Ben Nevis Formation is located in pools 1, 2, and 3 with 70% of recoverable resources expected from Pool 1.

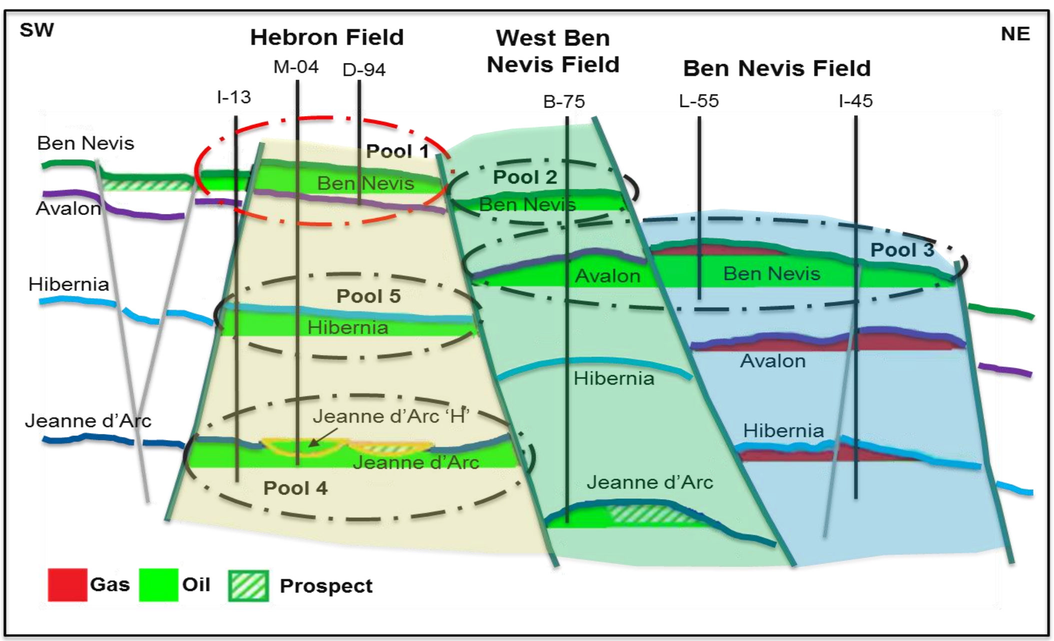

Figure 2.2 *Schematic Cross-Section Across the Hebron Project Area*

(after CNLOPB, 2011)

From a geological point of view, the quality of the Ben Nevis reservoir on pool 1 is fair to good with a very high net to gross ratio, and the density of the oil is between 17 to 24 °API (CNLOPB, 2011). The Ben Nevis Formation is composed predominantly of laminated and bioturbated medium to fine grained sandstones with a high content of quartz. The reservoir quality decreases upwards, presenting an increment of carbonate that averages less than 20 %. In addition, laboratory test revealed that the Ben Nevis Formation is weakly water-wet (CNLOPB, 2011).

The producing life of a reservoir is composed of three phases: primary, secondary and tertiary. Primary recovery is defined as oil recovery derived from natural mechanisms; whereas, secondary recovery involves water or gas injection. Finally, the last stage of the reservoir, which is called tertiary recovery or enhanced oil recovery (EOR), is governed by injection of materials that are not originally present in petroleum reservoir (Lake et al., 2014). These materials aim to modify the fundamental physics or chemistry of the reservoir conditions to improve the recovery (Shepherd, 2009), and are generally classified into thermal techniques, gas injections and chemical methods. Each one of EOR techniques has a particular methodology, and the method applied will depend on the reservoir properties and conditions.

Nanoparticle injection is classified as chemical EOR. It aims to generate interaction between injected fluid and oil to reduce interfacial tension, as well as the interaction between injected fluid and the rock to alter the wettability. The interfacial tension is a well-defined interface that appears in the contact of two immiscible fluids such as gas-liquid or liquid-liquid. The IFT represents only a few molecular diameters in thickness, and it is measured in force per unit length (mN/m) (Donaldson et al., 1985). When this force is low enough, it increases the capillary number, which affects the microscopic pore-level oil displacement (Lake et al., 2014). Wettability is an essential rock property for enhancing oil recovery because it describes the preference of a solid to be in contact with one liquid rather than another in a three-phase system. The wetting character of the rock surface can be divided in three main types: water wet, oil wet, and intermediate wet (Morrow & Heller, 1985).

In the past few years, SiO_2 as an EOR agent has been gaining ground because of its successful results at laboratory scale. SiO_2 is shown to reduce IFT and alter the wetting character of the rock surface (Al-Anssari, et al., 2015; Aurand, et al., 2014; Hendraningrat et al., 2012; Hendraningrat & Torsæter, 2014; Li, et al., 2013; Li & Torsæter, 2015).

The limitation of these studies is that the nanoparticles are dispersed in a solution of sodium chloride (NaCl) or synthetic brine, and the experiments were conducted at ambient conditions. Using sodium chloride solution for nanoparticle dispersant is unrealistic for offshore applications, such as Hebron Field, since seawater will be used for nanoparticle injection. Mg^{2+} and Ca^{2+} present in seawater is known to highly compromise the stability of nanoparticle dispersed in aqueous phase (Metin, et al., 2011). This research aimed to reduce the uncertainties between laboratory and field conditions; hence, the experiments were conducted at the reservoir pressure and temperature of the Hebron Field. In addition, fluids and rocks were chosen to mimic the Ben Nevis Formation as closely as possible, and will be validated using Hebron core after experimental confirmation.

2.3 Experimental Methodology

Hydrophilic silicon dioxide (SiO_2) nanoparticles used as an EOR agent were ordered from US Research Nanomaterials, Inc., which consisted of 99.9% of SiO_2, with particle sizes between 5 to 35 nm. Seawater from Grand Banks, which is the area surrounding the Hebron Field, is used as a dispersant fluid for the nanoparticles. To mitigate challenges of obtaining a stable SiO_2 nanoparticles dispersed in seawater, hydrochloric acid (HCl) was used as a stabilizer. Two types of standard cores, Berea and Bandera, were used for contact angle experiments, since they best represented the main two facies of the Ben Nevis Formation. Berea was ordered from Berea Sandstone Petroleum Cores, and Bandera was ordered from Kocurek Industries Inc. The cores were cut in sizes of 25.4 mm in diameter and 3 mm in thickness. The compositions of Bandera and Berea rocks according to mineral liberation analysis (MLA), performed on MLA 650 FEG manufactured by FEI, are shown in Figure

2.3 and Figure 2.4. Berea sandstone represent the lower section of Ben Nevis formation with high content of quartz and low content of carbonate minerals. Ben Nevis reservoir quality decreases upwards, which means that the mineralogical composition of the upper section is richer in carbonate minerals. Therefore, Bandera sandstone was chosen to represent the upper section of the reservoir. Bandera is composed of 14.24 % of carbonate minerals, as can be seen in Figure 2.4.

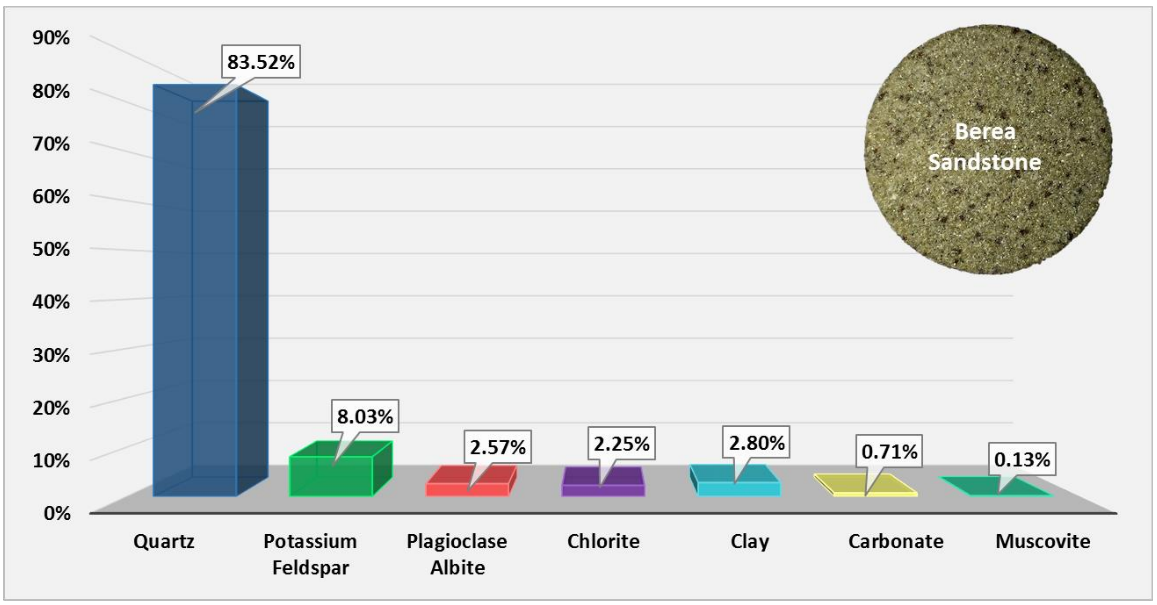

Figure 2.3 *Mineralogical Composition of Berea Sandstone*

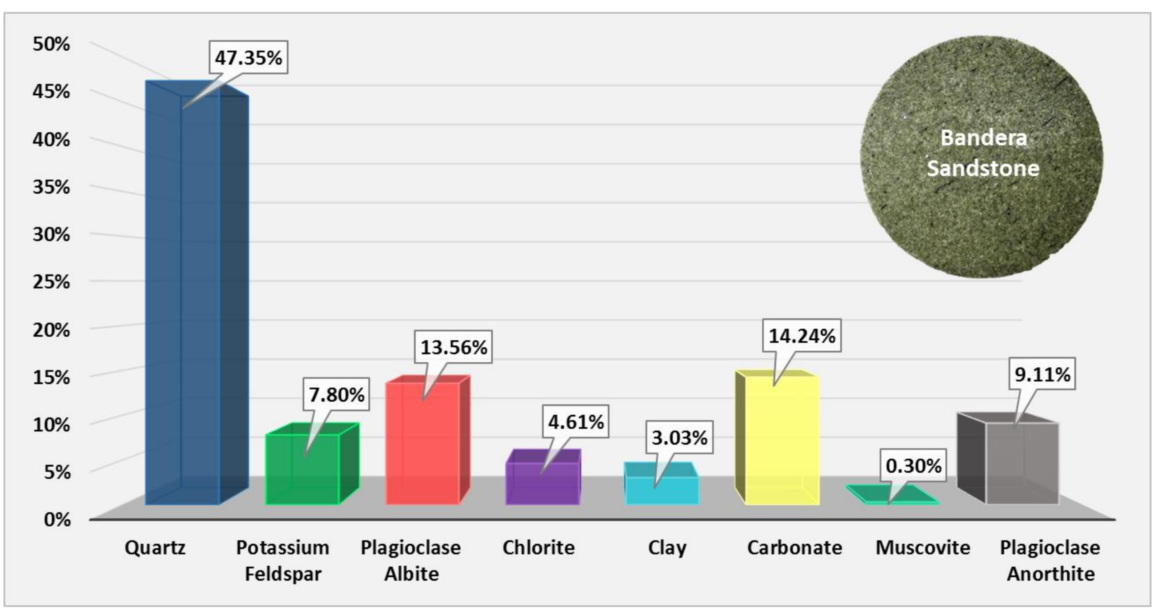

Figure 2.4 *Mineralogical Composition of Bandera Sandstone*

To determine effectiveness SiO_2 nanofluids as an EOR agent, the interfacial tension and contact angle measurements were made using IFT 700, developed by Vinci Technologies. All interfacial tension and contact angle experiments were conducted through drop shape method, under Hebron reservoir temperature and pressure, which is 62°C and 19.00 MPa, respectively. The IFT instrument was calibrated by measuring interfacial tension of deionized water/air, and toluene/air, and comparing it to the literature value. Data for each IFT and contact angle experiments were recorded every 5 seconds for 15 minutes. Standard deviation for the data set is then calculated for each experiment. In addition, 20 % of each IFT and contact angle experiments were duplicated to ensure the accuracy of the instrument.

The interfacial tension and contact angle measurements alterations are tested for 0.01, 0.03, and 0.05 wt% SiO_2 nanofluids. To obtain stable 0.01, 0.03, and 0.05 wt% nanofluids, HCl was added to each solution, while keeping the same ratio between HCl concentration and SiO_2 nanoparticle concentration for all three nanofluids. The detailed make-up of the nanofluids are organized in Table 2.1.

Table 2.1 *Nanofluid Composition*

Nanoparticle	Nanoparticle Concentration (wt%)	Stabilizer	HCl Concentration (wt%)	Ratio HCl:SiO_2	Dispersant
SiO_2	0.01	HCl	0.0046	0.46	Seawater
	0.03		0.0138	0.46	Seawater
	0.05		0.0230	0.46	Seawater

To understand the contribution of SiO_2 nanoparticle on the degree of interfacial tension alteration, IFT between seawater/oil and three different nanofluids/oil are compared. IFT between seawater containing 0.0046, 0.0138 and 0.0230 wt% HCl and oil were also measured. This was to ensure that the IFT reduction is resulting from nanoparticles, not the stabilizing agent, HCl.

For wettability alteration experiments using SiO_2 nanoparticle, Berea and Bandera core plugs were aged in oil from offshore Newfoundland at 62°C for 2 weeks. Immediately after aging in oil, contact angles of the core plugs were measured. These measurements represented the initial contact angle for future comparison. Then, the core plugs aged in oil were aged in SiO_2 nanofluid at 62°C. The wetting character changes on the rock surfaces were identified by comparing initial contact angle of the rock surface aged in oil, and the contact angle after nanofluid application.

2.4 Results and Discussion

According to Das et al. (2008), the main challenges of making nanofluid from nanopowder is that the nanoparticles agglomerate when they are in suspension. The stability of SiO_2 nanoparticle is extremely sensitive to the salinity of the dispersant. Since the dispersant used in this research is seawater from offshore Newfoundland, a stabilizer was needed. Hydrochloric acid successfully generated a stable SiO_2 nanofluid dispersed in seawater, under Hebron field temperature and pressure conditions (62°C and 19.00 MPa), over extended periods of time. From Figure 2.5, effectiveness of HCl as a SiO_2 nanoparticle stabilizer in seawater can be observed. The unstable solutions of SiO_2 nanoparticles in seawater can easily be recognized on the left-hand side, compared to the stable nanofluids on the right-hand side of 0.01, 0.03, and 0.05 wt% SiO_2 nanofluids used for this research.

Figure 2.5 *Unstable Nanofluid Solutions (Left) Versus Stable Nanofluid Solutions (Right)*

The reduction of interfacial tension is desirable in terms of oil recovery, because reducing interfacial tension increases the capillary number. The capillary number is defined as the relationship between viscous forces and interfacial tension (Eq. 1). Increased capillary number means improved mobilization of the residual oil (Donaldson et al., 1985).

Preliminary IFT experiments were conducted with deionized water and 0.05 wt% SiO_2 nanoparticles dispersed in deionized water. The experiments showed that the nanoparticles reduced the IFT from 39.70 ± 1.09 mN/m (deionized water) to 21.54 ± 1.12 mN/m (0.05 wt% SiO_2 nanoparticles dispersed in deionized water). These results share the same trend as results obtained by (Li et al., 2013). They measured IFT for ranging concentrations of hydrophilic SiO_2 nanoparticles dispersed in a solution of sodium chloride at 3 wt%. They claimed that when the SiO_2 nanoparticle concentration is increased, the IFT decreased.

$$N_c = \frac{v\mu}{\sigma} \text{ ,……………. (1)}$$

Where:

N_c = Capillary Number

v = Darcy velocity (m/sec)

μ = Displacing fluid viscosity (Pa.s)

σ = Interfacial tension (N/m)

IFT results for 0.01, 0.03 and 0.05 wt% are presented in Figure 2.6, and are compared to IFT of seawater/oil to examine the effect of nanoparticles on the interfacial tension. IFT of seawater/oil is measured to be 21.80 ± 0.31 mN/m. It is observed that 0.01 wt% SiO_2 nanofluid has minimal effect on the interfacial tension, since only small change is observed from 21.80 ± 0.31 mN/m to 21.02 ± 0.32 mN/m. For 0.03 wt% SiO_2 nanofluid, IFT was reduced from 21.80 ± 0.31 mN/m to 17.90 ± 0.89 mN/m. Finally, the test with 0.05 wt% SiO_2 nanofluid generated the highest IFT reduction from 21.80 ± 0.31 mN/m to 16.61 ± 0.96 mN/m. The IFT of seawater with HCl/oil was also measured to ensure interfacial tension reduction is not owing to HCl. The seawater containing 0.0046, 0.0138 and 0.0230 wt% HCl were tested, which is the HCl concentrations present in 0.01, 0.03, 0.05 wt% nanofluid, respectively. The stabilizer, HCl, in fact was unfavorable in terms of IFT reduction, as it can be seen in Figure 2.7. When comparing IFT of the seawater versus the

IFT of seawater and HCl mixture, the IFT increases. There is a trend in which the IFT increases as HCl concentration increases. Despite these findings, SiO_2 nanofluids consisting of seawater, HCl, and nanoparticles, are found to decrease IFT. Further, the higher the SiO_2 concentration, the more reduction in IFT.

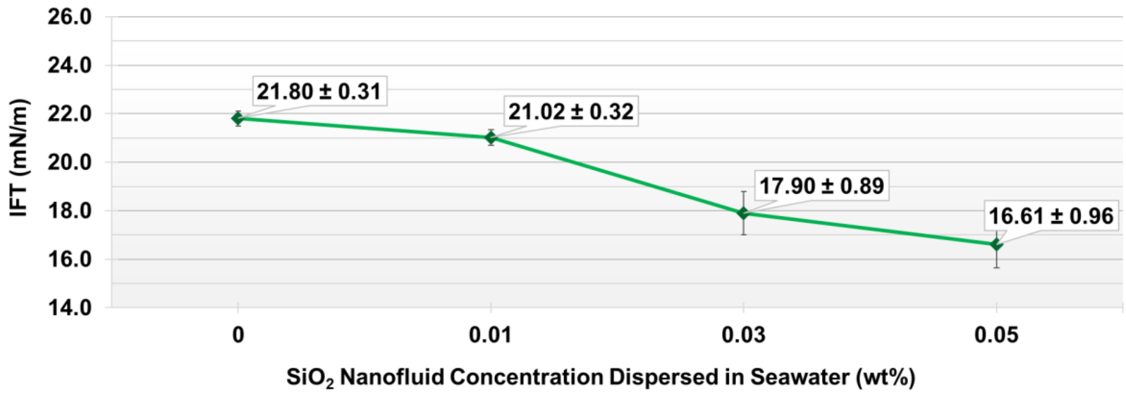

Figure 2.6 *SiO_2 Nanoparticle Contribution on the Interfacial Tension Alteration*

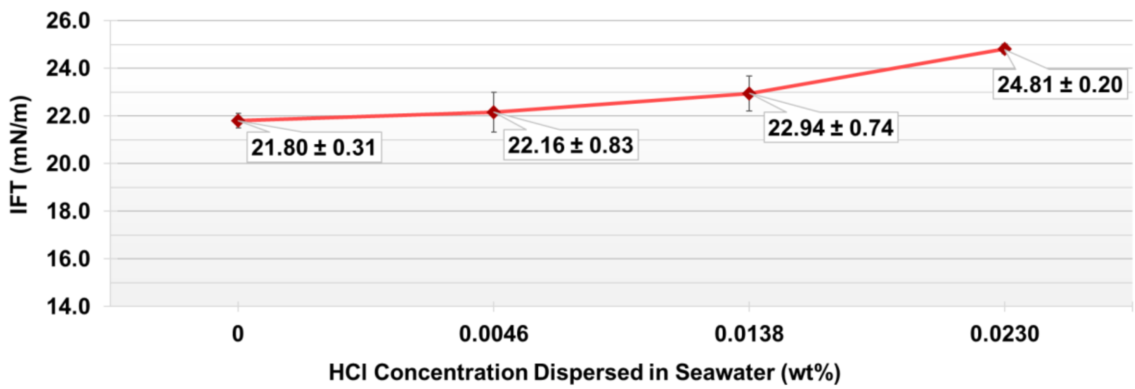

Figure 2.7 *HCl Contribution on the Interfacial Tension Alteration*

The alteration of wettability is another important aspect of nanoparticles EOR application. Modification of the wetting character of the reservoir from a tendency towards oil wet to water wet has a positive effect on the oil recovery. The most efficient oil displacement is obtained in reservoirs with strong wetting preferences for water and with strong capillary imbibition forces (Morrow, 1990). One of the methods for defining wettability is the contact angle test, which is expressed in terms of wettability index (WI). -1 describes oil wet condition, and 1 describes water wet condition. The wettability index is equal to the cosine of the contact angle, as shown in Figure 2.8.

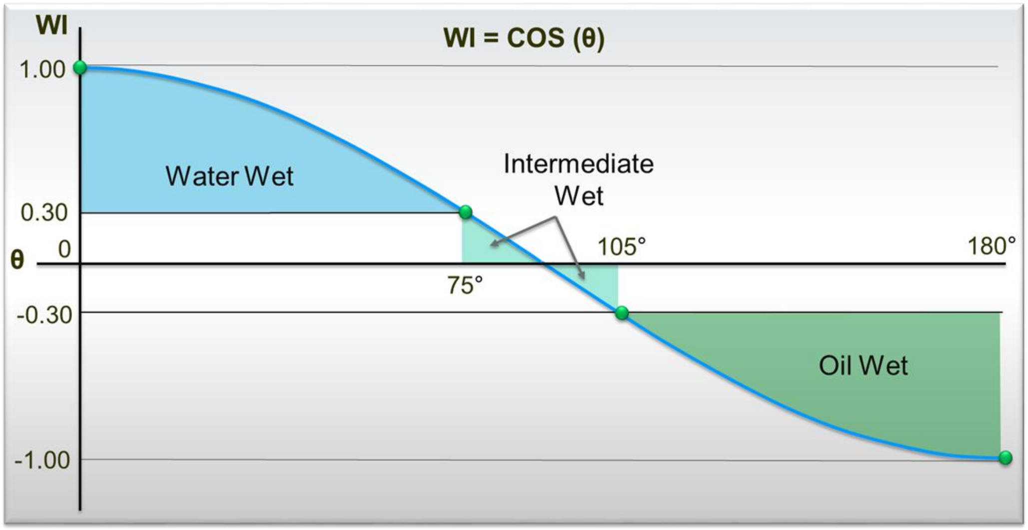

Figure 2.8 *Visual Representation of the Relationship Between Contact Angle and Wettability Index*

(Treiber & Owens, 1972)

The contact angle experiments on Berea sandstones showed a clear decrease in the contact angle when they were aged in nanofluids (Figure 2.9). The contact angle of the Berea sample aged in oil was 51.4° ± 1.0. The contact angle in the case of the sample in 0.01 wt% nanofluid was 37.3° ± 0.7, which is a reduction of 14.1°. The experiment conducted with 0.03 wt% SiO_2 nanofluid generated a contact angle of 32.4° ± 0.6, showing 19.0° of reduction. Finally, the test using a 0.05 wt% SiO_2 nanofluid produced a contact angle of 31.4° ± 0.9; resulting in the highest reduction in the contact angle of 20.0°. The experiments using Bandera sandstone showed the same trend as Berea sandstone (Figure 2.10). The contact angle of the Bandera sample aged in oil was 76.7° ± 1.5. Bandera core plug aged in 0.01 wt% SiO_2 nanofluid showed a reduction of 37.5° in contact angle compared to initial contact angle, since the contact angle was measured to be 39.2° ± 0.6. For Bandera core plug aged in 0.03 wt% SiO_2 nanofluid, the contact angle was 37.0° ± 0.3, with a reduction of 39.7°. The last contact angle experiment with Bandera core plug in 0.05 wt% SiO_2 nanofluid gave contact angle of 34.1° ± 0.4. This is a decrease of 42.6° in contact angle, and is the biggest contact angle reduction observed in this study. The contact angle experiments showed that the SiO_2 nanoparticle is an effective agent to reduce the contact angle of the rock surface, making the rock more water wet. Based on the results, Bandera seems to be more sensitive to wettability alteration via SiO_2 nanoparticles compared to Berea, possibility resulting from differences in mineralogical compositions between two rocks. Moreover, the results also indicated that the greatest alterations were obtained with the highest concentration of the nanofluid.

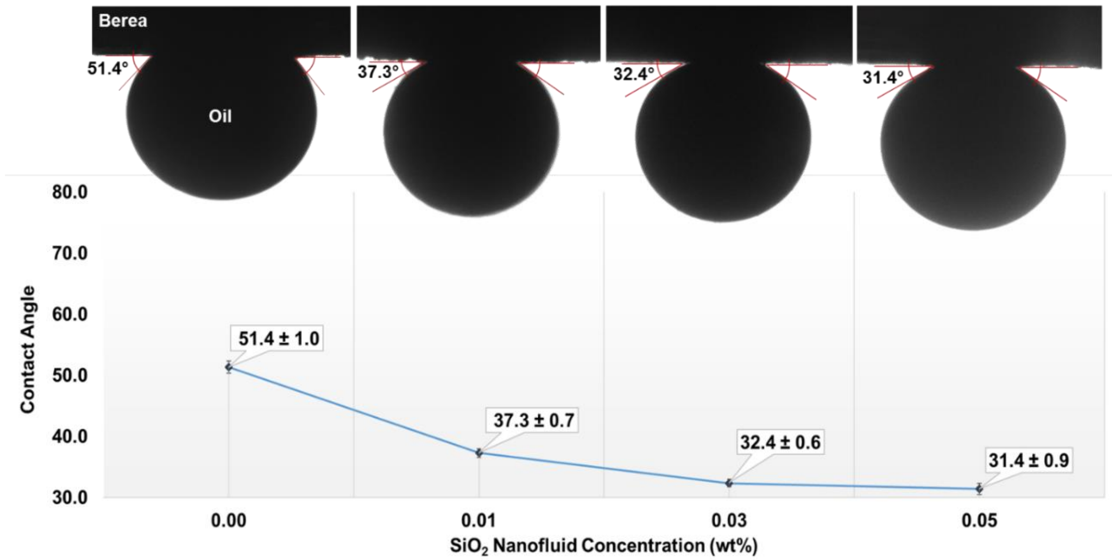

Figure 2.9 *Contact Angle Measurement on Berea Sandstone with Various SiO_2 Nanofluid Concentration*

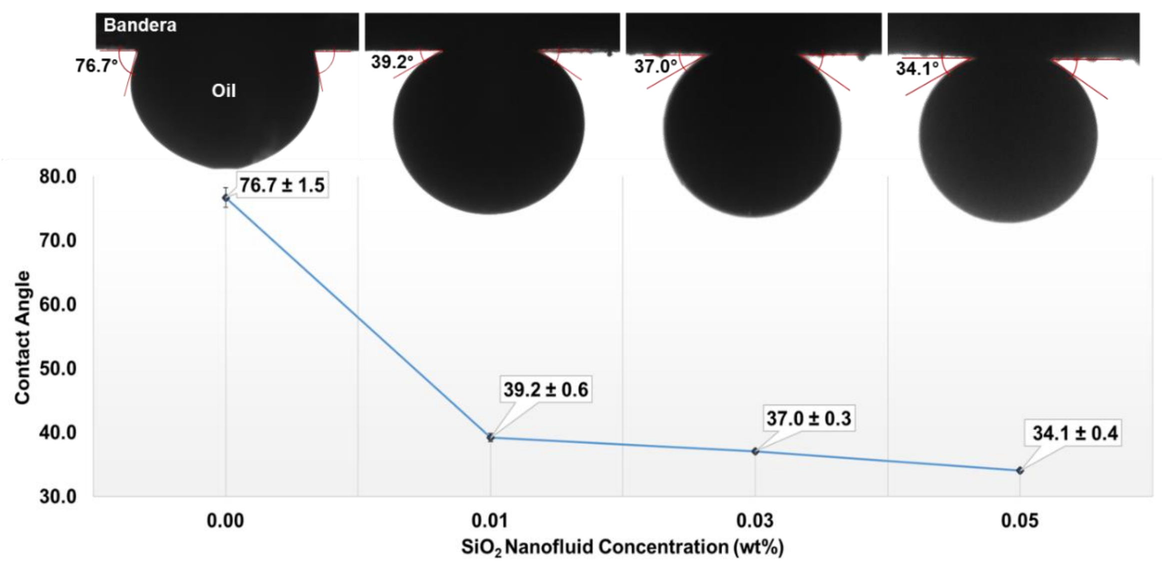

Figure 2.10 *Contact Angle Measurements on Bandera Sandstone with Various SiO_2 Nanofluid Concentration*

The wettability alteration during nanofluid injection can be explained using the disjoining pressure theory proposed by Wasan & Nikolov, 2003; Chengara et al., 2004; and Wasan, et al., 2011. They suggested that nanoparticles disperse in a solution will arrange themselves into geometrical structures at the wedge film formed between an oil drop and the rock surface. The nanoparticles present at the wedge exert excess pressure, called disjoining pressure, forcing themselves into a confined region forward until the nanofluid spreads on the rock surface, and detaching the oil drop (Figure 2.11). The disjoining theory involves energies such as potential attraction energy of van der Waals' between the particles, repulsion energy of electric double layers, and Brownian motion. The forces applied will depend on the number of particles. One single particle will apply a very weak force, whereas large number of particles will exert a significant disjoining pressure (McElfresh, et al., 2012). Furthermore, the disjoining pressure is directly correlated to the adsorption characteristics of the nanofluid (Chengara et al., 2004).

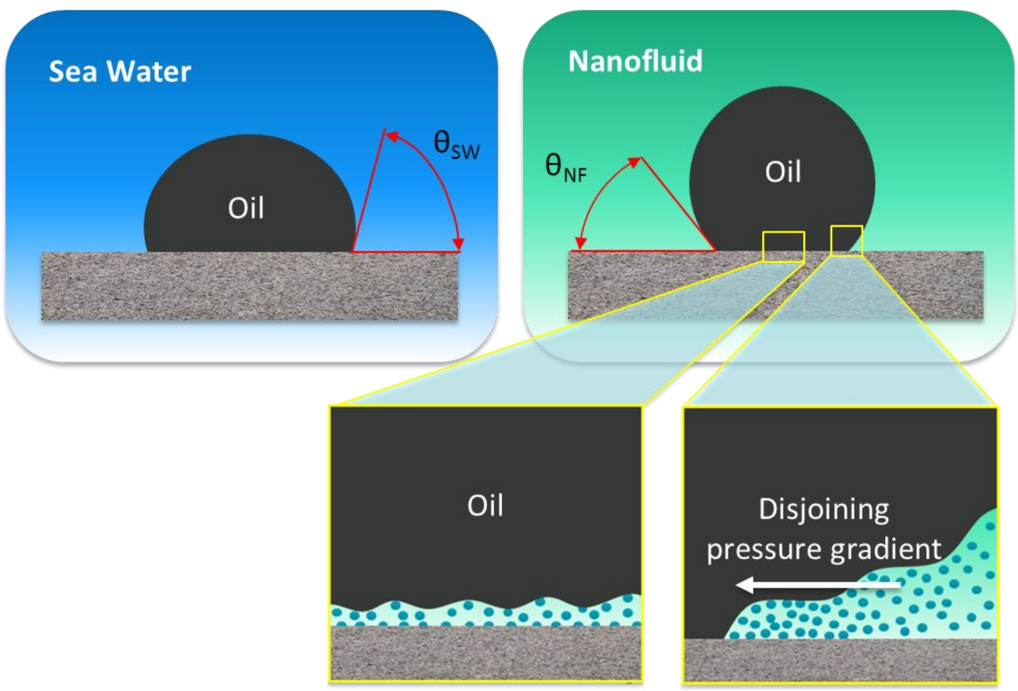

Figure 2.11 *Contact Angle in a Three-Phase System Decrease from Seawater-Oil-Rock to Nanofluid-Oil-Rock ($\theta_{SW} > \theta_{NF}$) Due to Disjoining Pressure Gradient at the Wedge-Film (after Wasan et al., 2011)*

2.5 Conclusions

The remarkable goals achieved during this research are listed as follows:

1. Stable SiO_2 nanoparticle dispersed in seawater reduces the interfacial tension at Hebron field pressure and temperature (62°C and 19.00 MPa).

2. The interfacial tension between the stabilizer, hydrochloride acid, in seawater and oil is greater than the interfacial tension without hydrochloric acid. As concentration of hydrochloric acid increases, the interfacial tension of oil-water also increases.

3. Despite of the increment on IFT caused by hydrochloride acid, the interfacial tension decreases in the presence of SiO_2 nanoparticle. The greater the concentration of SiO_2 nanofluid, the lower the interfacial tension of oil-water.

4. Hydrophilic SiO_2 nanofluid has the ability of reduce the contact angle, making the wetting character of the Berea and Bandera rock surface more water wet under Hebron field pressure and temperature conditions (62°C and 19.00 MPa).

5. Berea sandstones treated with 0.05 wt% stable SiO_2 nanofluid showed a maximum contact angle reduction of 20.0°. The concentration of the nanofluid is inversely proportional contact angle, hence 0.05 wt% nanofluid is most effective in wettability alteration.

6. Contact angle measurements on Bandera sandstone exhibited a reduction in contact angle when the rock was aged in stable SiO_2 nanofluid. The highest alteration was achieved using a 0.05 wt% SiO_2 nanofluid, reaching total reduction of 42.6°.

2.6 Acknowledgements

The authors would like to thank Hibernia Management and Development Company (HMDC), Research and Development Corporation of Newfoundland and Labrador (RDC), the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Hibernia EOR Research Group for technical and financial support.

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CHAPTER III - WETTABILITY ALTERATION AND INTERACTIONS BETWEEN SILICON DIOXIDE (SiO_2) NANOPARTICLES AND RESERVOIR MINERALS IN STANDARD CORES MIMICKING HEBRON FIELD CONDITIONS FOR ENHANCED OIL RECOVERY

D. J. Sivira, H. Kim, L.A. James, D. Wilton, and Y. Zhang

Memorial University of Newfoundland, St. John's, Newfoundland and Labrador, Canada.

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3.1 Abstract

The use of innovative economically and environmentally suitable techniques is becoming a main objective for the oil and gas industry. Adding SiO_2 nanoparticles to water for enhanced oil recovery (EOR) has been gaining ground as such a technique over the last few years because of favorable laboratory results; however, field applications have yet to be attempted. The goal of nanofluid injection is to promote fluid-rock interaction, therefore, determination of the nature of these interactions is a key research question. This research studied interaction between 0.01, 0.03, and 0.05 wt% SiO_2 nanofluids and standard cores through 1) contact angle experiments, 2) scanning electron microscopy - mineral liberation analyzer (SEM - MLA) analysis; and 3) inductively coupled plasma optical emission spectroscopy (ICP-OES), to predict EOR mechanisms with SiO_2 nanofluids in the Hebron field. The Hebron field is the 4th offshore development in Canada. Located 350 km offshore Newfoundland and Labrador, it contains an estimated of 2620 million barrels of oil in place. First oil production is planned for 2017. Berea and Bandera standard cores were selected

to represent the mineralogical compositions of the Ben Nevis Formation, the most important reservoir containing approximately 80 % of the Hebron's crude oil. The SiO_2 nanoparticles were dispersed in seawater collected from the vicinity of the Hebron field and the oil used was from offshore Newfoundland (Hibernia Field). Contact angle measurements at standard Hebron Field temperature and pressure conditions (62 °C and 19.00 MPa) indicated that maximum angle decrease occurred after six hours of aging the core plugs in nanofluids. Berea core had a decrease from 51.4° to 30.2°, whereas the Bandera rock decreased from 76.7° to 29.6°. The adsorption of nanoparticles is believed to have been responsible for changing the wettability of the rock, but unfortunately SEM-MLA and ICP-OES results were not able to verify the adsorption of SiO_2 nanoparticle on the rock surface. However, SEM-MLA and ICP-OES analysis confirmed the dissolution of carbonate minerals on Berea and Bandera by the hydrochloric acid (HCl) used as stabilizer in the nanofluids.

3.2 Introduction

The Hebron project is the 4th major Canadian offshore development with first oil expected in 2017. It is located 350 km offshore Newfoundland and Labrador, Canada, as shown in Figure 3.1. The best oil in place estimation is 2620 million barrels of oil, of which 30 % is considered recoverable (CNLOPB, 2011). The goal of this research is to quantify the wettability alteration caused by nanoparticles as part of screening nanoparticle EOR. The research is part of a larger Hebron EOR Screening project considering suitable enhanced oil recovery (EOR) methods applicable to this heterogeneous (mixed wettability, upward fining), medium crude oil (17-24 °API) field.

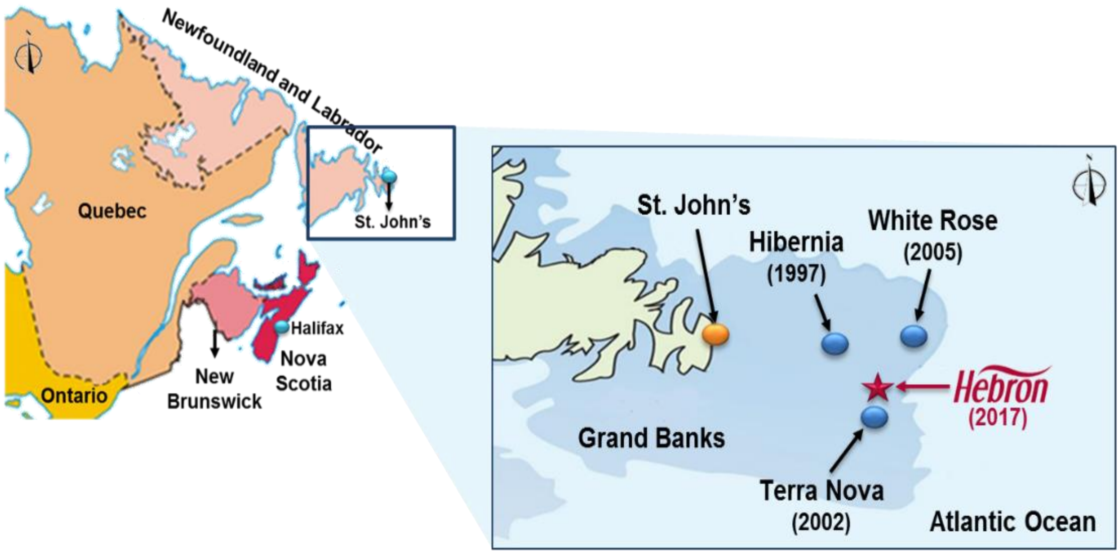

Figure 3.1 *Hebron Project Area Location*

The Hebron development is divided into three fields: Hebron, West Ben Nevis, and Ben Nevis. These fields are subdivided into five pools, as shown in Figure 3.2, hosted by four formations: Ben Nevis, Hibernia, Avalon and Jeanne d'Arc. The Ben Nevis Formation in Pool 1 is estimated to contain 70 % of the total recoverable oil of the entire project (CNLOPB, 2011). The reservoir pressure and reservoir temperature are 19.0 MPa and 62 °C respectively and the oil is medium crude with 17 - 24 °API. The Ben Nevis Formation is composed predominantly of laminated and bioturbated medium to fine grained, sandstones with high quartz contents. The reservoir quality decreases upwards with increasing carbonate content (Valencia et al., 2017). Laboratory testing revealed that the Ben Nevis Formation is weakly water-wet (CNLOPB, 2011). In addition to oil characteristics and reservoir conditions, the geological characteristics of the reservoir are important to ensure compatible geochemistry, wettability alteration, and sweep efficiency in EOR applications.

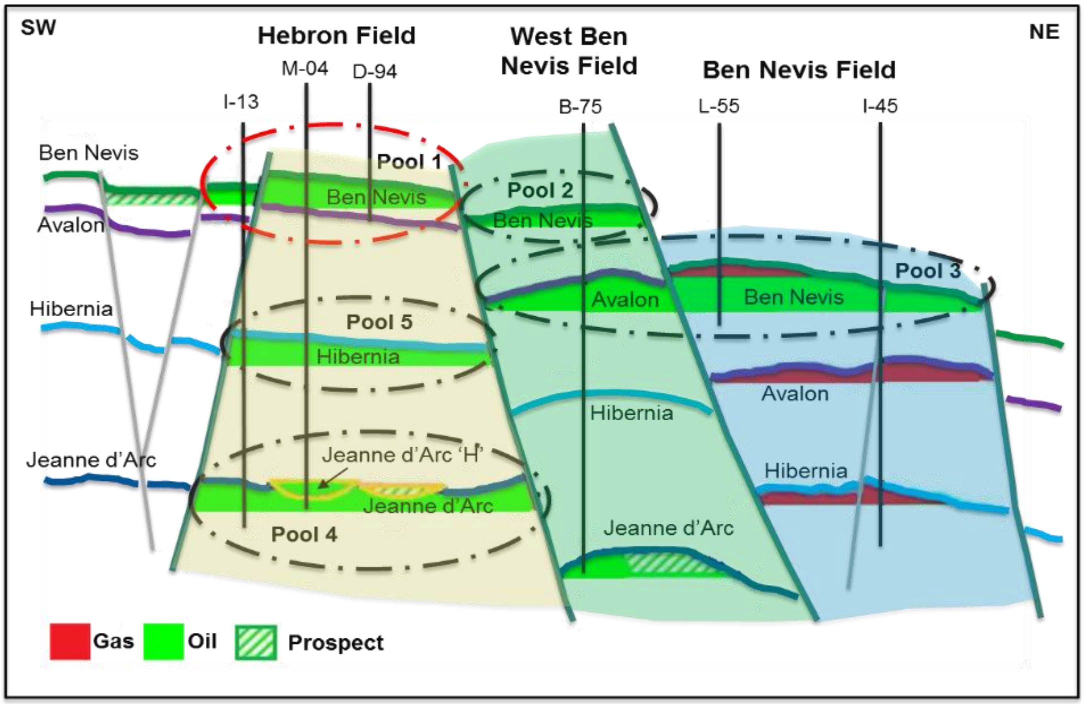

***Figure 3.2** Schematic Cross-Section Across the Hebron Project Area*
(after CNLOPB, 2011)

The list of EOR methods is extensive and screening of a particular method requires specific information; as a result, the most suitable EOR method for a field involves the consideration of the location, properties, and reservoir conditions. Nanoparticle injection is considered a viable method for remote harsh locations, such as the Hebron field location, due to the cost, volume and ease of nanoparticle transportation, minimal facility requirements, and environmental concerns. Injecting silicon dioxide (SiO_2) nanoparticles as a water additive looks to reduce the interfacial tension between the water and the oil as well as alter the wettability of the rock, hence enhancing recovery.

The presence of nanoparticles on a rock surface tends to alter the wetting character of the rock due to disjoining pressure as proposed by Chengara et al., 2004; D. Wasan et al., 2011; and Wasan & Nikolov, 2003. This theory is based on the potential attraction energy of Van der Waals' forces between the particles, repulsion energy of electric double layers, and Brownian motion. It states that nanoparticles dispersed in a solution will arrange themselves into geometrical structures at the wedge film between an oil drop and the rock surface. The nanoparticles present at the wedge exert excess pressure, called disjoining pressure, forcing themselves forward into a confined region until the nanofluid spreads on the rock surface, and detaching the oil drop (Figure 3.3).

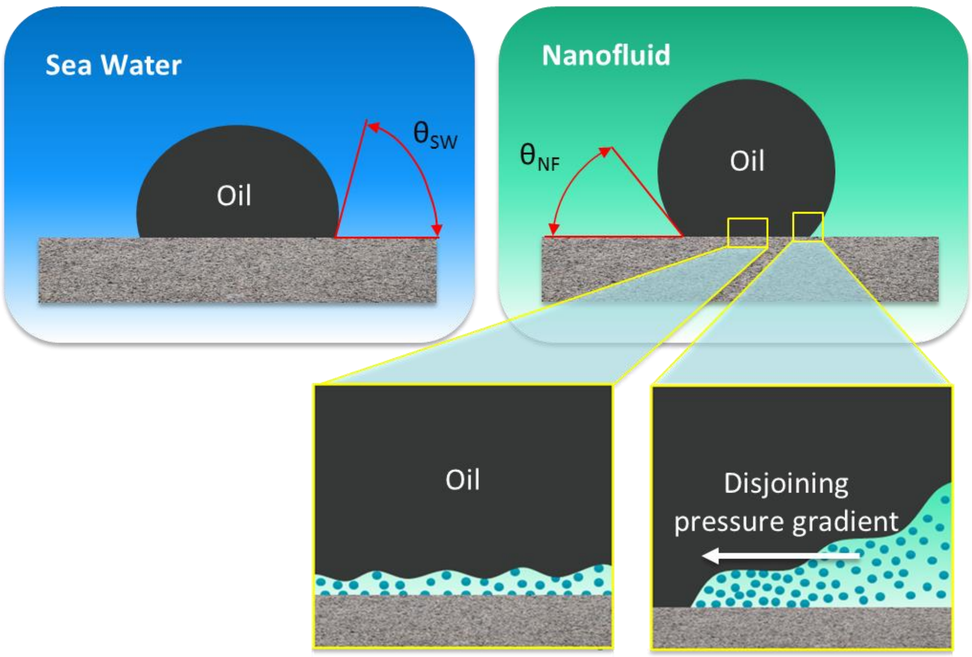

Figure 3.3 *Contact Angle in a Three-Phase System Decrease from Seawater-Oil-Rock to Nanofluid-Oil-Rock ($\theta_{SW} > \theta_{NF}$) Due to Disjoining Pressure Gradient at the Wedge-Film (after Wasan et al., 2011)*

Nanoparticle injection is an innovative EOR technique that is gaining favor because of potential results at laboratory scale, as shown in other research such as: Al-Anssari et al., 2015; Aurand et al., 2014; Hendraningrat, et al., 2013; Hendraningrat & Torsæter, 2014; Li et al., 2013; Li & Torsæter, 2015. All of these research projects performed experiments to measure wettability alteration using hydrophilic SiO_2 nanoparticles as a modifier. They determined the alteration through either contact angle experiments or Amott tests, and their results are consistent with making the wetting character more water wet. Unfortunately, most of these researches considered unrealistic conditions (for example, sodium chloride (NaCl) or synthetic brine as a dispersant and/or conducting the experiments at ambient conditions); however, Sivira et al., 2016 showed promising results with IFT reduction and wettability alteration at field conditions. The aim of this research is to continue filling the gap between laboratory and field conditions of applying silicon dioxide (SiO_2) nanoparticles as a water additive for EOR, determining the optimum time of interaction, as well as the level of interaction between the SiO_2 nanoparticles and rock. The optimum time is achieved by testing the contact angle at different aging time, and the level of interaction is evaluated by analyzing the mineralogical composition of rock and the characteristics of the solution before and after the procedure.

3.3 Experimental Methodology

Three types of experiments were conducted to analyze the fluid-rock interaction. Contact angle experiments were performed to measure the alteration of the wetting character; SEM-MLA (scanning electron microscopy - mineral liberation analyzer) analysis to determine the variation on the mineralogical composition of the rock surface including any adsorbed SiO_2 nanoparticles; and finally, inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis to quantify the chemical changes in the nanofluid solution. All these experiments were conducted before and after aging the core in the nanofluid to prove effectiveness of the nanoparticle on the wettability alteration.

The materials were chosen to mimic the Hebron field conditions closely. The 99.9 % hydrophilic silicon dioxide (SiO_2) nanoparticles (US Research Nanomaterials, Inc.) have a particle size ranging from 5 to 35 nm. The seawater used as a dispersant is from the Grand Banks (ocean surrounding the Hebron field). To guarantee a stable nanofluid, hydrochloric acid (HCl) was used as a stabilizer (Kim, et al. 2017). Berea (Berea Sandstone Petroleum Cores) and Bandera (Kocurek Industries Inc.) standard cores were used to represent the lower and upper sections of the Ben Nevis Formation, respectively (Figure 3.4 and Figure 3.5).

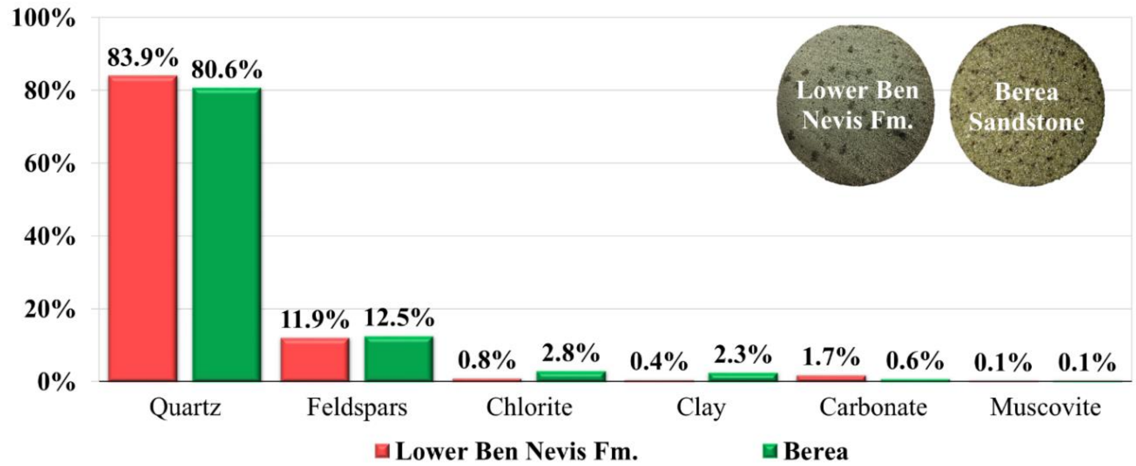

Figure 3.4 *Mineralogical Composition of Lower Ben Nevis Formation and Berea Sandstone Analyzed by SEM-MLA*

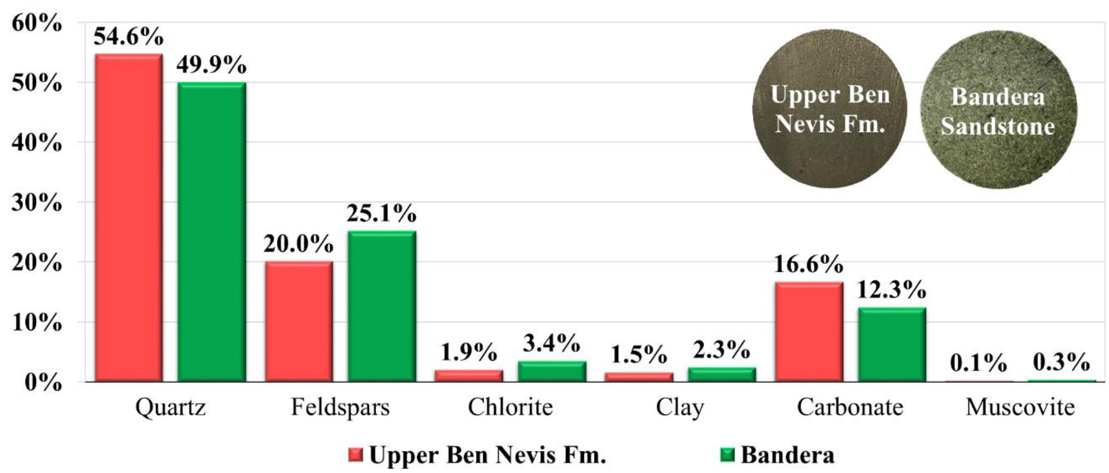

Figure 3.5 *Mineralogical Composition of Upper Ben Nevis Formation and Bandera Sandstone Analyzed by SEM-MLA*

The nanofluids were prepared at three different concentrations: 0.01, 0.03 and 0.05 wt% SiO_2, as shown in Table 1. Nanoparticles were dispersed in seawater with HCl as a stabilizer. The ratio between HCl concentration and SiO_2 nanoparticle concentration for all three nanofluids were kept constant. Three solutions without the nanoparticles (i.e. seawater and HCl only) with the same HCl concentrations as nanofluids were also prepared.

The same experiments for nanofluids were performed on these solutions of seawater and HCl only, to ensure that the nanoparticles are responsible for wettability alterations rather than HCl.

Table 3.1 *Composition of the Fluids*

Name	SiO_2 Concentration (wt%)	HCl Concentration (mol/L)	Ratio HCl:SiO_2	Dispersant
Nanofluid 1	0.01	0.002	0.2	Seawater
Nanofluid 2	0.03	0.006	0.2	Seawater
Nanofluid 3	0.05	0.010	0.2	Seawater
HCl 1	-	0.002	-	Seawater
HCl 2	-	0.006	-	Seawater
HCl 3	-	0.010	-	Seawater

Tests were conducted on the core slices before and after aging in the nanofluid to optimize the nanofluid concentration and aging time. Contact angle experiments were conducted on 25.4 mm in diameter and 3 mm in thickness core slices of both Berea and Bandera. The core slices were first aged in oil from offshore Newfoundland for 2 weeks at 62 °C. After aging the core slices in oil, initial wetting characters were measured and recorded at 62 °C and 19.00 MPa (reservoir conditions). Then, these core slices were aged in three different nanofluid concentrations (0.01, 0.03, and 0.05 wt% SiO_2) at 62 °C for different time periods to determine the level of interaction between the rock and the fluids. Figure 3.6 shows the aging process of the rocks in nanofluid. The aging time periods chosen were 1 hour, 3 hours, 6 hours, 1 day and 3 days. Once the core slices have been aged in the stable nanofluid solutions for each of these time periods, the contact angles were measured again at 62 °C and 19.00 MPa.

Contact angle experiments were performed using a Vinci Technologies IFT 700 instrument through the drop shape method. The contact angle was measured every 10 seconds for 15 minutes, and three drops were measured for each sample. The standard deviation of the contact angle measurements within the sample were lower than two degrees for all the samples. To ensure the accuracy of the results, 20 % of the measurements were replicated.

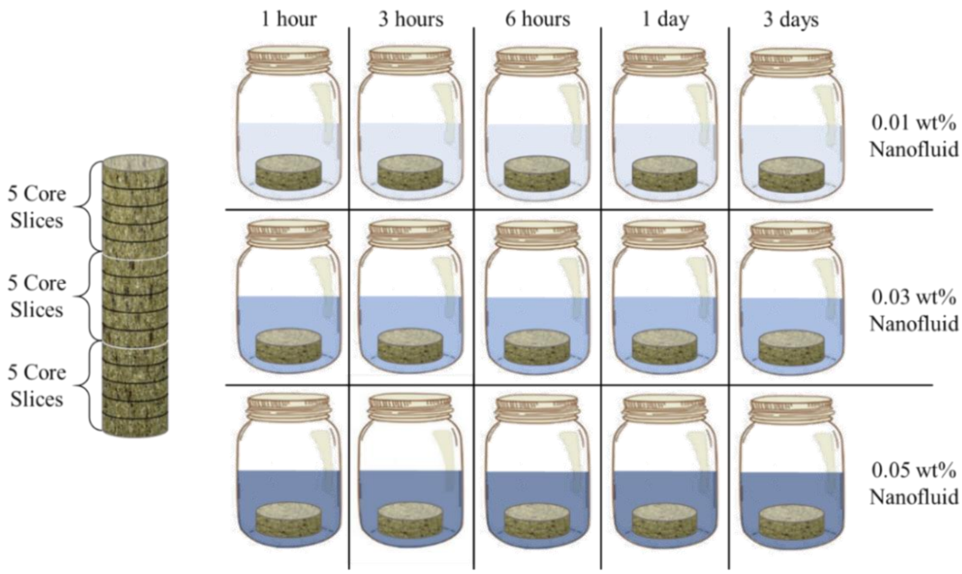

Figure 3.6 *Preparation of Cores for Contact Angle Experiments*

SEM-MLA analyses were performed on Berea and Bandera core slices before and after aging in three different nanofluid concentrations for six hours, using an FEI 650 FEG SEM instrument. SEM analysis take high definition images on the rock surface with a level of the detection of 10 nm, and MLA tests quantify the minerals content on the rock surface with a level of detection of 500 nm. ICP-OES analysis was performed using a Perkin-Elmer 5300 DV inductively coupled plasma-optical emission spectrometer with a detection limit of 10 ppm, to quantify the changes in the concentrations of key chemical elements in the nanofluid before and after aging the rocks. Figure 3.7 illustrates the methodology applied for MLA-SEM and ICP-OES experiments.

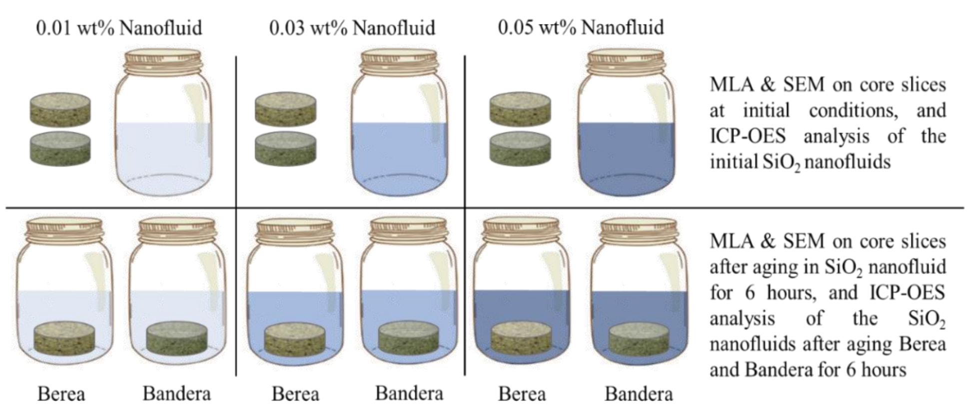

Figure 3.7 *Diagram of MLA-SEM and ICP-OES Experiments*

To understand the contribution of the HCl stabilizer on the interaction between the nanofluid and the rock, contact angle experiments were conducted on both Berea and Bandera standard cores with seawater and HCl, following the same procedure and aging times (1 hour, 3 hours, 6 hours, 1 day, and 3 days) as contact angle experiments using nanofluid. ICP-OES analysis were also conducted on the solutions of seawater and HCl before and after aging the rocks for six hours.

3.4 Results and Discussion

Alteration of rock wetting character is a crucial parameter for increasing the oil recovery. According to Morrow (1990), strongly water wet reservoirs reach higher oil recovery. The wetting character of the rock surface can be expressed in either wettability index (WI) or contact angle, and they share a linear relationship because the wettability index is equal to the cosine of the contact angle (Figure 3.8). The contact angle describes the wetting character of the rock through the angle formed from a drop of oil placed on a surface rock, surrounded by formation water or in our case, nanofluid or seawater with HCl. When the effective contact angle of the oil is between 0° to 75°, the surface is referred as water-wet. The surface is intermediate wet when the effective contact angle ranges from 75° to 105°, and oil-wet for contact angles between 105° and 180°. Intermediate wet conditions can be subdivided into weakly water wet (75° to 84°); neutral wet (84° to 96°), and weakly oil wet (96° to 105°) (Treiber & Owens, 1972).

The goal of this research is to determine if and how SiO_2 nanofluids can alter the wettability from weakly water wet to strongly water wet. A successful alteration on the wetting character mimicking Hebron conditions was shown in Sivira et al. (2016), where soaking Berea sandstone in nanofluid reached a maximum alteration from 51.4° ± 1.0 to 31.4° ± 0.9, and in the case of Bandera sandstone, from 76.7° ± 1.5 to 34.1° ± 0.4. These measurements were taken under Hebron temperature and pressure (62 °C and 19.00 MPa).

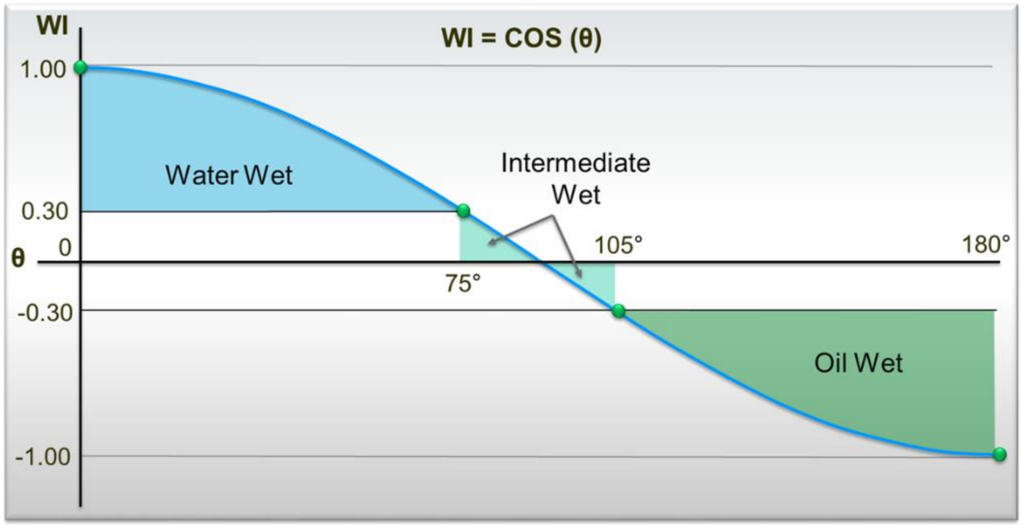

Figure 3.8 *Visual Representation of the Relationship Between Contact Angle and Wettability Index*

(Treiber & Owens, 1972)

Extensive contact angle experiments were conducted in this research to optimize the potential alteration of the wetting character of the rock surface. First, the contact angles of Berea core plugs aged in seawater and HCl solutions were measured. These results shown in Figure 3.9 reveal a clear increment in the contact angle as a function of time. The contact angle goes up from 51.4° ± 1.0 to 73.9° ± 0.9 for Berea core aged in 0.002 mol/L after 3 days. Similarly, the contact angle for Berea rock aged in 0.006 mol/L HCl in seawater goes up from 51.4° ± 1.0 to 72.4° ± 0.8 after 3 days. Berea rock aged in 0.010 mol/L HCl also goes up from 51.4° ± 1.0 to 71.5° ± 1.2 after 3 days. The average maximum increment due to 0.002, 0.006 and 0.010 mol/L HCl is 21.2°. The contact angle increment may be due to pH reduction with increasing HCl concentration. Seawater has a pH of 7.84, but with addition of HCl, the pH decreases to 2.64, 2.40 and 2.12 (0.002, 0.006, and 0.010 mol/L HCl, respectively). These results are consistent with previous research such as Nasralla & Nasr-el-din (2014) and Buckley, et al. (1996). They reported that the contact angle increases as the pH decreases. The contact angle measurements across 3 different HCl concentrations are similar through 0 hour and 3 days in this research. This is because there is only a slight difference in the HCl concentrations, resulting in only a small variation in the pH.

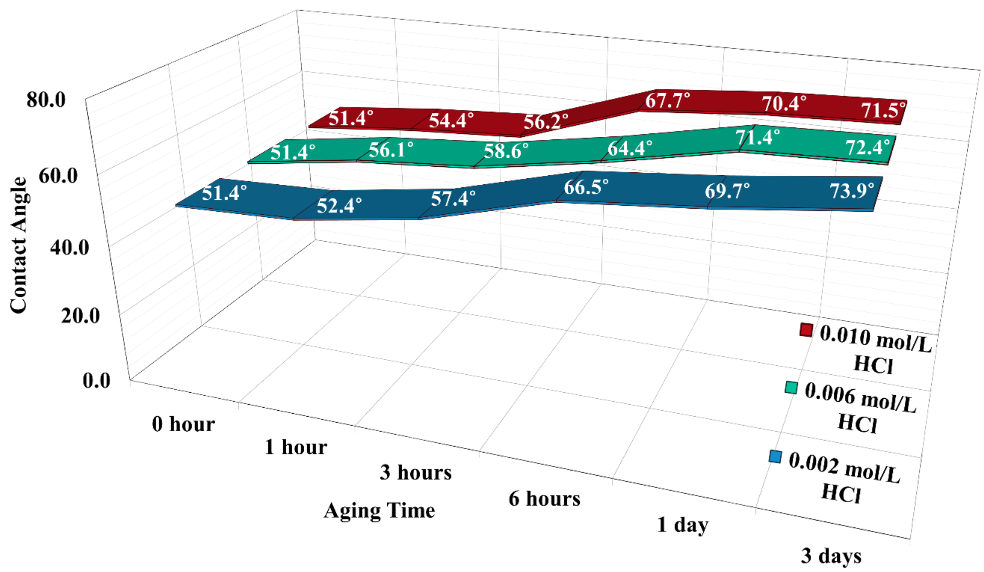

Figure 3.9 *Contact Angles of Oil and Seawater + HCl on Berea as a Function of Aging Time*

The contact angles of the Berea core plugs aged in nanofluid were then measured. The contact angle experiments on Berea sandstone aged in 0.01 wt% SiO_2 nanofluid (with 0.002 mol/L HCl) has two clear trends – one before and another after six hours of aging. The contact angle decreases from 51.4° ± 1.0 (core aged in oil) to 31.0° ± 0.5 after six hours of aging; however, the contact angle increases from 31.0° ± 0.5 (6 hours) to 41.2° ± 0.2 (after 3 days). Similar tendencies in contact angle results are observed when Berea cores were aged in 0.03 wt% SiO_2 nanofluid (with 0.006 mol/L HCl) and 0.05 wt% SiO_2 nanofluid (with 0.010 mol/L HCl). The maximum reduction on the contact angle from aging Berea sandstone in 0.03 wt% SiO_2 was observed after six hours of aging, reaching 30.6° ± 1.0 from 51.4° ± 1.0. Then, the contact angle starts increasing until 34.0° ± 1.0, which occurs on the third day of aging. The contact angle of the Berea sample aged in 0.05 wt% SiO_2 nanofluid changes from 51.4° ± 1.0 to 30.2° ± 0.8 with a maximum reduction of 21.2° after six hours of aging. The contact angle increases after this time with the contact angle measured at 43.4° ± 0.6 after 3 days (Figure 3.10). The analysis proves that SiO_2 nanoparticles successfully reduce the contact angle of oil – nanofluid – Berea rock making the wetting character more water wet regardless of the HCl contribution on the contact angle.

Bandera plugs were also aged in seawater containing HCl in concentrations of 0.002, 0.006 and 0.010 mol/L. The contact angle was measured before and after aging for comparison. Figure 3.11 shows that the contact angle increases from initial conditions as time passes, as it did for Berea. The greatest contact angles are 102.0° ± 1.3, 99.7° ± 1.2 and 97.8° ± 1.0, when Bandera rocks are aged in 0.002, 0.006 and 0.010 mol/L HCl respectively for 3 days. The average of total contact angle increment is 23.1° from the initial contact angle measured (76.7° ± 1.5).

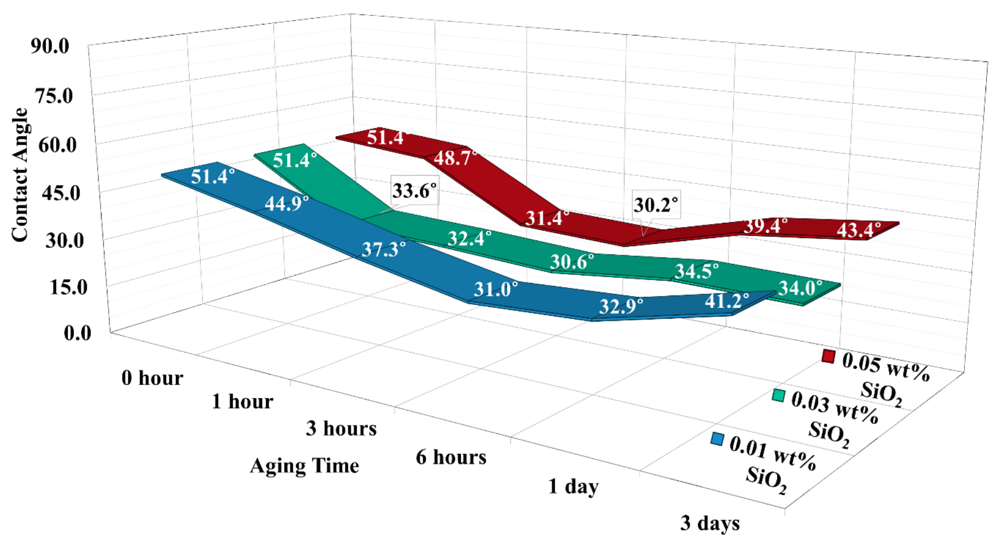

Figure 3.10 *Contact Angles of Oil and SiO_2 Nanofluids on Berea as a Function of Aging Time*

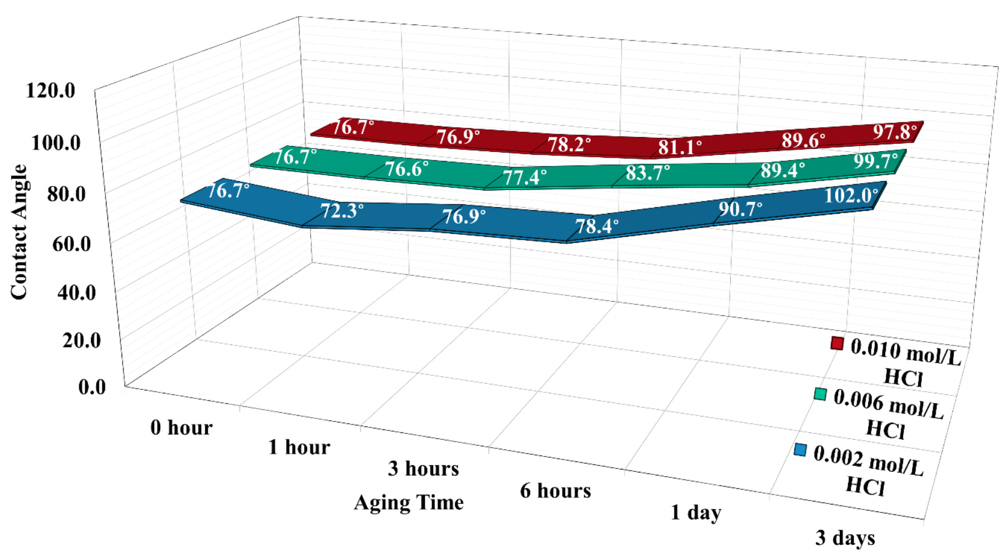

Figure 3.11 *Contact Angles of Oil and Seawater + HCl on Bandera as a Function of Aging Time*

The contact angle experiments on Bandera sandstones aged in nanofluid also show the greatest decrease in contact angles after six hours of aging, reaching similar contact angles (average 30.4° ± 0.6°) irrespective of the nanofluid concentration in which the samples were aged. Bandera samples after aging in oil have an initial contact angle equal to 76.7° ± 1.5. This angle reduces depending on the time and the nanofluid concentration in which the Bandera core plug is aged. The contact angle experiments performed with Bandera sandstone aged in 0.01 wt% SiO_2 nanofluid showed a maximum reduction of 46.2° (from 76.7° ± 1.5 to 30.5° ± 0.9). This reduction was obtained after six hours of aging; however, the contact angle tends to increase after this time up to the last measurement at the third day, as shown in Figure 3.12. Bandera sample aged in 0.03 wt% SiO_2 nanofluid show an alteration from 76.7° ± 1.5 to the lowest contact angle measurement of 31.0° ± 0.7 (at 6 hours of aging), which then increases to 37.2° ± 1.0 (on day 3). The experiment conducted with 0.05 wt% SiO_2 nanofluid generated the lowest contact angle of 29.6° (maximum reduction of 47.1° at 6 hours) increasing again to a maximum of 38.7° ± 0.9 after 3 days. Despite the increment in the contact angle as a consequence of the HCl, SiO_2 nanofluids are found to have the ability to reduce the contact angle making the wetting character of Bandera rock strongly water wet.

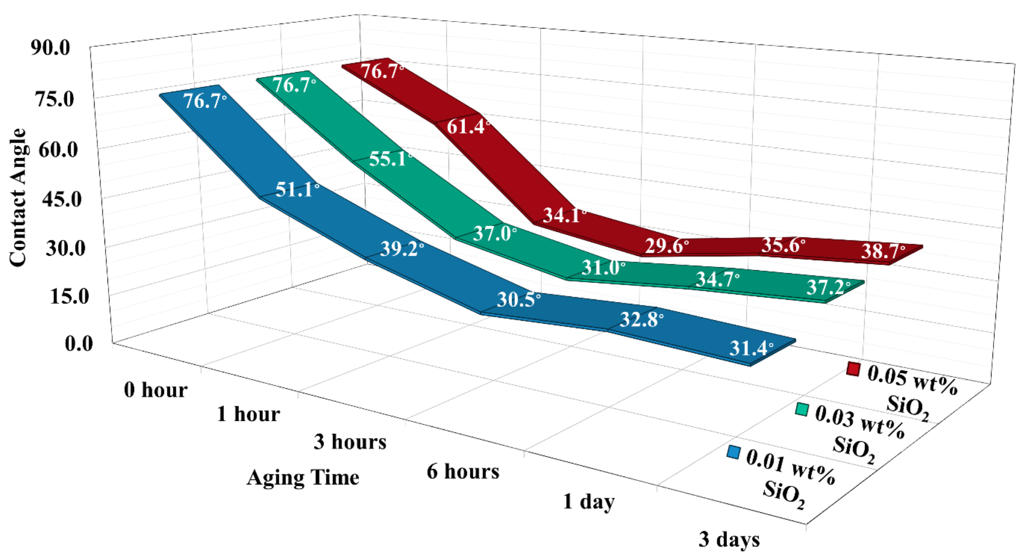

Figure 3.12 *Contact Angles of Oil and SiO_2 Nanofluids on Bandera as a Function of Aging Time*

In general, the maximum decrease in contact angle occurs at six hours of aging, and all of the experiments on Berea and Bandera sandstone reached a similar contact angle of around 30°, regardless of the nanofluid concentration, after 6 hours. Bandera seems to be more sensitive to wettability alteration via SiO_2 nanoparticles compared to Berea because the maximum degree of reductions on Bandera is approximately 45° while on Berea is approximately 20°. The differences in the contact angle reduction are possibly due to different mineralogical compositions of two rocks. It was also observed after six hours of aging, the contact angles in both type of rocks start increasing again. Despite the increment in contact angle because of the HCl, SiO_2 nanoparticles are able to reduce the contact angle making both rocks (Berea and Bandera) strongly water wet.

SEM-MLA analysis revealed that the mineralogical compositions of Berea and Bandera sandstones vary from initial conditions (before any treatment) to after six hours of aging nanofluid across concentrations of 0.01, 0.03 and 0.05 wt%. The major mineralogical variations are in quartz, clay and carbonate content, as shown in Figure 3.13, Figure 3.14, and Figure 3.15, respectively. In all samples, the quartz content increases while the clay minerals and carbonate decrease after the nanofluid aging. The MLA instrument cannot distinguish the SiO_2 nanoparticles from the rock quartz content because the chemical formula of quartz is SiO_2 as well. The results showed that as the nanoparticle concentration increases, the quartz content measured by the MLA on the rock surface also increases after the nanofluid aging (Figure 3.13). At this point, we are not certain as to the reason the quartz contents increase after aging. It could be because of either or a combination of the following reasons: 1) the adsorption of nanoparticles on the rock surface; 2) residual nanofluid on the rock surface at the moment of the analysis, since the MLA analysis was performed at low vacuum when the samples are still wet; and/or 3) dissolution of the clay/carbonate thereby exposing more quartz. If the adsorption of the nanoparticle successfully occurs and this is detected by the MLA, the nanoparticles must have attached to a quartz mineral making this quartz mineral bigger in surface area because SiO_2 nanoparticles by itself cannot be detected by the MLA since its level of detection is 500 nm. The clay minerals in Berea and Bandera decrease after aging regardless of the nanofluid concentration (Figure 3.14). The carbonate content is also reduced after nanofluid aging. This is attributed to hydrochloric acid, used as a stabilizer in the preparation of the stable nanofluid, which dissolves carbonate content in both rocks (Figure 3.15). The reduction of carbonate content is higher in Bandera than Berea because of the higher carbonate content in Bandera at initial condition. In the discussion to be followed, we confirm this by comparing the fluids' composition results from ICP-OES before and after aging.

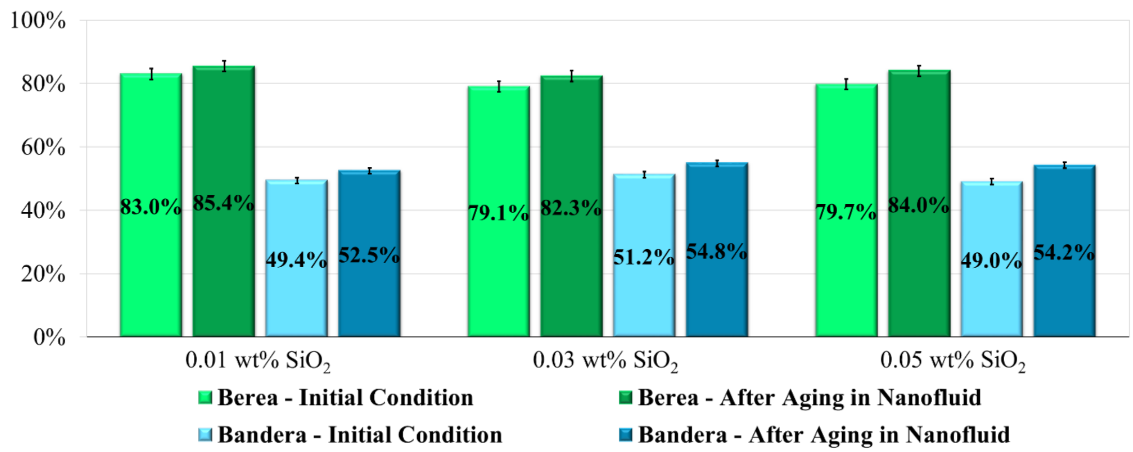

Figure 3.13 *Quartz Content in Berea and Bandera Before and After Aging in SiO_2 Nanofluid for 6 Hours*

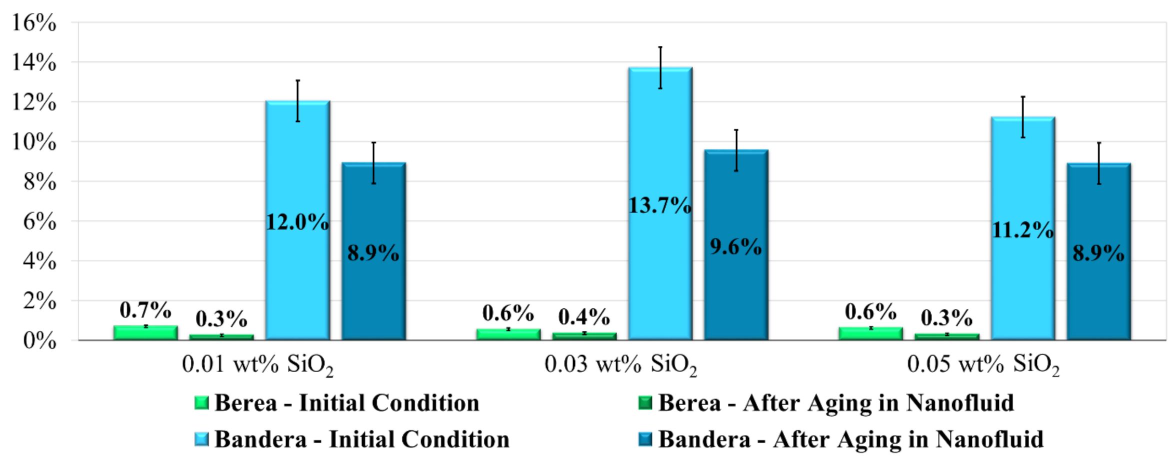

Figure 3.14 *Clay Content in Berea and Bandera Before and After Aging in SiO_2 Nanofluid for 6 Hours*

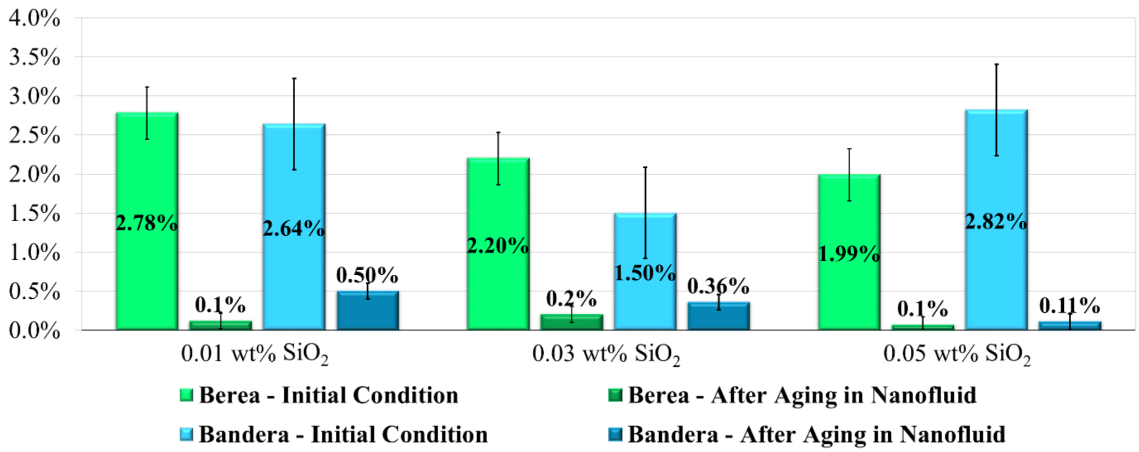

Figure 3.15 *Carbonate Content in Berea and Bandera Before and After Aging in SiO_2 Nanofluid for 6 Hours*

As the results obtained in the MLA are not conclusive for nanoparticle absorption, high definition images were taken by a scanning electron microscopy. Figure 3.16 shows one of the comparative images of Berea sandstone before and after aged in 0.05 wt% SiO_2 nanofluid. Unfortunately, there was no evidence of SiO_2 nanoparticles on the rock surface after nanofluid treatment in the sections analyzed. However, this does not necessarily mean that nanoparticles are not being adsorbed on the rock surface because the images analyzed before and after treatment at a nanoscale represent less than 1% of the core slice area. The core plug area in nanometer is equal to 5.07 x 1014 nm^2 (506.71 mm^2) and the image area just cover 2.19 x 104 nm^2. Had more areas were analyzed, adsorption of nanoparticles might have been visible, as MLA results suggest. From these images, the disappearance of the clay minerals, however, is noticeable after aging core slices in the nanofluid. The absence of carbonate cement after the aging in nanofluid is also visible.

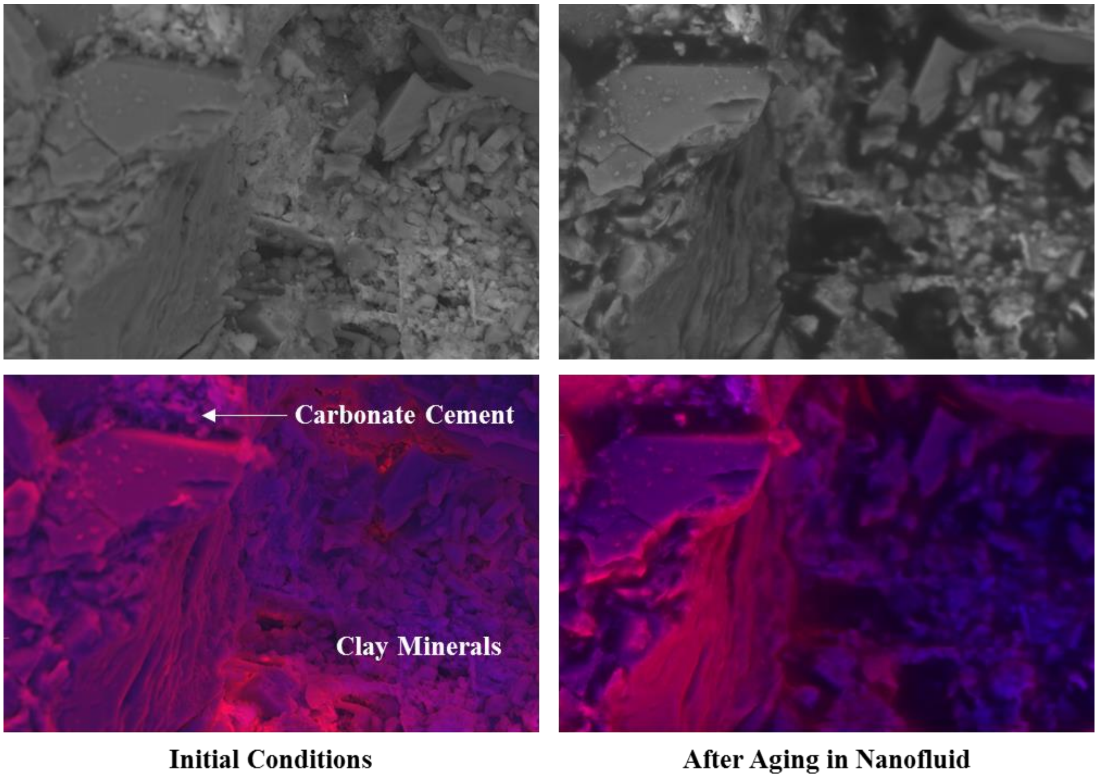

Figure 3.16 *SEM Images of Berea at Initial Conditions (Left), and the Same Sample After Aged in 0.05 wt% SiO_2 Nanofluid (Right) (Analyses were Completed by SEM-MLA)*

Finally, to analyze the nanofluid composition before and after the aging process, an ICP-OES was conducted. The decrease in Si concentration in the nanofluid would prove that nanoparticles are adsorbed on the rock surface. However, the ICP-OES equipment has some limitations regarding Si detection and nanoparticle measurements. Silicon is a tricky element to measure, because it can come from borosilicate glasses, which is what the laboratory glassware is made of. In addition, OES detector has challenges of distinguishing the background signal from the signal generated from a small particle (i.e. nanoparticles). The Si content measured by this equipment on the initial solution 0.01, 0.03, and 0.05 wt% SiO_2 nanofluid was 13.6, 116.1, and 250.2 ppm respectively. These results do not clearly show expected concentrations of 100, 300 and 500 ppm. We can infer that the ICP-OES results are not reliable for Si content from nanoparticles because of the limitation on the equipment generating signals for nano sized particles. ICP-OES tests were conducted on the seawater with 0.002, 0.006, and 0.010 mol/L HCl before and after aging Berea and

Bandera rocks to measure a possible dissolution of a mineral containing silicon due to HCl, increasing the silicon content in solution. The results of these tests show that the silicon content was too low to be measured in initial solution as well as solution after aging, demonstrating that there is no additional silicon content by the dissolution of minerals in Berea or Bandera rocks.

Despite the challenges of measuring silicon nanoparticle content, the ICP-OES analysis show reliable result on calcium and magnesium content. Increased calcium and magnesium content in the solution indicate the dissolution of carbonate minerals, and the ICP-OES result for these elements are consistent with MLA results. Figure 3.17 and Figure 3.18 show increased calcium and magnesium in solutions after aging as HCl concentration increase (and pH decreases) due to greater degree of carbonate dissolution. A higher calcium and magnesium content is observed in the solution in which Bandera was aged rather than in the solution after aging Berea, since there is higher carbonate content in Bandera rocks.

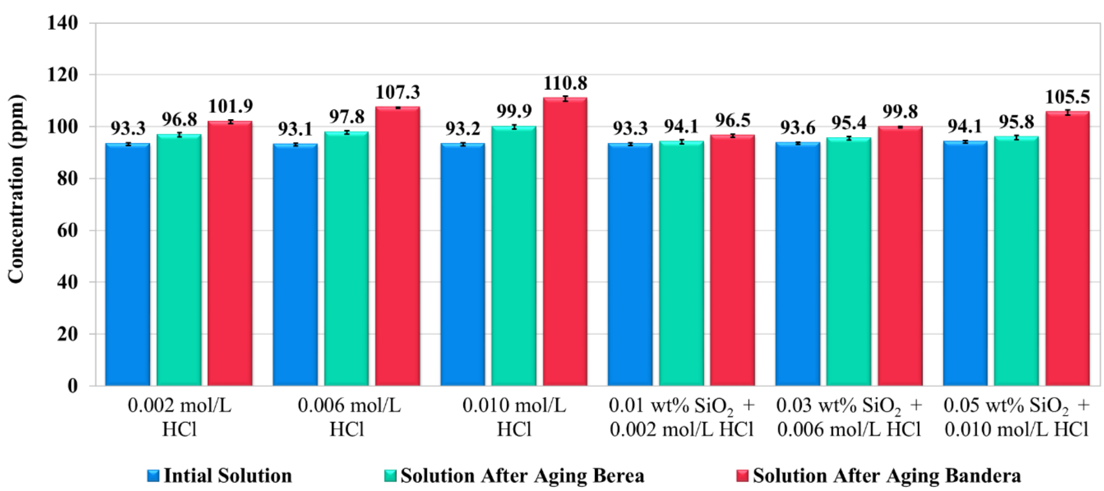

Figure 3.17 *Calcium Concentration in the Six Different Solutions Before and After Aging Berea and Bandera Analyzed by ICP-OES*

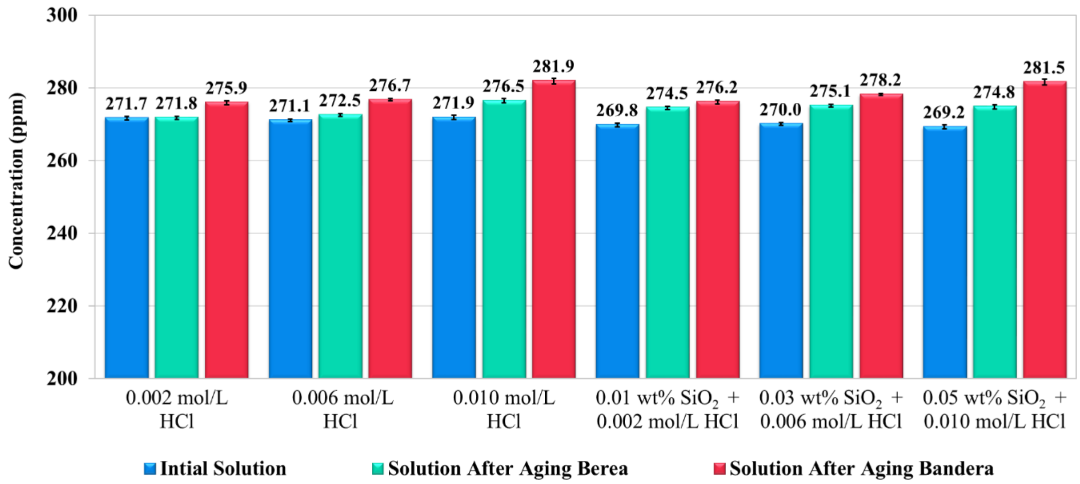

Figure 3.18 *Magnesium Concentration in the Six Different Solutions Before and After Aging Berea and Bandera Analyzed by ICP-OES*

3.5 Conclusions

The conclusions of this research on the wettability alteration of are listed as follows:

1. Stable SiO_2 nanofluid is able to alter the wetting character of the Berea and Bandera rock surface at Hebron field conditions (62°C and 19.00 MPa).

2. HCl (used to stabilize the SiO_2 nanoparticles in seawater) has the ability to increase the contact angle of Berea and Bandera rocks, making them less water wet. The maximum average increase in contact angle was 21.2° in Berea and 23.1° in Bandera after three days of aging in a solution of seawater and HCl.

3. However, when the same HCl concentrations were used with SiO_2 nanoparticles, the rock surfaces become more water wet:

    a. The contact angle reduced from 51.4° to a minimum average contact angle of 30.6° on Berea rock after six hours of aging regardless of nanofluid concentration.

b. The contact angle reduced from 76.7° to a minimum average contact angle of 30.4° on Bandera rock after six hours of aging irrespective of nanofluid concentration, showing a greater reduction in contact angle. The change from weakly to strongly water wet conditions should impact oil recovery.

4. MLA tests before and after aging the rock in nanofluid confirm an increase in the quartz content of the rock possibly due to the adsorption of SiO_2 nanoparticles on the rock surface, residual SiO_2 nanofluid on the rock surface at the moment of the analysis, and/or exposing more quartz surface by dissolving carbonate with HCl and reducing the clay minerals.

5. SEM analysis compliments the dissolution of carbonate and the reduction of clay minerals, but there is no evidence of SiO_2 nanoparticle on the on the rock surface analysed. However, this does not mean that the nanoparticles are not being adsorbed on the rock surface because the images analyzed before and after treatment at a nanoscale represent less than 1% of the core slice area.

6. ICP-OES experiment results confirms the dissolution of carbonate minerals on Berea and Bandera because an increment on the calcium and magnesium content. Unfortunately, the adsorption of nanoparticle on the rock surface can not be verified because of the equipment limitation on nanoparticles measurements.

3.6 Acknowledgements

The authors would like to thank Hibernia Management and Development Company (HMDC), Chevron Canada, the Research and Development Corporation of Newfoundland and Labrador (RDC), the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Hibernia EOR Research Group for technical and financial support.

3.7 References

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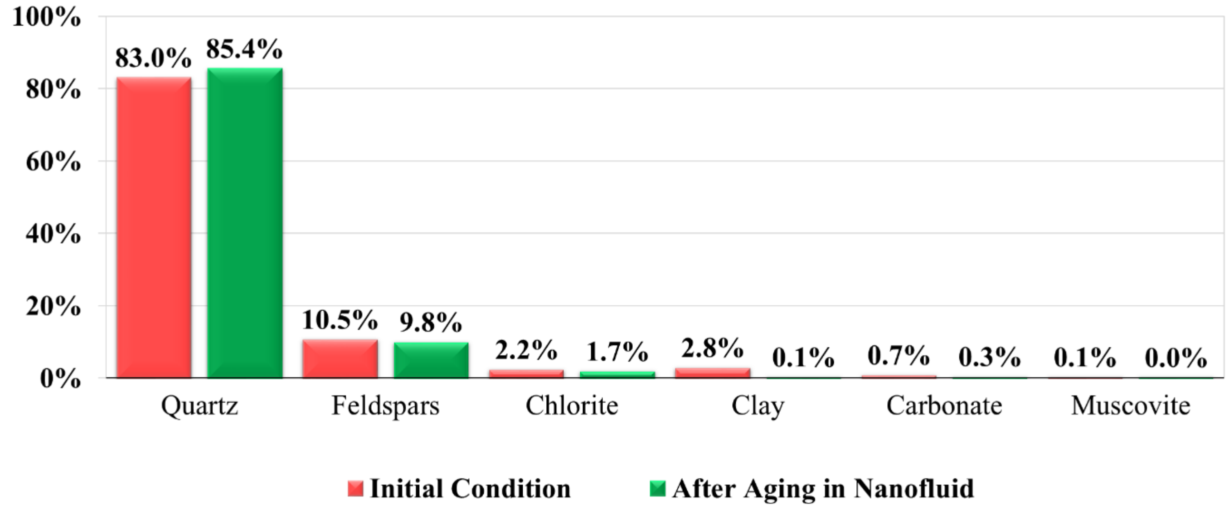
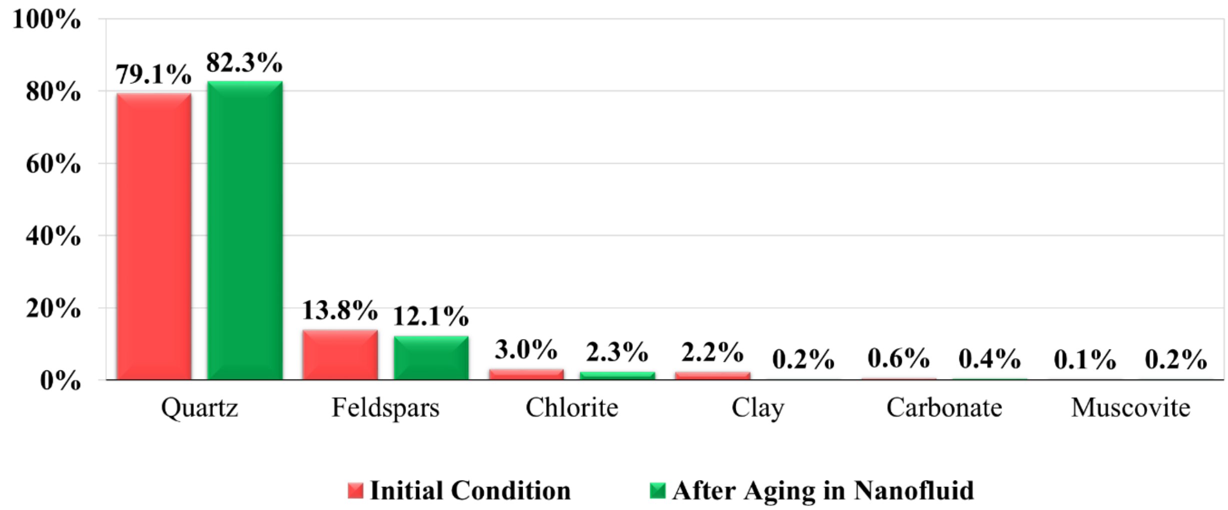
3.8 Appendices

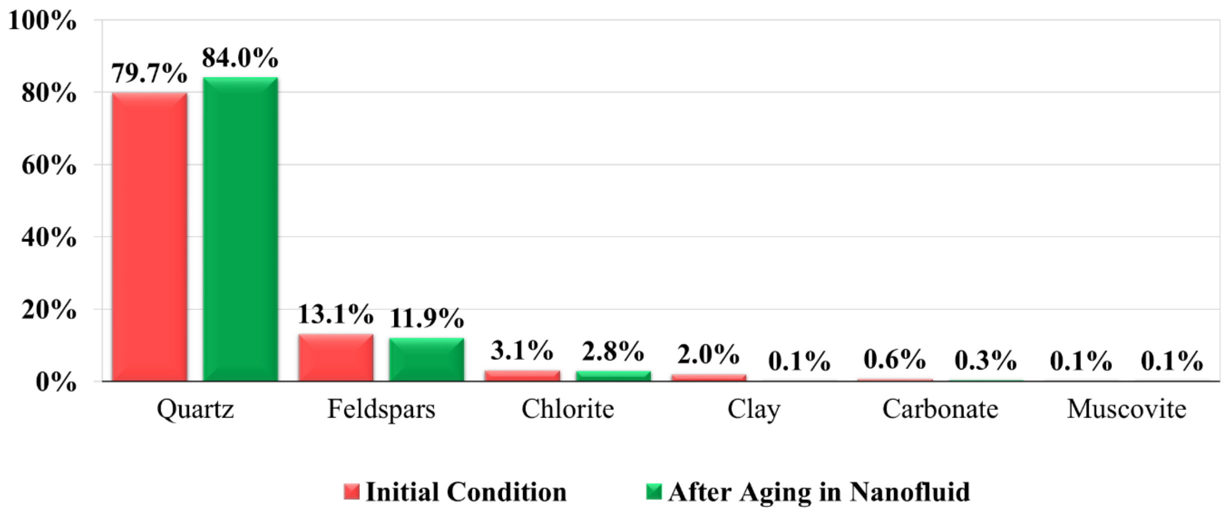
Appendix 3.A Mineralogy of Berea Before and After Aging in 0.01 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



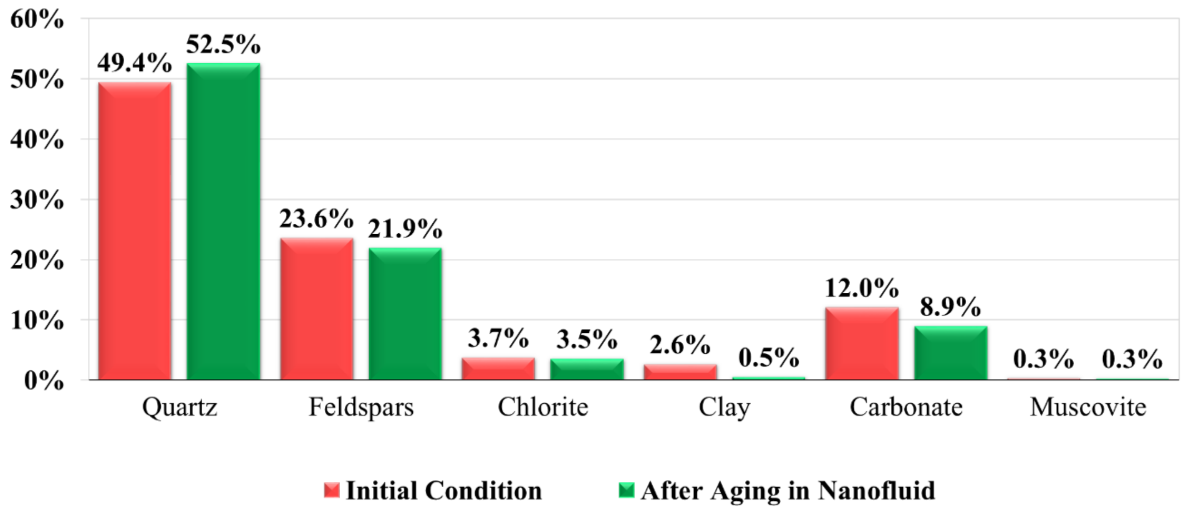
Appendix 3.B Mineralogy of Berea Before and After Aging in 0.03 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



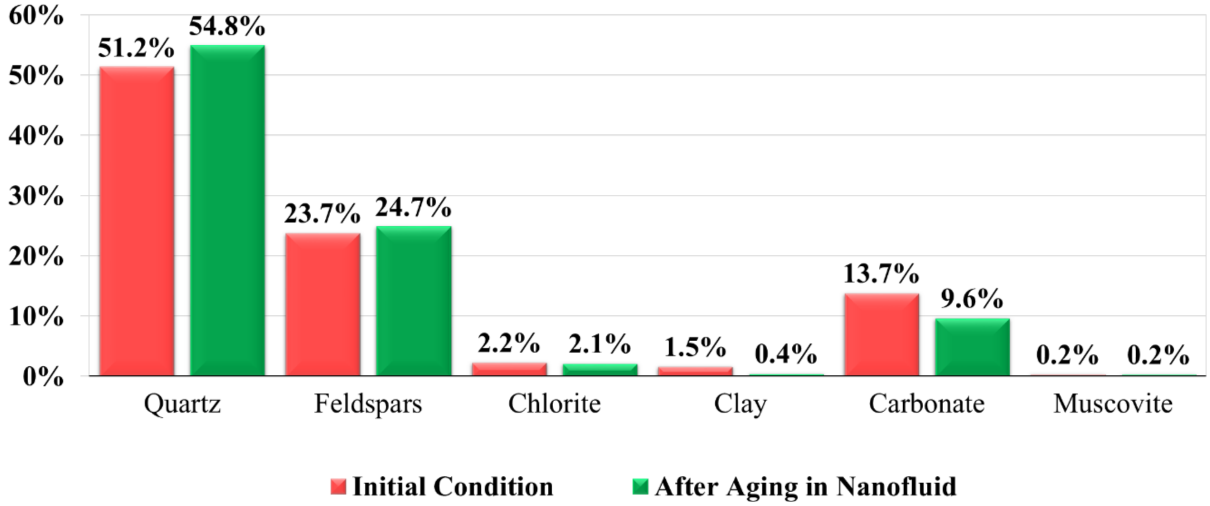
Appendix 3.C Mineralogy of Berea Before and After Aging in 0.05 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



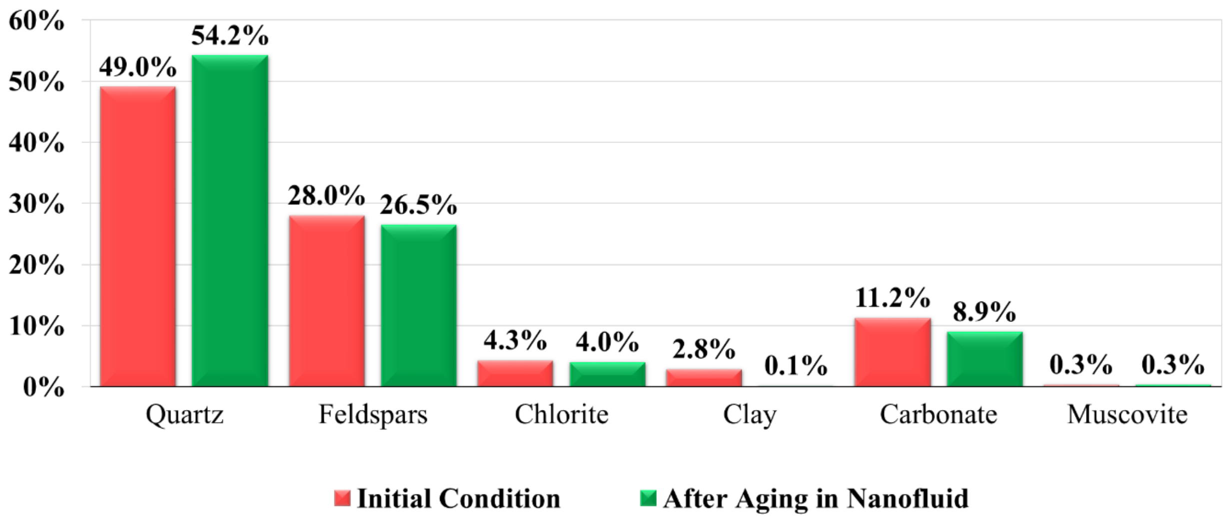
Appendix 3.D Mineralogy of Bandera Before and After Aging in 0.01 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



Appendix 3.E Mineralogy of Bandera Before and After Aging in 0.03 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



Appendix 3.F Mineralogy of Bandera Before and After Aging in 0.05 wt% SiO_2 Nanofluid for 6 Hours, Analyzed by SEM-MLA



CHAPTER IV – OPTIMIZATION OF SILICON DIOXIDE NANOPARTICLE (SIO_2) AS A WETTABILITY MODIFIER FOR ENHANCED OIL RECOVERY IN HEBRON FIELD, OFFSHORE EASTERN CANADA

D. J. Sivira, H. Kim, L.A. James, D. Wilton, Y. Zhang and E. Sripal

Memorial University of Newfoundland, St. John's, Newfoundland and Labrador, Canada.

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4.1 Abstract

The Hebron field is located approximately 350 km offshore eastern Canada with an estimated reserve of 2620 million barrels of oil. It is the 4th major Canadian offshore development with first oil expected in 2017. The Ben Nevis Formation contains approximately 80% of the total crude oil of the Hebron field. Geologically, the Ben Nevis Formation is composed of two main facies. The lower section is represented by medium to fine grain sandstone with elevated quartz content. The upper section contains increased carbonate contents (up to approximately 20%), and decreased permeability. Enhanced oil recovery (EOR) screening for the Hebron field is a major research project for the Hibernia EOR research group. One possible EOR method under investigation is nanoparticle EOR using silicon dioxide (SiO_2) nanoparticle enhanced water to potentially increase oil recovery. Nanoparticles, being surface active agents, can reduce the interfacial tension between oil and water and may also alter the wettability of the reservoir.

The goal of this research is to evaluate the ability of silicon dioxide (SiO_2) nanoparticles to modify the wettability of predominately quartz rich sandstones, as well as sandstones with increasing calcium carbonate contents such as the Ben Nevis Formation. The experiments

were conducted using Berea and Bandera standard cores to mimic the mineralogy of the Ben Nevis Formation lower and upper facies, respectively. Water imbibition followed by oil drainage were carried out according to standard procedures in centrifugal core holders with overburden pressure. The cores were first aged to restore the wettability to reservoir conditions. Then, the core plugs were aged in a stable brine suspension of silicon dioxide (SiO_2) nanoparticles for different periods of time. Finally, the wettability of the core plugs was measured at reservoir conditions (62°C and 19.00 MPa). The results indicated that silicon dioxide (SiO_2) nanoparticles are an effective wettability modifier as they altered the wettability of the rock, reducing the contact angle making the rock surface more water wet. Additionally, the contact angles decreased the most within the first hour of aging in silicon dioxide (SiO_2) nanofluid, and after that time, the contact angles oscillate in the range of 10° with no sign of a tendency to go back to their initial contact angle. The higher the SiO_2 nanoparticle concentration in suspension, the greater the alteration in the contact angle.

4.2 Introduction

The Hebron asset is the fourth major development offshore Newfoundland and Labrador, Canada with first oil expected in 2017. This asset is in the Jeanne d'Arc basin, which is located 340 km offshore Newfoundland and Labrador. The Hebron field is surrounded by three other major offshore fields, Hibernia, Terra Nova, and White Rose, as shown in Figure 4.1.

The Hebron asset is composed of three discovered fields (Hebron, West Ben Nevis, and Ben Nevis); four reservoirs (Ben Nevis Formation, Avalon Formation, Hibernia Formation, and Jeanne d'Arc Formation); and five pools, as shown in Figure 4.2. The best estimation of oil in place is 2620 MMBO, however, just 30 % of the oil is considered recoverable. Additionally, the Pool 1, which is in the Hebron field, Ben Nevis reservoir, represents 70 % of the total oil in place (CNLOPB, 2011). This research is focused on the Pool 1 due to its significance. The reservoir pressure and temperature are 19.0 MPa and 62 °C respectively, and the oil is medium crude with 17 – 24 °API. Ben Nevis Formation is composed predominantly of laminated and bioturbated medium to fine grained, sandstones with high quartz contents. The reservoir quality decreases upwards with increasing carbonate content (Valencia et al., 2017). The wettability of Ben Nevis Formation was tested to be weakly water-wet (CNLOPB, 2011).

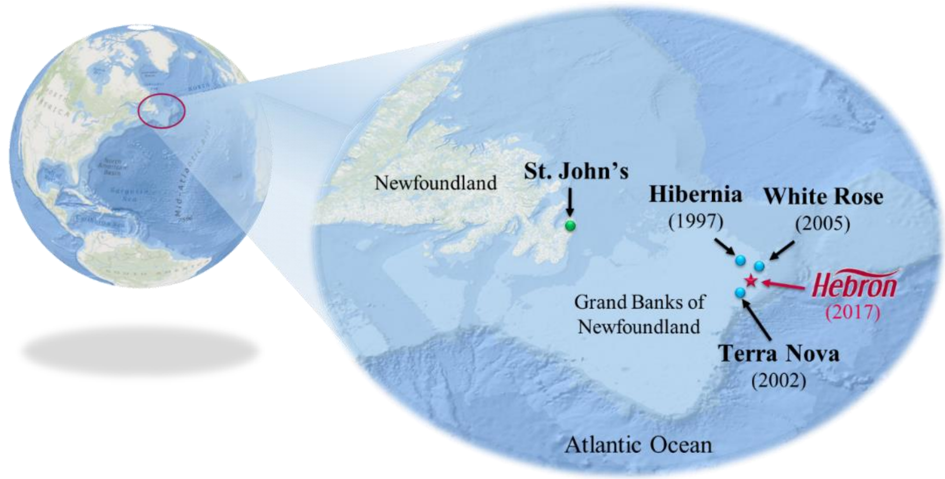

Figure 4.1 *Hebron Project Area Location*

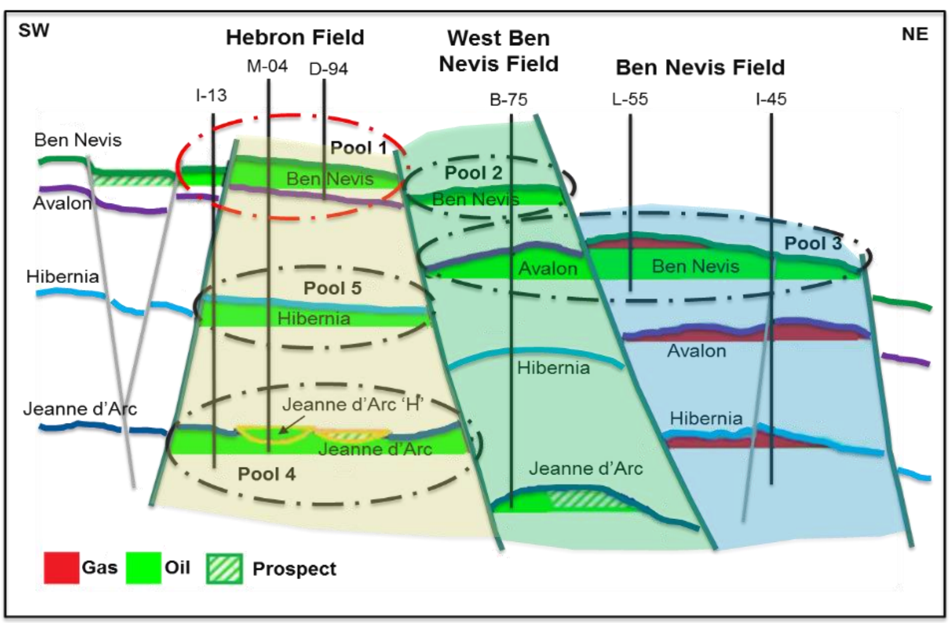

Figure 4.2 *Schematic Cross-Section Across the Hebron Project Area (after CNLOPB, 2011)*

The wetting character of the rock defines the preference of the rock to be in contact with a fluid over another in a three-face system (rock-oil-seawater), and it is a crucial parameter for increasing the oil recovery. According to Morrow (1990), strongly water wet reservoirs have higher oil recovery. The wettability of rock is expressed as either the wettability index (WI) or contact angle. The wettability index is equal to the cosine of the contact angle sharing a linear relationship. The wetting character of the rock can be water wet; intermediate wet; or oil wet. In water wet, the contact angle ranges between 0° and 75°, as shown in Figure 4.3. When the contact angle is between 75° and 105°, the wettability referred to as intermediate wet, and the intermediate wet condition is subdivided into weakly water wet (75° to 84°); neutral wet (84° to 96°), and weakly oil wet (96° to 105°). Finally, when the contact angle is higher than 105° up to 180°, it indicates oil wet condition.

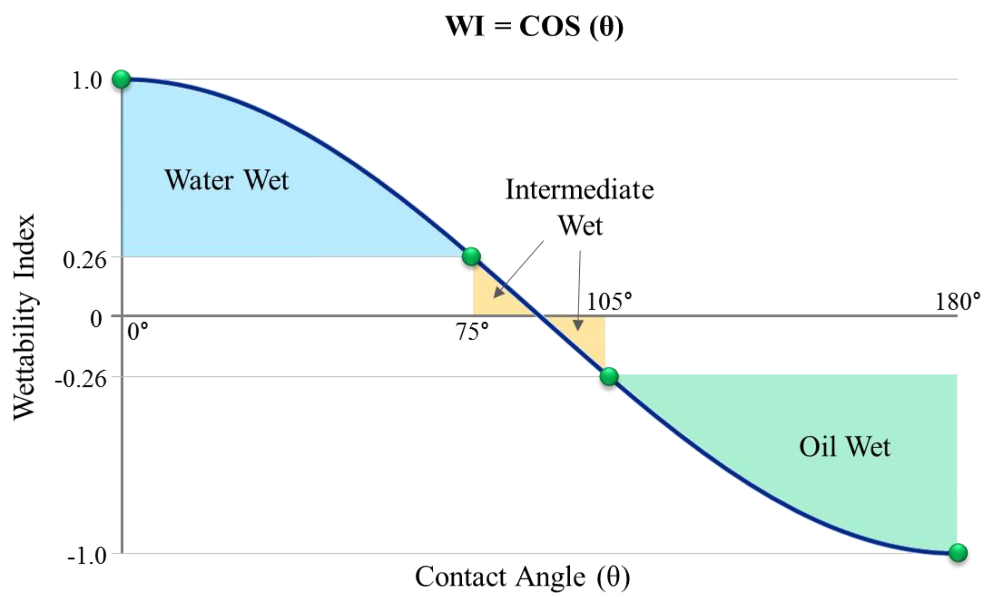

Figure 4.3 *Relationship Between the Contact Angle and Wettability Index (Treiber & Owens, 1972)*

Numerous enhanced oil recovery (EOR) methods aim to alter the wetting characteristics of the rock surface. Considering the remote, harsh location of the Hebron field, and its reservoir properties, silicon dioxide nanoparticle injections has a potential to be the most viable methods. A few advantages of this method over other EOR methods include low cost, ease of nanoparticle transportation, minimal facility requirements, and minimal environmental concerns.

Previous research studies have proven that silicon dioxide (SiO_2) nanoparticles reduce the interfacial tension, and the contact angle, making the wetting character of the rock surface more water wet. Although many of these researches Al-Anssari, et al., 2015; Aurand, 2017; Aurand, et al., 2014; Hendraningrat, et al., 2013; Hendraningrat & Torsæter, 2014; Li, et al., 2013; Li & Torsæter, 2015; and Youssif, et al., 2017 published positive results at laboratory scale measuring the wettability alteration, most of them were conducted in unrealistic conditions, using sodium chloride (NaCl) or synthetic brine as a nanoparticle dispersant in their experiments and/or conducting the experiments at ambient conditions. Hence, there was a need for studies to close the gaps between the laboratory experiments and field conditions using SiO_2 nanoparticle as water additive for EOR. Studies by Kim et al. (2017), Sivira et al. (2016), and Sivira et al. (2017) have recently shown promising results from experiments that mimic field conditions (i.e. using seawater as a nanoparticle dispersant, and real reservoir temperature and pressure). Those researches proved that SiO_2 nanofluid injection at field conditions can reduce interfacial tension, alter the wetting character of the rock, and alter the mineralogical composition of the rock to produce an additional oil recovery.

Nanoparticles succeed in altering the wettability of the rock surface due to disjoining pressure (Chengara, et al., 2004; Wasan, et al., 2011; and Wasan & Nikolov, 2003). The disjoining pressure theory suggests that nanoparticles dispersed in a solution will arrange themselves into geometrical structures at the wedge film between an oil drop and the rock surface. Then the nanoparticles apply an additional pressure or force (disjoining pressure), pushing themselves forward into a confined region until the nanofluid spreads on the rock surface, and detaching the oil drop, as shown in Figure 4.4.

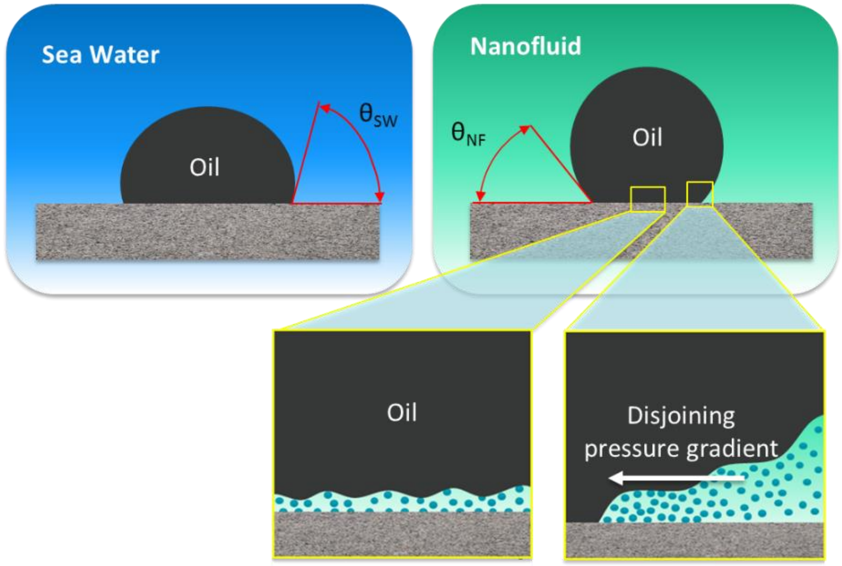

Figure 4.4 *Contact Angle in a Three-Phase System Decrease from Seawater-Oil-Rock to Nanofluid-Oil-Rock ($\theta_{SW} > \theta_{NF}$) Due to Disjoining Pressure Gradient at the Wedge-Film (after Wasan et al., 2011)*

The uses of silicon dioxide nanoparticles as a water additive in enhanced oil recovery methods is an innovative technique that can modify wettability. The research preceding this study (Sivira et al., 2016; and Sivira et al., 2017) saturated cores with oil and aged them for over two weeks under temperature. When the contact angle was measured before and after the treatments with nanofluid, changes in wetting character of the rock surface were observed. The research presented in this paper attempts to improve upon these two previous research reports. The core samples were treated to restore true wettability of the Hebron Field applying the method suggested by Sripal & James (2016). The cores were then aged in nanofluid to observe whether the nanofluid altered the wetting character of the rock. The aim is to even further reduce the gap between field and lab conditions, mimicking as much variables as possible present in the Hebron field.

4.3 Experimental Methodology

The goals of this research are to evaluate the ability of the silicon dioxide (SiO_2) nanoparticles to modify the wettability of the rock surface, and to analyze the effect of this method on the mineralogical composition of the rock. To achieve these goals, two main experiments were conducted: contact angle measurements and mineral liberation analyser (MLA) analysis. The contact angle determines the variations of the wetting character, and the MLA quantifies the mineralogical content of the rock surface. These two experiments were conducted before and after aging the samples in nanofluid.

Another focus of this research was to mimic Hebron field challenges; therefore, the materials were carefully selected. The most important characteristic of the Hebron field is its reservoir formation. The Ben Nevis Formation is divided in two facies based on its mineralogical composition, one facie predominately comprises quartz rich sandstones (lower section of Ben Nevis Formation), and another sandstone with a higher carbonate content (upper section of Ben Nevis Formation). These two facies were analysed in the MLA laboratory, as well as available standard cores. Then, the standard cores that best matched the mineralogical composition of the Ben Nevis Formation were selected, as shown in Figure 4.5 and Figure 4.6. Berea (Berea Sandstone Petroleum Cores) and Bandera (Kocurek Industries Inc.) standard cores were used to represent the lower and upper sections of the Ben Nevis Formation, respectively.

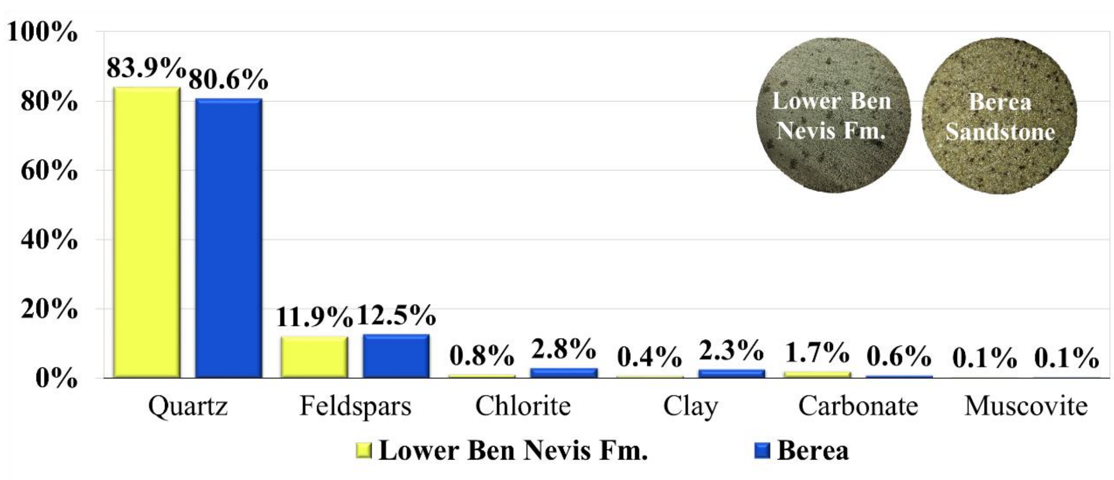

Figure 4.5 *Mineralogical Composition of Lower Ben Nevis Formation and Berea Sandstone, analyzed by MLA*

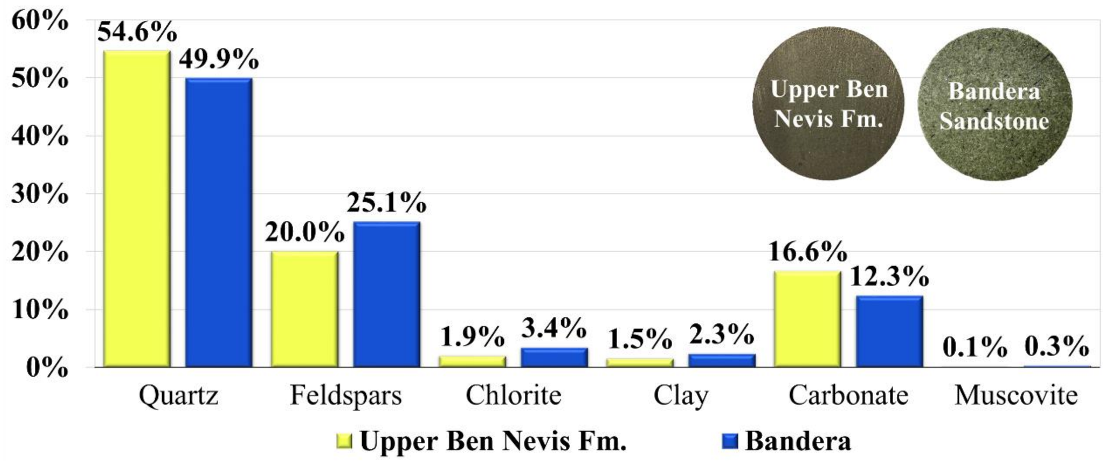

Figure 4.6 *Mineralogical Composition of Upper Ben Nevis Formation and Bandera Sandstone, analyzed by MLA*

The nanofluid is composed of SiO_2 nanoparticle, hydrochloric acid (HCl), and seawater as a dispersant. The hydrophilic silicon dioxide (SiO_2) nanoparticles were ordered from US Research Nanomaterials, Inc. with a particle size ranging from 5 to 35 nm. To guarantee a stable nanofluid, hydrochloric acid (HCl) was used as a stabilizer (Sivira et al., 2016). The dispersant, seawater, was collected from Grand Banks, surrounding the Hebron field. The nanofluids were prepared at three different concentrations: 0.01, 0.03 and 0.05 wt% SiO_2, as shown in Table 4.1. The ratio between the stabilizer (HCl) concentration and SiO_2 nanoparticle concentration for all three nanofluids were kept constant.

Table 4.1 *Composition of the Fluids*

Name	SiO_2 Nanoparticle Concentration (wt%)	Stabilizer: HCl Concentration (mol/L)	Ratio HCl:SiO_2	Dispersant
Nanofluid 1	0.01	0.002	0.2	Grand Banks Seawater
Nanofluid 2	0.03	0.006	0.2	Grand Banks Seawater
Nanofluid 3	0.05	0.010	0.2	Grand Banks Seawater

Experiments were conducted on Berea and Bandera core slices of 38.1 mm in diameter and 3 mm in thickness. The core slices were treated to restore the wettability following the procedure of Sripal & James (2016). After cutting the core slices, they were sonicated for 45 minutes to remove fines grains from the pores. Then, the slices were dried at 100 °C for a 24-hour period. The dried core slices were loaded in a pressure cell as a composite core and then vacuumed to 100 microns. The samples were saturated with formation water, by injecting formation water to the vacuumed pressure cell for a 24-hour period. The saturated core was then loaded in a core holder for centrifuge, and the overburden pressure was set to 20.68 MPa using silicon oil. The core holder was centrifuged with a Vinci Roto Silenta 630RS refrigerated centrifuge to bring the saturated composite core to connate water conditions. Then a drainage test was conducted with oil (from offshore Newfoundland) displacing the formation water. The core holder had a receiving tube attached, which allowed the collection of the displaced fluid. During the drainage test, the receiving tube was filled up with the formation water and a couple of pore volumes of crude oil (excess oil displaced). Centrifugation was completed in eight steps from 500 to 3000 rpm with three hours of equilibration time per rpm step. At this point, the composite core in the core holder is saturated with oil and connate formation water. The overburden pressure of the core holder was reduced to 10.34 MPa to compensate for the pressure build up due to heating the samples to aging temperature. Once the temperature reached 90 °C (the aging temperature), the overburden pressure was stabilized at 20.68 MPa. The composite core was then aged at 90 °C and 20.68 MPa for 4-weeks period (as recommend in the procedure of Sripal & James (2016)), to complete the restoration of wettability.

The Berea and Bandera core slices that had been restored to reservoir wettability were aged in three different nanofluid concentrations (0.01, 0.03, and 0.05 wt% SiO_2) at 62 °C (Hebron reservoir temperature) for different time periods as shown in Figure 4.7. The time periods selected were 1 hour, 3 hours, 6 hours, 1 day, and 3 days.

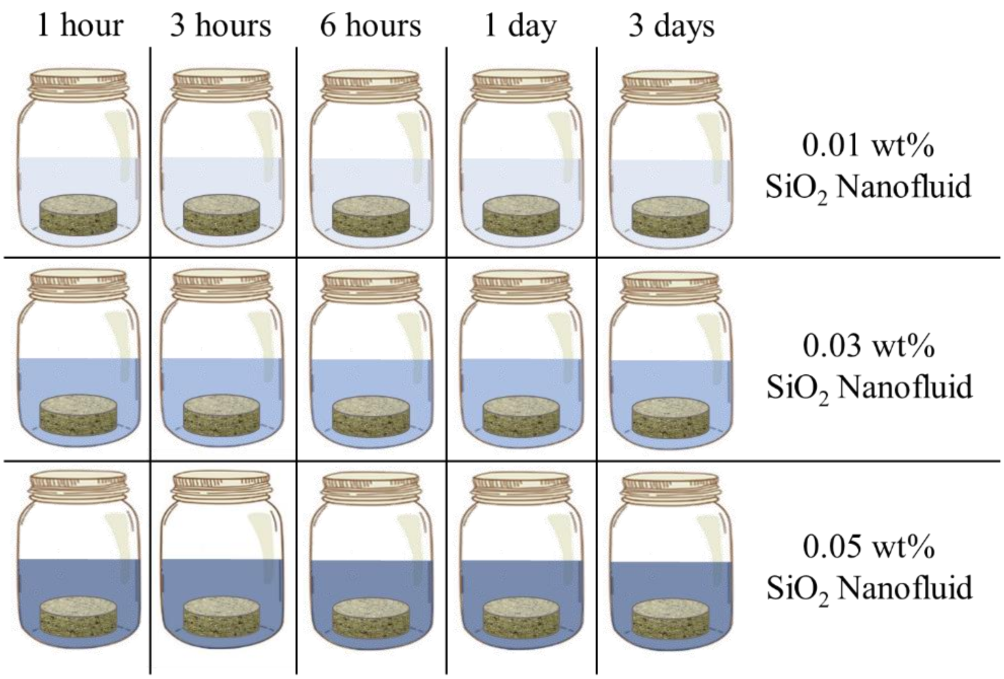

Figure 4.7 *Preparation of Cores for Contact Angle Experiments*

When the nanofluid aging finished, the contact angle was measured by a Vinci Technologies IFT 700 instrument through the drop shape method at 62 °C (Hebron reservoir temperature) and 19.00 MPa (Hebron reservoir pressure). The contact angle was measured every 10 seconds for 15 minutes, and three drops were measured from each sample. The standard deviations of the contact angle measurements within the sample were lower than two degrees for all the samples. To ensure the accuracy of the results, 20% of the measurements were replicated.

Mineral liberation analyzer (MLA) was also conducted using a FEI 650 FEG SEM instrument before and after aging the rock surface in three nanofluid solution at 0.01, 0.03, and 0.05 wt. % SiO_2 for 1 hour under reservoir temperature (62 °C), as shown in Figure 4.8. MLA tests quantify the minerals contents on the rock surface with a level of detection of 500 nm.

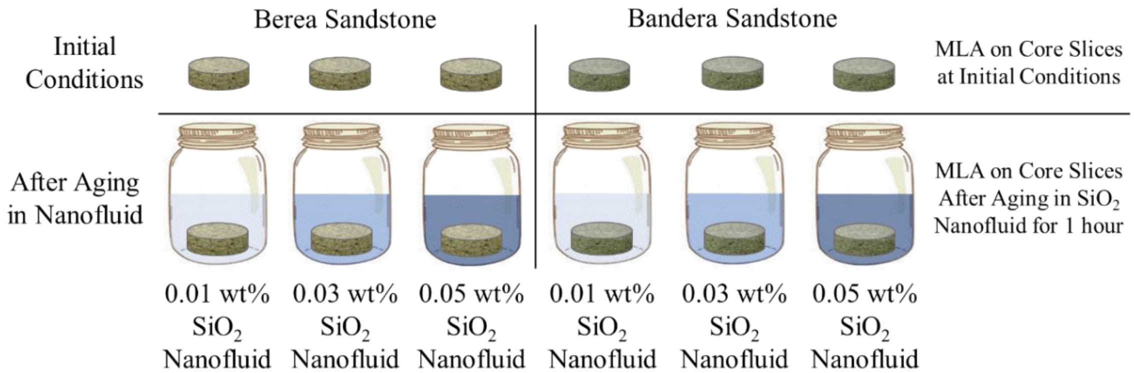

Figure 4.8 *Diagram of MLA-SEM Experiments*

4.4 Results and Discussion

The contact angle experiments were conducted to understand the ability of silicon dioxide (SiO_2) nanoparticles to modify the wettability of Berea (quartz rich sandstone) as well as Bandera (sandstone with a considerable carbonate content). The contact angle on Berea sandstone core at the end of the wettability restoration to reservoir conditions was measured to serve as a reference angle to compare contact angle changes on Berea over time in 0.01, 0.03, and 0.05 wt% nanofluids, and this angle was 103.4°. Then, the contact angles were measured systematically based on the aging time and nanofluid concentration (Figure 4.9). The contact angle of Berea drastically decreased from 103.4° to 60.7° after 1 hour of aging in 0.01wt% SiO_2 nanofluid. After three hours of aging in 0.01 wt% nanofluid, the Berea rock had a contact angle of 62.4°, resulting in an increment of 1.7° from the angle measured at one hour. The next measurement at six hours on Berea showed an angle of 65.6°. The last two measurements were after 24 and 72 hours of aging in 0.01wt% SiO_2, and the angles obtained were 62.5° and 63.3° respectively. In summary, Berea aged in 0.01wt% SiO_2 over a maximum of 72-hour period shows a drastic decrease in the contact angle within the first hour of nanofluid aging, and on the following hours the contact angle's behavior tends to be cyclical between 60.7° (lowest contact angle reported) and 65.6° (highest contact angle reported).

All of the contact angles on the Berea samples aged in 0.03 wt% SiO_2 nanofluid were slightly lower compared to the samples aged in 0.01 wt% SiO_2, and followed the same tendency that of 0.01 wt% SiO_2 nanofluid contact angle experiments. In the first hour of aging in a solution of 0.03 wt% SiO_2, the contact angle of a Berea sample went from 103.4° to 56.0°, and then to 58.7° at the end of 3 hours. After six hours of aging, the contact angle keeps increasing from the measurement at 3 hours up to 61.3°, and then it decreases to 57.6° at 24 hours. Finally, the sample aged over 72 hours in 0.03 wt% SiO_2 shows 60.3° contact angle.

The last nanofluid concentration used to age Berea rocks was 0.05 wt%. The contact angles measured at 1 hour, 3 hours, 6 hours, 24 hours and 72 hours were: 50.6°, 52.1°, 58.4°, 51.3°, and 57.9° respectively. These angles also show the same trend as observed in the results when the rock slices were treated with 0.01 and 0.03 wt% SiO_2 nanofluids. It seems that a sharp decrease in contact angle occurs within the first hour, and then the contact angles fluctuate within a few degrees. This fluctuation can be due to stabilization of the nanoparticle-rock interaction on the rock surface after detaching the oil from the rock. During this process, there may be a constant equilibrium and disequilibrium on the rock surface, and depending on what state it is in, the contact angle may be affected.

In the preceding research (Sivira et al., 2017), the nanofluid concentration did not show a clear trend in contact angles between the Berea samples analysed. It also could not fully explain coreflood experimental work conducted by Kim et al. (2017), who proved that the higher nanofluid concentration produced the higher oil recovery. This brought up doubts in the wettability restoration procedure applied in the previous research. The wettability restoration technique stated by Sripal & James (2016) was now implemented to dissipate those doubts. In this study, the degree of contact angle changes on Berea between 0.01, 0.03 and 0.05 wt% nanofluids observed in this study (as the nanofluid concentration increases, the contact angles decrease) are now consistent with the coreflood studies done by Kim et al. (2017). The comparison between the two investigations shows the importance of a proper the wettability restoration methods for SCAL experiments.

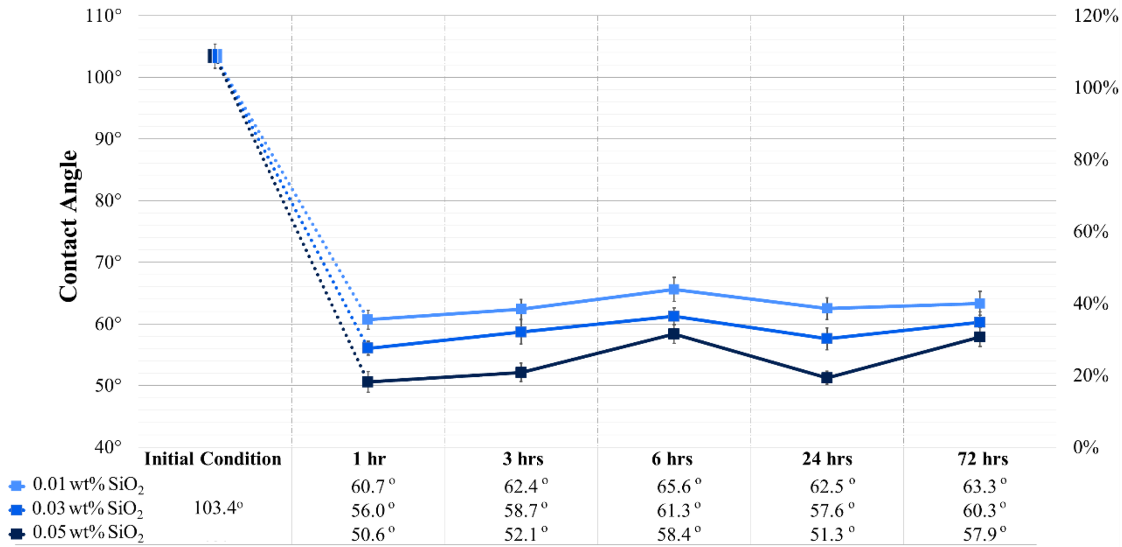

Figure 4.9 *Contact Angles of Oil and SiO_2 Nanofluids on Berea (Preaged in Oil Over 6 Weeks) as a Function of Aging Time*

The contact angle experiments conducted on Bandera samples have shown a similar trend as the results obtained with Berea sandstone (Figure 4.10). The initial contact angle of Bandera sandstone after the wettability restoration procedure stated by Sripal & James (2016) was equal to 111.8°. The contact angles recorded on the Bandera rock slices aged in 0.01 wt% SiO_2 nanofluid exhibit a significant decrease after the first hour of aging from 111.8° to 54.3°, followed by an increased angle equal to 57.7° at 3 hours. This increment continues up to 6 hours with an angle of 60.4°. After this period, the measurement taken at 24 hours showed a decrease in the angle of 56.7°. The last contact angle tested was 62.5° at 72 hours of aging, which is an increment from the angle at 24 hours of aging.

For the Bandera samples in 0.03 wt% nanofluid, the contact angle was 54.3° at 1 hour, 53.2° at 3 hours, 59.6° at 6 hours, 50.9° at 24 hours, and 57.6° at 72 hours. Again, the contact angles are slightly lower than the Bandera samples in 0.01 wt% nanofluids, and the trend is comparable to the angles on Bandera in 0.01 wt% nanofluid.

Finally, the experiments on the Bandera rocks aged in 0.05 wt% SiO_2 nanofluid were performed, and the trend was consistent to the ones with the Bandera rocks aged in 0.01

and 0.03 wt% SiO_2 nanofluid. Strong decrease within the first hour of aging is also seen in the rocks aged 0.05 wt% SiO_2 nanofluid, when the angle goes from 111.8° (initial condition) to 45.6° (at 1 hour of aging). Then, the contact angle increases from 1 hour to 6 hours of aging (45.6° to 56.0°). Lastly, the contact angle has a decrease period between 6 hours to 24 hours (56.0° to 49.0°), and an increase period from 24 hours to 72 hours aging (49.0° to 54.4°). The difference in these results compared to 0.01 and 0.03 wt% were that the change in contact angles were greater, giving lower magnitudes in the angles.

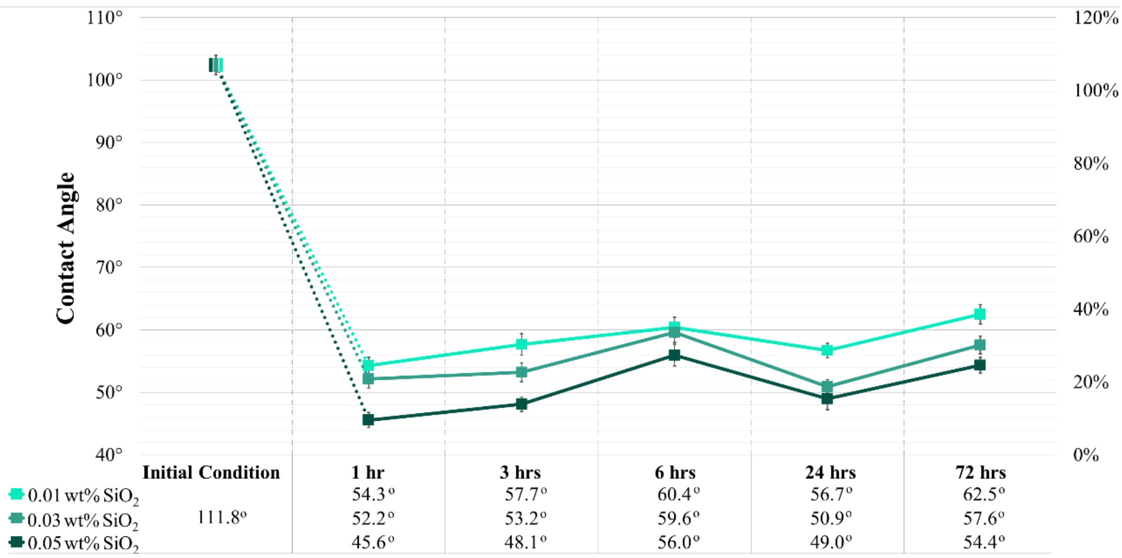

Figure 4.10 *Contact Angles of Oil and SiO_2 Nanofluids on Bandera (Preaged in Oil Over 6 Weeks) as a Function of Aging Time*

It is demonstrated that the SiO_2 nanoparticle has the ability to change the wetting character of Berea and Bandera rock surfaces from oil wet to strongly water wet, which is consistent with preceding research (Sivira et al., 2017). The tendency for both Berea and Bandera rocks are similar, as they exhibit the major alterations at the higher nanofluid concentration. The greatest reduction occurs within the first hour of aging in 0.05 wt% SiO_2 nanofluid, where the Berea rock experiences a reduction in its contact angle of 52.8°, and the reduction in Bandera, 66.2°. After the first hour and up to 72 hours (the analysed period), the contact angles oscillate in the range of 10°, and they do not show a tendency to go back to their initial condition. The Bandera sandstone seems to be more sensitive to the wettability alteration by SiO_2 nanoparticle, since the contact angles at the different aging time periods and nanofluid concentrations were lower on Bandera sandstones than the contact angles on Berea sandstones. The reason behind the higher alterations on Bandera sandstones is because, the higher the nanofluid pH, the lower the contact angle (Nasralla & Nasr-el-din, 2014, and Buckley, et al., 1996). The resulting pH of 0.01 wt% SiO_2 nanofluid suspension after aging a Berea sample is equal to 2.75, whereas the resulting pH of the same suspension after aging a Bandera sample is 3.69. The pH is higher in Bandera sample (more basic) due to dissolution of carbonate content after the aging process, and as a result, the contact angle is lower in Bandera sandstone in comparison with Berea sandstone.

The mineralogical composition of the Berea and Bandera sandstones were defined by MLA analyses before and after aging the rock slices in three different concentrations of SiO_2 nanofluids. The MLA instrument can not discriminate host rock quartz from SiO_2 nanoparticles because the chemical formula of both is SiO_2. The quartz content is an important measurement because an unusual increment can result from the detection of SiO_2 nanoparticles on rock surfaces. Figure 4.11 shows the change in quartz contents from both the Berea and Bandera rock slices. In both samples, the quartz content increases as the SiO_2 nanofluid concentration increases. This is consistent with previous research (Sivira et al., 2017), however, an explanation for this alteration is still unclear. Several possible reasons have been proposed including 1) successful adsorption of SiO_2 nanoparticles on the Berea and Bandera rock surfaces, 2) residual SiO_2 nanoparticles on the rock surface, 3) increment of exposed quartz on the rock surface from the dissolution of carbonate content and the reduction of clay content at the end of the aging process. All these reasons are valid, and the increase can might can be a consequence of either one or a combination. Further analysis of the rock surface should be performed to provide an explanation.

The carbonate (Figure 4.12) and clay contents (Figure 4.13) are decreased from initial condition of both Berea and Bandera. The carbonate content of the rock samples decreases due to the addition of hydrochloric acid (HCl) with the nanofluids. The stabilizer HCl reacts with the carbonate minerals in the rock and dissolves them. Clay minerals, on the other hand, seems to have been washed away in the aging process, and their concentration reduction is not affected by the nanofluid concentration.

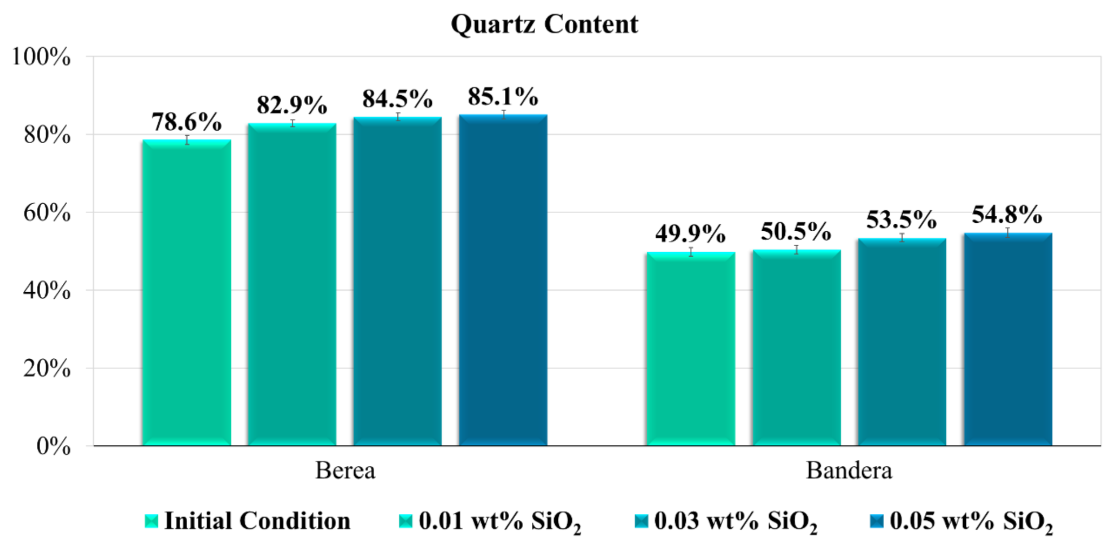

Figure 4.11 *Quartz Content in Berea and Bandera Samples Pre-Aged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour*

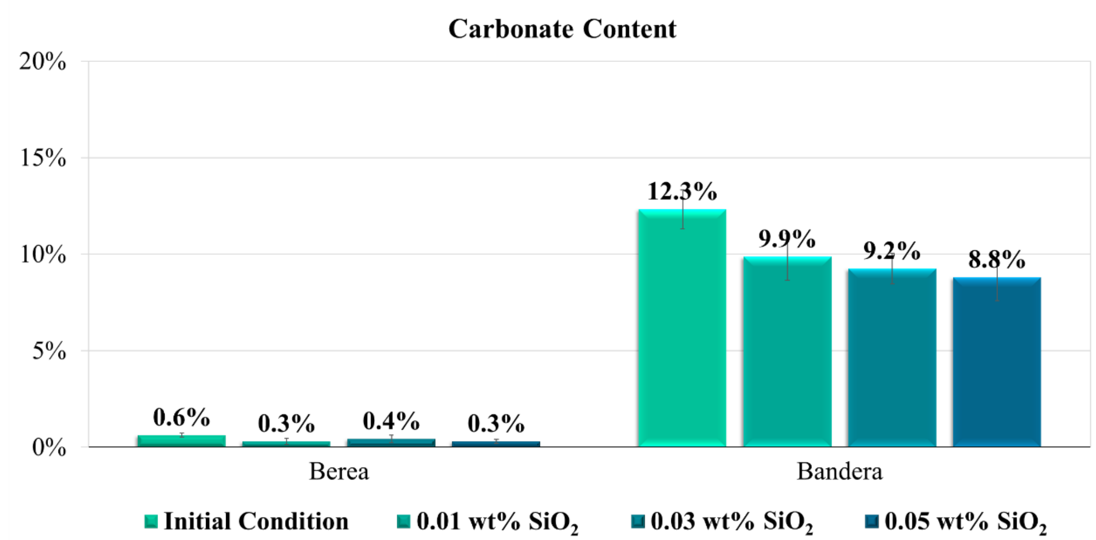

Figure 4.12 *Carbonate Content in Berea and Bandera Samples Pre-Aged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour*

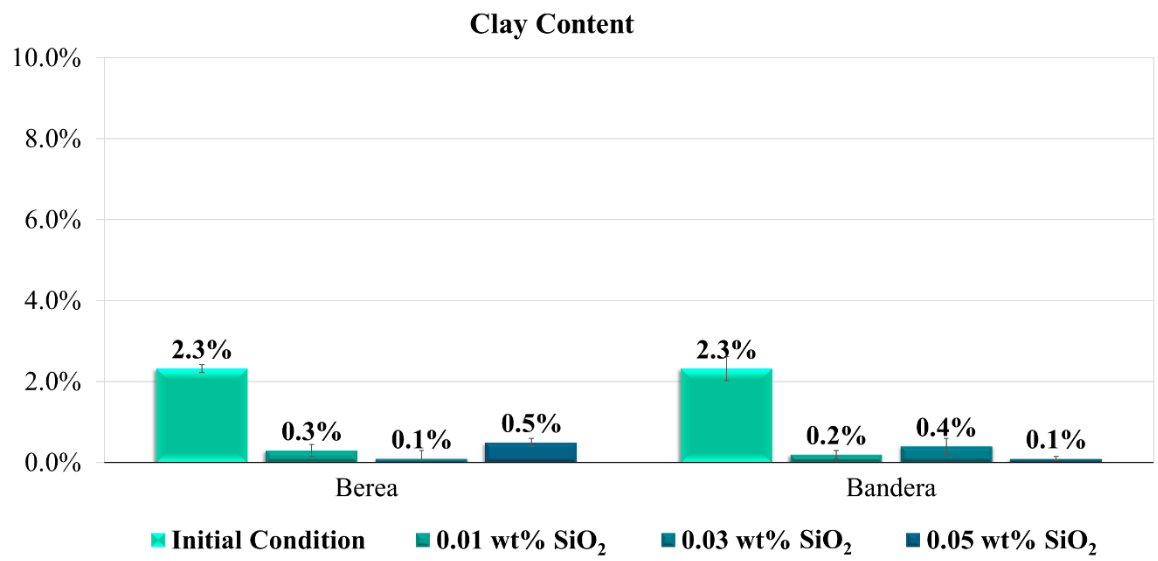

Figure 4.13 *Clay Content in Berea and Bandera Samples Preaged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour*

4.5 Conclusions

The main conclusions from this research are:

1. The contact angles in the Berea and Bandera core samples decrease when the rocks are aged in SiO_2 nanofluid, indicating a wettability change from oil wet to strongly water wet.

    a. The higher the nanofluid concentration, the greater the alteration in the wetting character, making the rock surface more water wet.

    b. Berea sandstone after a wettability restoration procedure has a contact angle equal to 103.4°. This angle decreases up to 50.6° when the rock is aged in 0.05 wt% SiO_2 for one hour, with maximum total reduction of 52.8°.

    c. The initial contact angle (measured after the wettability restoration process) of a Bandera sandstone is 111.8°, and after aging for one hour in 0.05 wt%

SiO_2, the resulting contact angle is equal to 45.6°. This is a reduction of 66.2°, the highest reduction reported on Bandera.

   d. Bandera rock is more sensitive to wettability alteration using SiO_2 nanofluids than Berea sandstone due to difference in the mineralogical composition and its effect on the pH of the nanofluid suspension.

2. The comparison between the two investigations shows the importance of proper wettability restoration methods for SCAL experiments. The wettability restoration technique applied in this research seems to provide more realist results, which are more consistent with the coreflood studies of Kim et al. (2017).

3. The mineralogical composition of Berea and Bandera rock was monitored before and after the aging process for quartz, carbonate and clay content.

   a. Host rock quartz has the same chemical formula as the nanoparticles used in the aging process. As the MLA can only detect SiO_2, it will quantify nanoparticles as quartz. An increase in quartz content was detected after the aging, and can be explained by one or combination of the following reasons:

      i. The successful adsorption of the SiO_2 nanoparticle on the Berea and Bandera rock surfaces

      ii. Residual SiO_2 nanoparticles on the rock surface from sample preparation

      iii. The increment of exposed quartz on the rock surface by the dissolution of carbonate content and by the reduction of clay content at the end of the aging process

   b. The reduction of the carbonate minerals is due to the effect of hydrochloric acid (HCl) used as a stabilizer in the nanofluid. As the nanofluid concentration increases, the reduction of the carbonate is higher because the concentration of HCl is higher.

c. The clay minerals experience a reduction in its content after the aging process regardless of the nanofluid concentration, and it seems that the clay minerals were washed away in the aging process.

4.6 Acknowledgements

The authors would like to thank Chevron Canada, Hibernia Management and Development Company (HMDC), InnovateNL, Natural Sciences and Engineering Research Council of Canada (NSERC), and the Canadian Foundation for Innovation (CFI) for financial support. We thank our colleagues in the Hibernia EOR Research Group for technical support.

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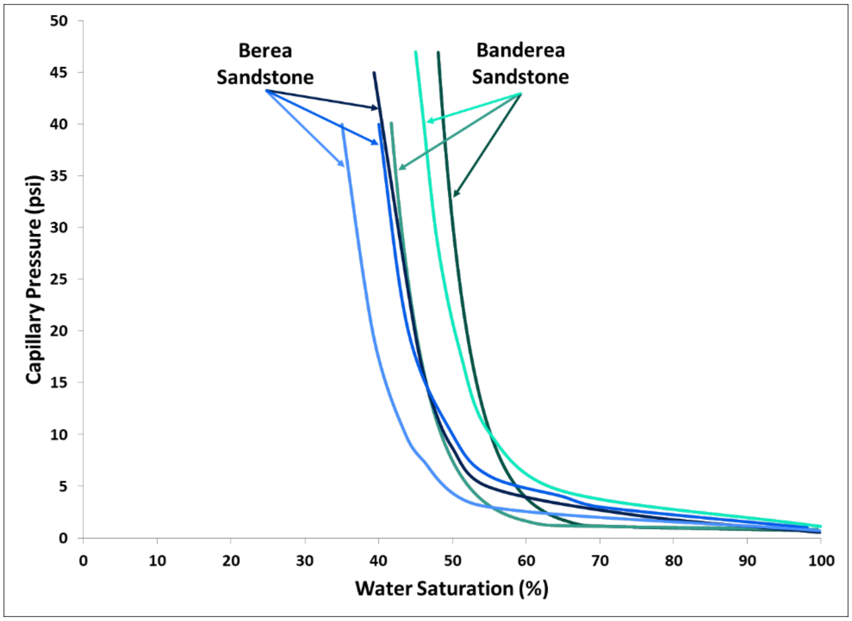
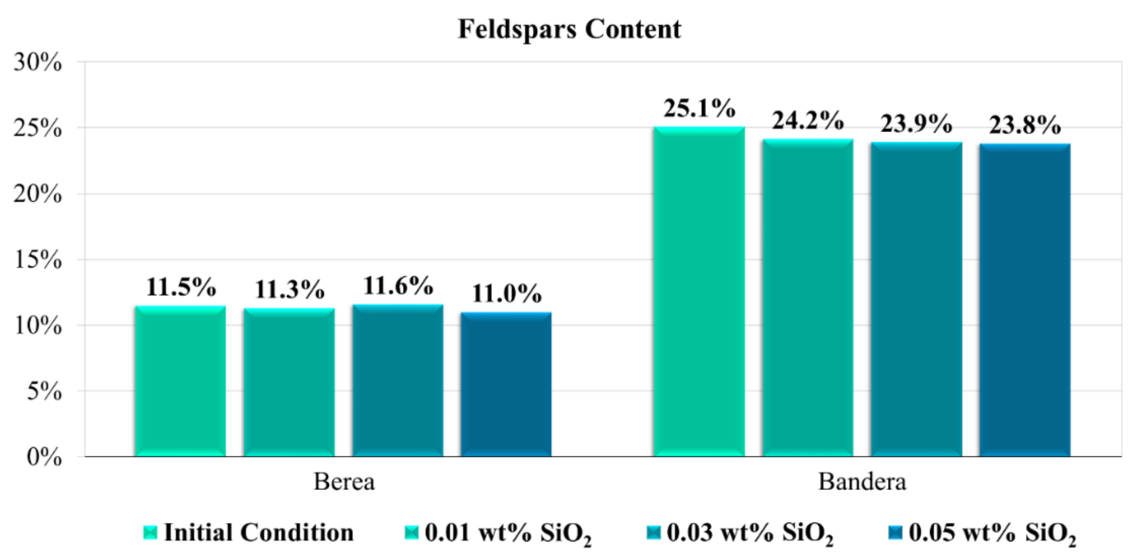
4.8 Appendices

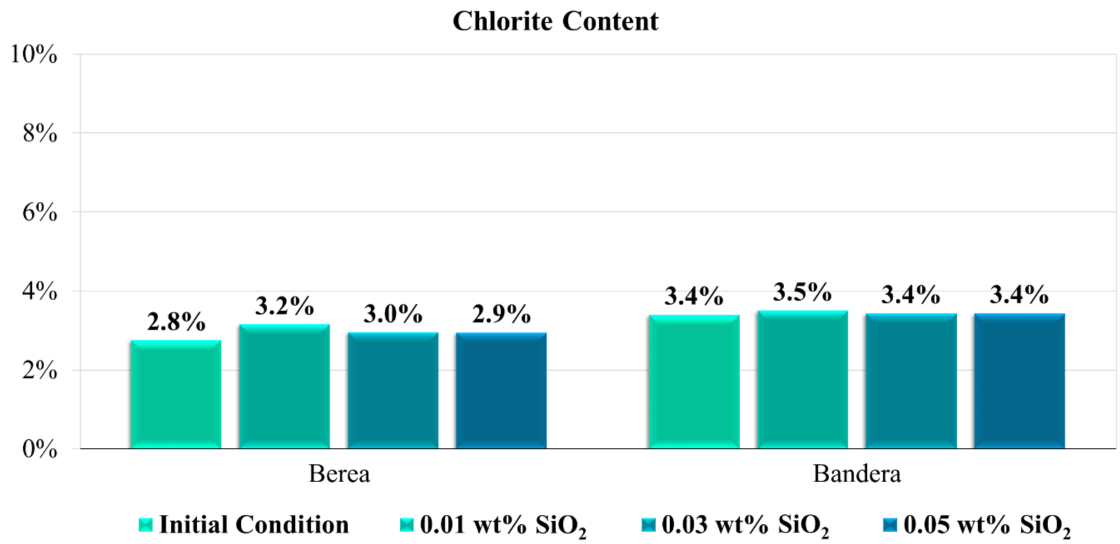
Appendix 4.A Capillary Pressure Curves for Berea and Bandera Sandstone samples in the Imbibition Process



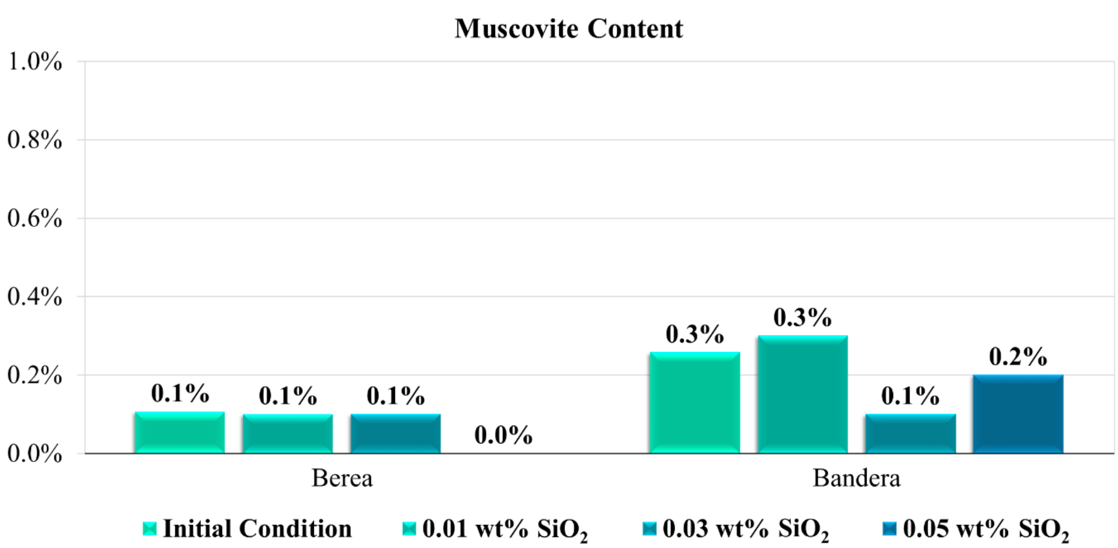
Appendix 4.B Fledspars Content in Berea and Bandera Samples Preaged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour



Appendix 4.C Cholite Content in Berea and Bandera Samples Preaged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour



Appendix 4.D Muscovite Content in Berea and Bandera Samples Preaged in Oil Over Six Weeks, Before and After Aging in Three Different Concentrations of SiO_2 Nanofluid for One Hour



CHAPTER V- SUMMARY

The research achieved several goals of incorporating new results regarding SiO_2 nanoparticles as a water additive for EOR techniques. This research also reduces the gap between laboratory and field conditions.

Silicon dioxide nanoparticles were successfully dispersed in seawater from Grand Banks at Hebron Field temperatures (62°C) by adding HCl (at the right concentration) as a stabilizer. This research concluded that the IFT between oil and seawater decreases in the presence of SiO_2 nanoparticles dispersed in seawater (from Grand Banks) and increases when hydrochloric acid (HCl) is added to the seawater. Despite the increase in on IFT caused by HCl, the interfacial tension still decreases when oil is in contact with the SiO_2 nanofluid. It was also found that the greater the concentration of SiO_2 nanofluid, the lower the interfacial tension of oil-water.

Stable SiO_2 nanofluids are also able to alter the wetting character of Berea and Bandera rock surfaces at Hebron field conditions (62°C and 19.00 MPa). When the Berea and Bandera rocks are treated by a proper wettability restoration technique, the resulting wetting character of these rocks is oil-wet. After treating these oil wet Berea and Bandera rock with nanofluid, the wetting character rapidly (within an hour) change to a strongly water wet conditions. The results also show that the SiO_2 nanoparticle concentration is directly proportional to the level of wettability alteration, as higher SiO_2 nanofluid concentrations result in the lowest contact angles after an nanofluid aging period.

MLA tests revealed alterations in the mineralogical compositions of Berea and Bandera rock surfaces, when the rocks were aged in SiO_2 nanofluid. These alterations are observed for three minerals: quartz, carbonate, and clay. The quartz content increases whereas the carbonate and clay contents reduce after aging the rock in SiO_2 nanofluid. Quartz mineral shares the same chemical formula as the nanoparticle used in the aging process, and when the MLA detects SiO_2, it quantifies nanoparticles as quartz. An increment in quartz is due to the adsorption of SiO_2 nanoparticles on the rock surface, residual SiO_2 nanofluid on the rock surface at the moment of the analysis, and/or exposing more quartz surface by dissolving carbonate with HCl and reducing the clay minerals. The carbonate content in the rock surface is dissolved by the HCl used as a stabilizer in the SiO_2 nanofluid. The clay minerals reduce because these minerals are washed away after the SiO_2 nanofluid aging process.

SEM and ICP-OES analyses did not confirm the adsorption of SiO_2 nanoparticle on the Berea or Bandera rock surfaces. However, both analyses compliment the dissolution of carbonate minerals and the SEM analysis proved the reduction of clay minerals.

5.1 Future Work

The following ideas are recommended to better understand the application of SiO_2 nanoparticle as a EOR technique:

- Upscaling the evaluation to other reservoir formations in offshore Newfoundland and Labrador oil fields
- Evaluation of long-term wettability alteration
- Economical analysis of nanoparticles as a water additive for EOR purposes
- Comparison with other EOR methods such as: Low-Salinity, Water Alternative Gas, or Alkali-Surfactant-Polymer
- Increasing SiO_2 nanoparticle concentration and determining the optimal concentration for the greatest IFT decrease and wettability alteration
- Analyzing the nanofluid-rock interaction using a more accurate SEM to determine the specific reason of the increment in quartz content
- Investigating the changes on the porosity and permeability of the rock before and after introducing the nanoparticles

- Determining the optimal concentration of SiO_2 nanoparticle on the rock surface by adsorption studies, and addressing the effect of the adsorption on the incremental oil recovery

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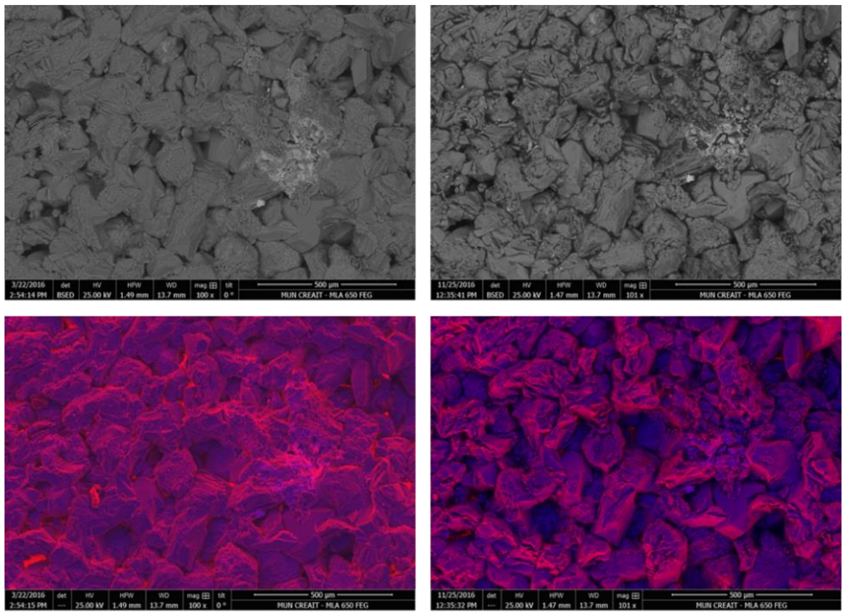
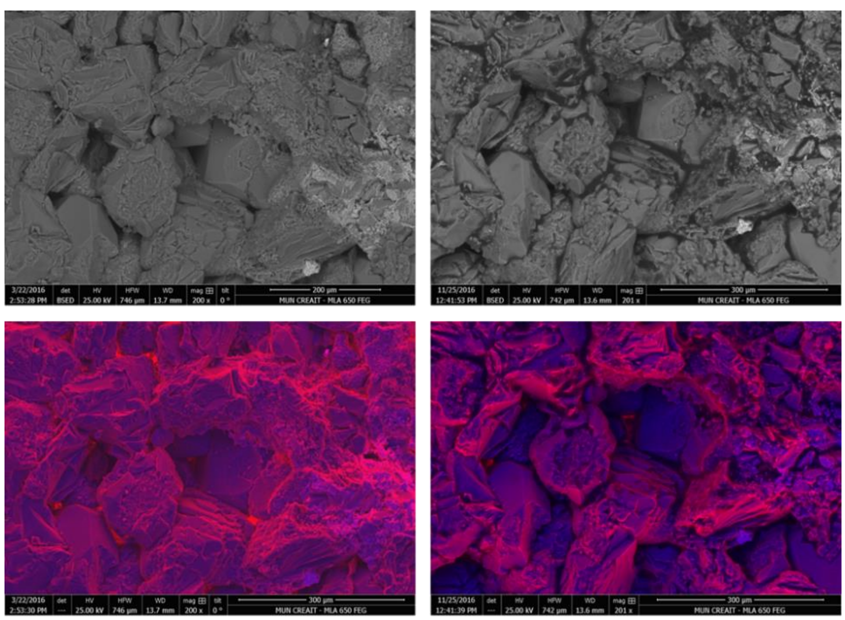
APPENDICES

Appendix A SEM Images of Berea Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 100X – 500μm (Analysed by SEM-MLA)



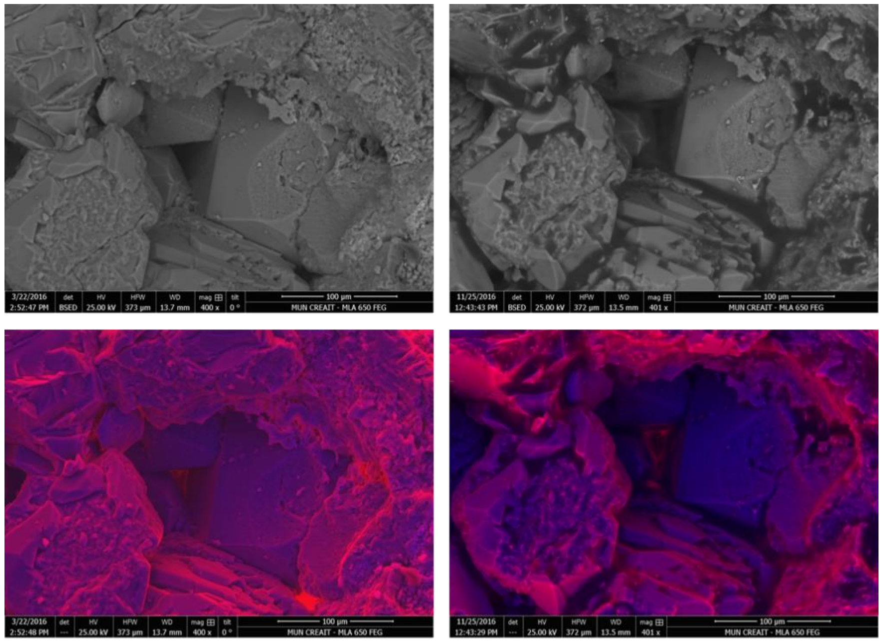
Initial Conditions After Aging in Nanofluid

Appendix B SEM Images of Berea Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 200X – 200μm (Analysed by SEM-MLA)



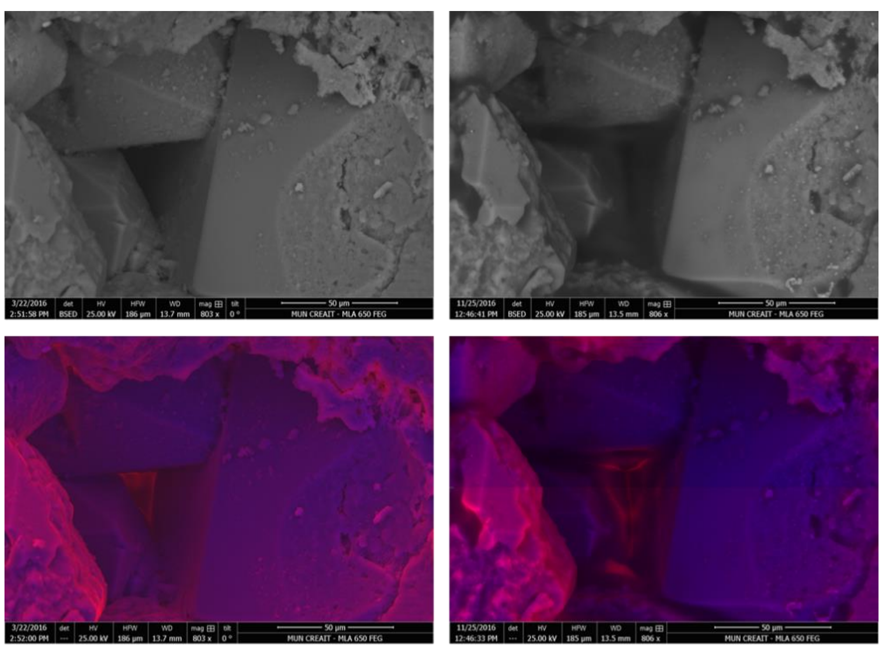
Initial Conditions After Aging in Nanofluid

Appendix C SEM Images of Berea Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 400X – 100μm (Analysed by SEM-MLA)



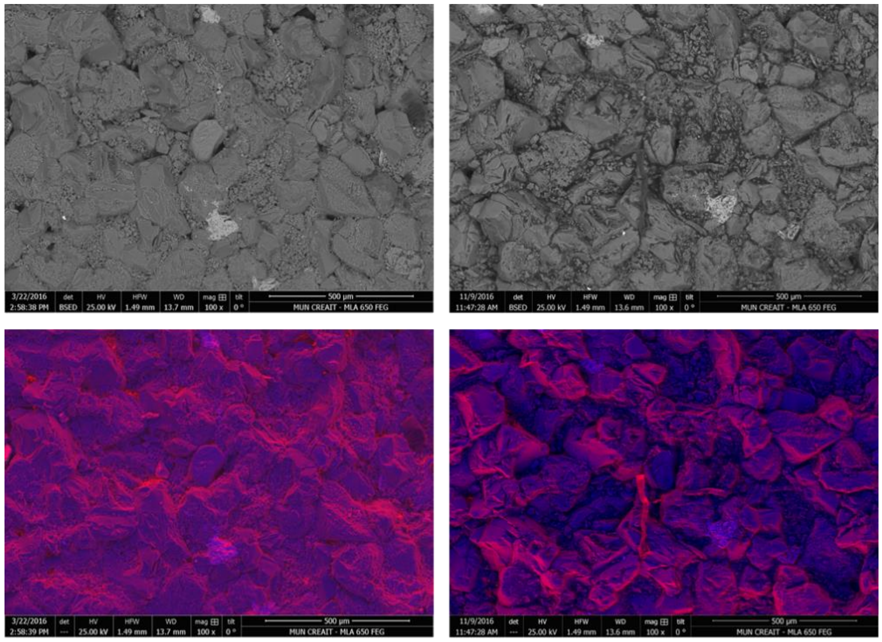
Initial Conditions After Aging in Nanofluid

Appendix D SEM Images of Berea Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 800X – 50μm (Analysed by SEM-MLA)



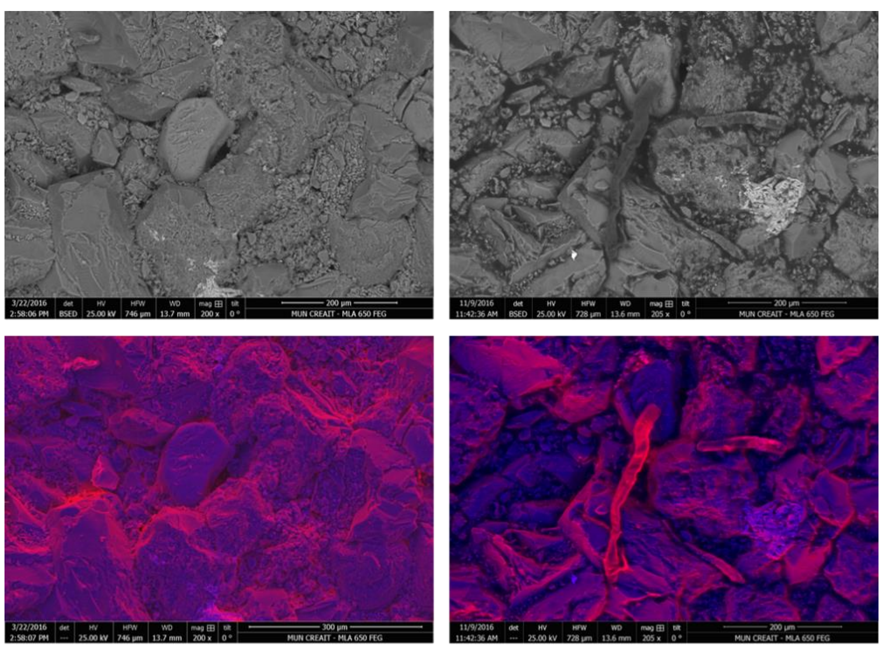
Initial Conditions After Aging in Nanofluid

Appendix E SEM Images of Berea Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 100X – 500µm (Analysed by SEM-MLA)



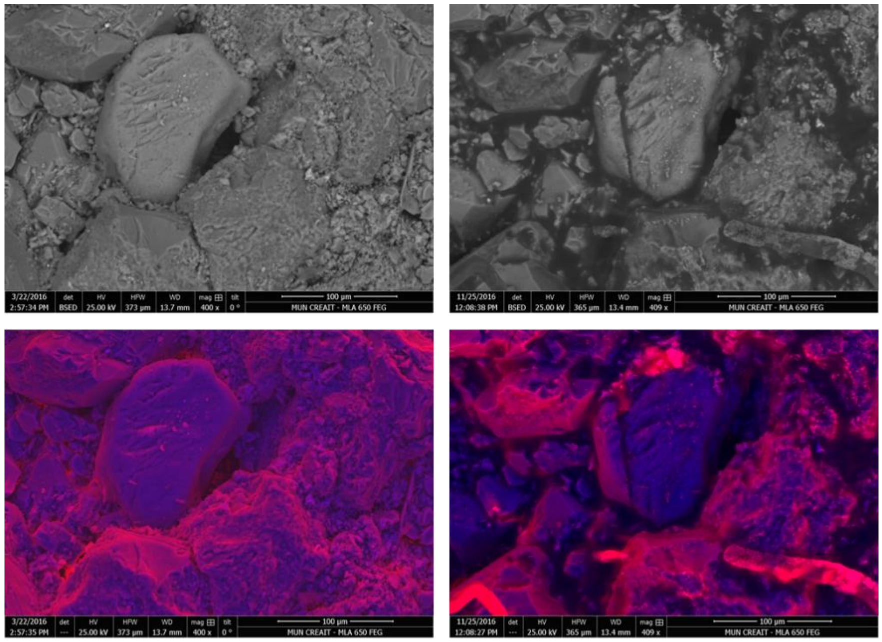
Initial Conditions | After Aging in Nanofluid

Appendix F SEM Images of Berea Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 200X – 200µm (Analysed by SEM-MLA)



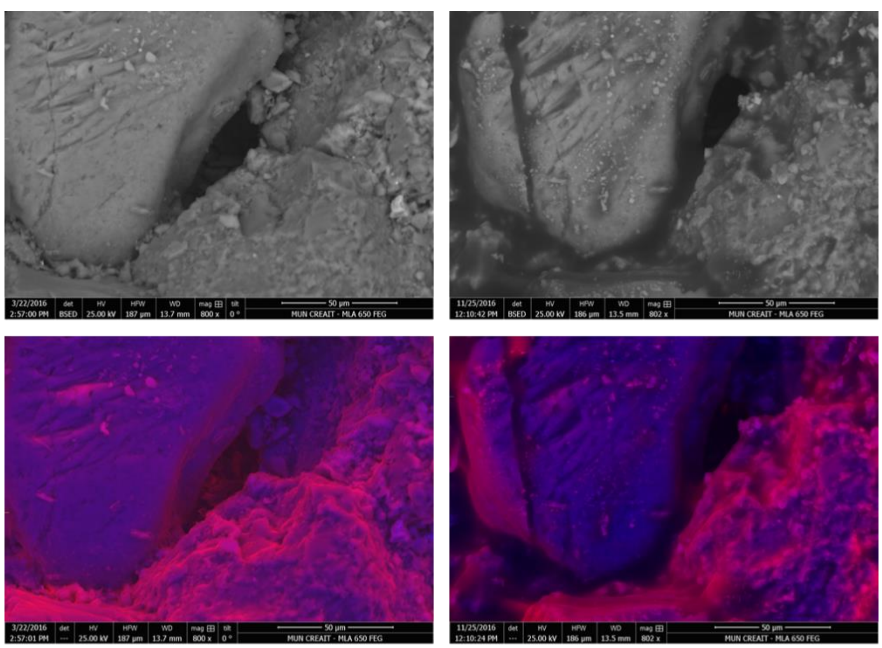
Initial Conditions | After Aging in Nanofluid

Appendix G SEM Images of Berea Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 400X – 100µm (Analysed by SEM-MLA)



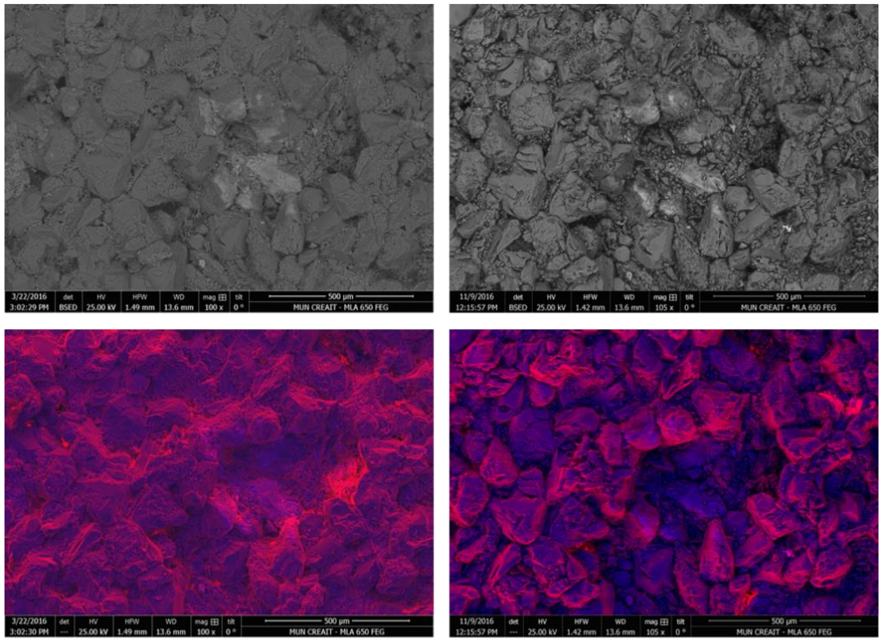
Initial Conditions After Aging in Nanofluid

Appendix H SEM Images of Berea Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 800X – 50µm (Analysed by SEM-MLA)



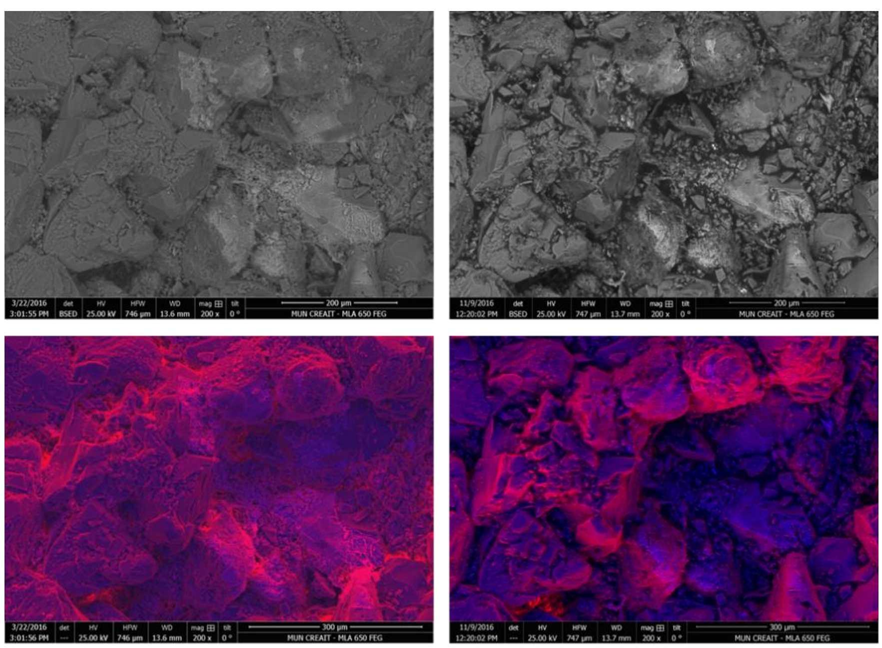
Initial Conditions After Aging in Nanofluid

Appendix I SEM Images of Berea Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 100X – 500µm (Analysed by SEM-MLA)



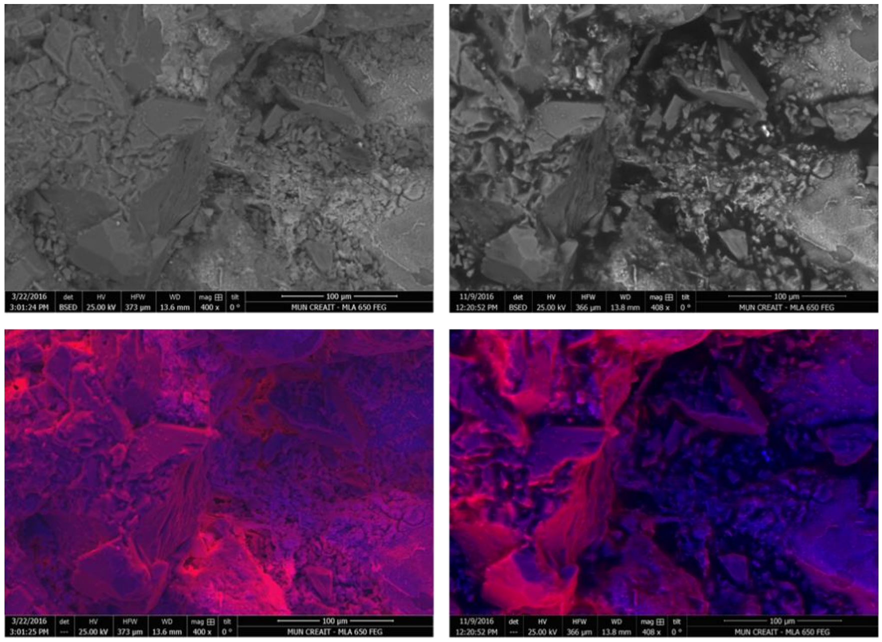
Initial Conditions After Aging in Nanofluid

Appendix J SEM Images of Berea Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 200X – 200µm (Analysed by SEM-MLA)



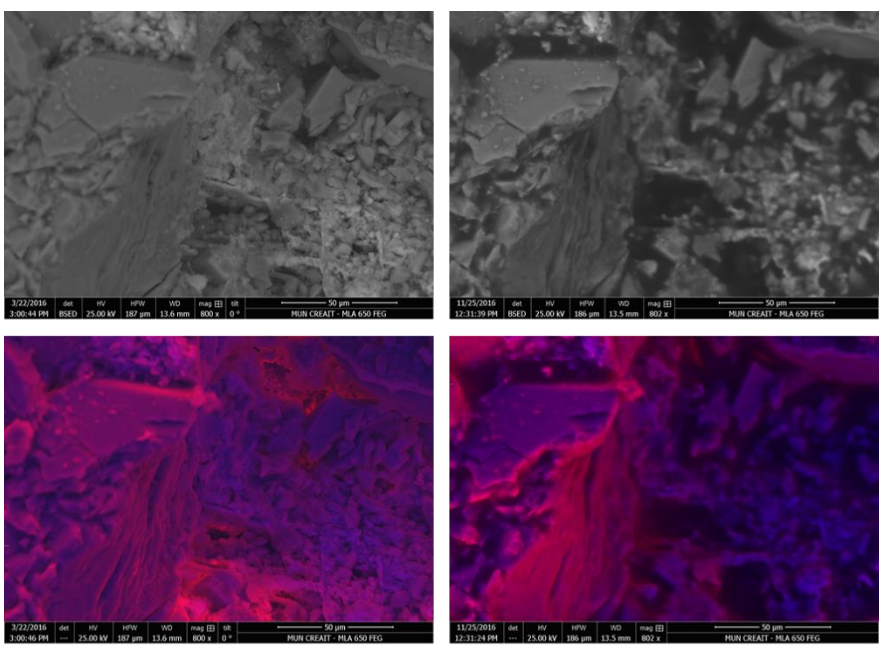
Initial Conditions After Aging in Nanofluid

Appendix K SEM Images of Berea Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 400X – 100µm (Analysed by SEM-MLA)



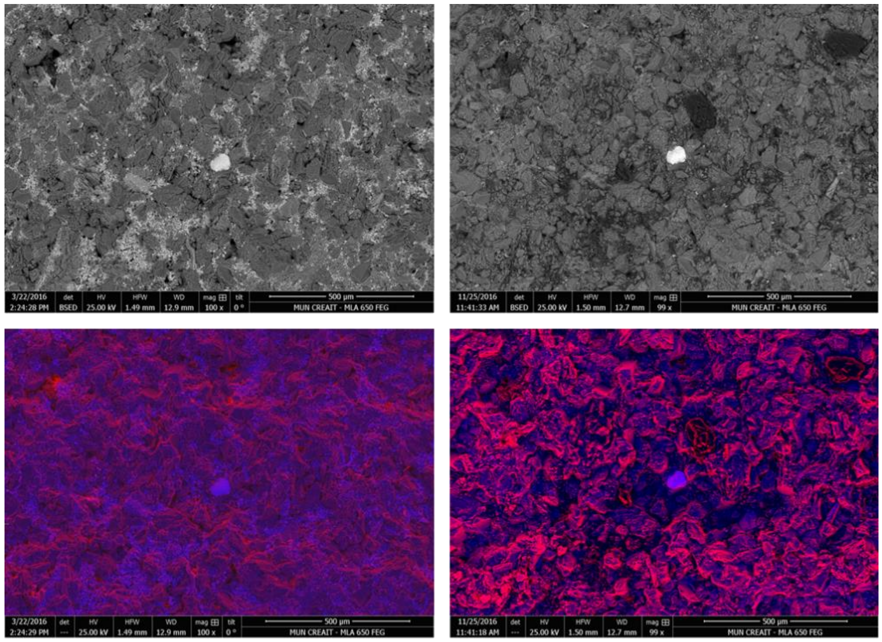
Initial Conditions After Aging in Nanofluid

Appendix L SEM Images of Berea Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 800X – 50µm (Analysed by SEM-MLA)



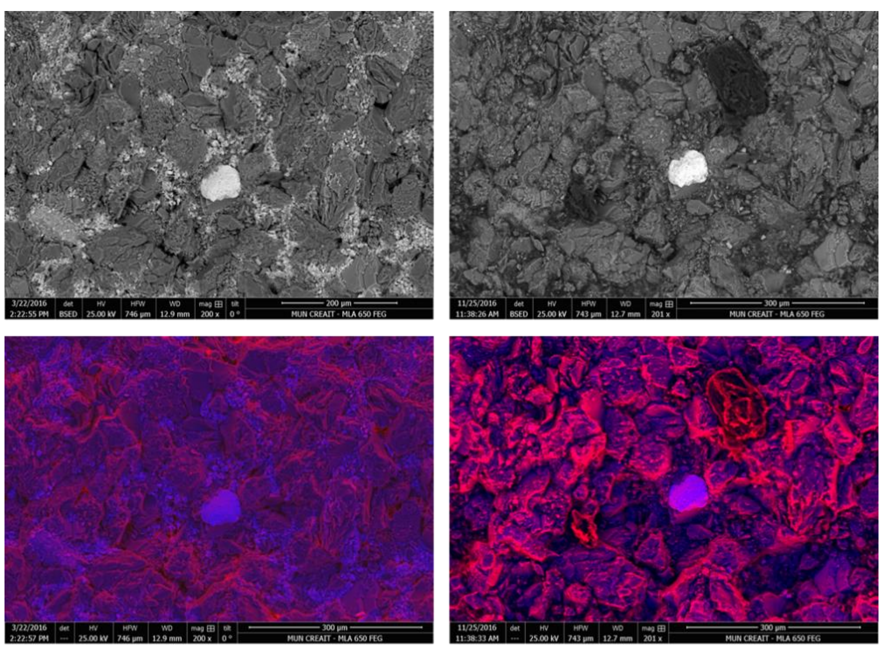
Initial Conditions After Aging in Nanofluid

Appendix M SEM Images of Bandera Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 100X – 500µm (Analysed by SEM-MLA)



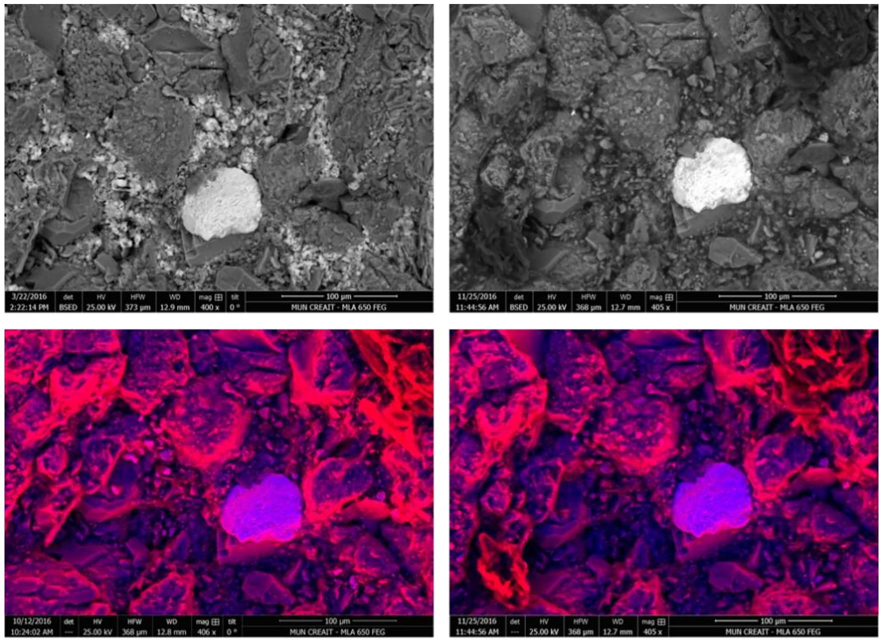
Initial Conditions | After Aging in Nanofluid

Appendix N SEM Images of Bandera Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 200X – 200µm (Analysed by SEM-MLA)



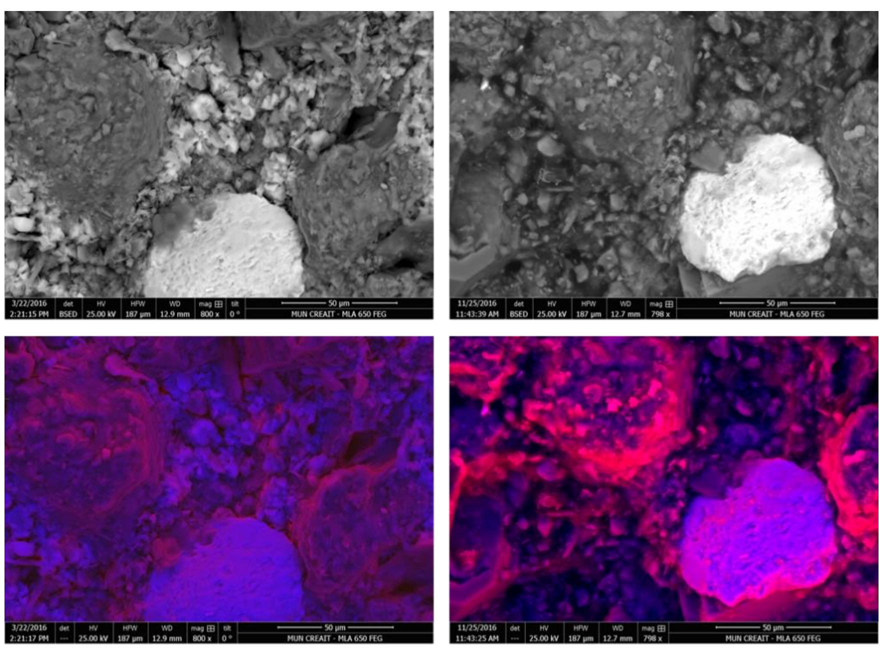
Initial Conditions | After Aging in Nanofluid

Appendix O SEM Images of Bandera Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 400X – 100µm (Analysed by SEM-MLA)



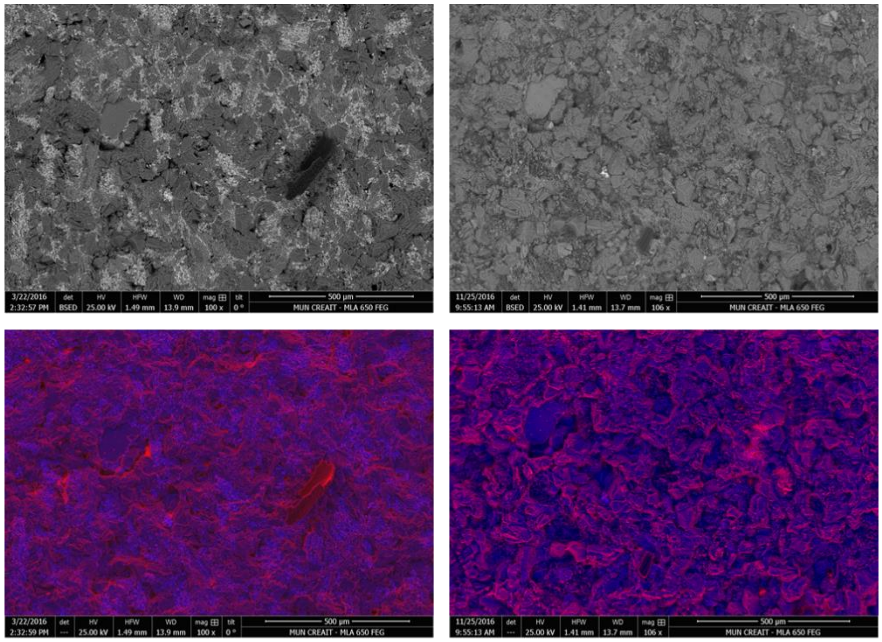
Initial Conditions After Aging in Nanofluid

Appendix P SEM Images of Bandera Before and After Aging in 0.01 wt% SiO_2 Nanofluid at Magnification of 800X – 50µm (Analysed by SEM-MLA)



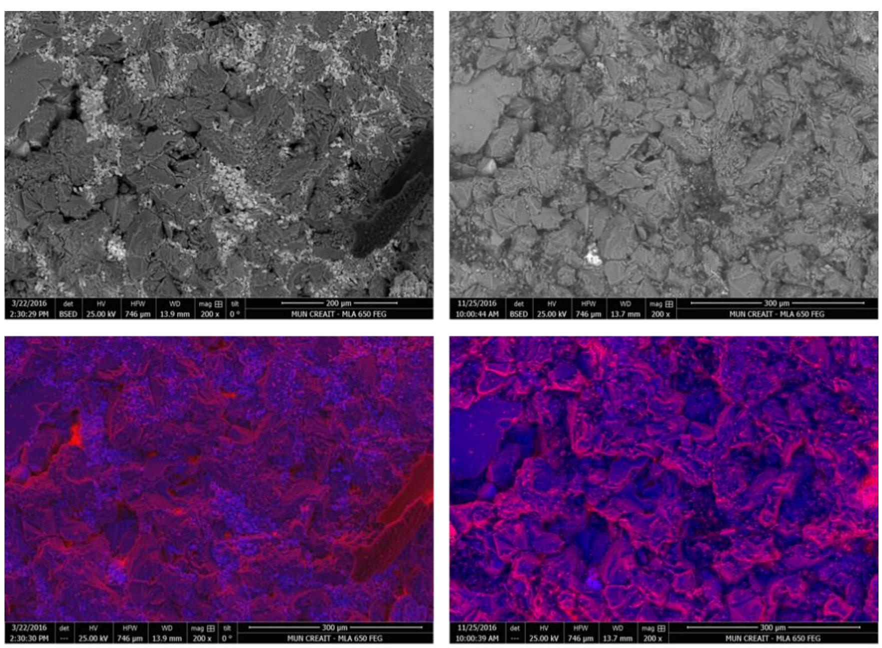
Initial Conditions After Aging in Nanofluid

Appendix Q SEM Images of Bandera Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 100X – 500μm (Analysed by SEM-MLA)



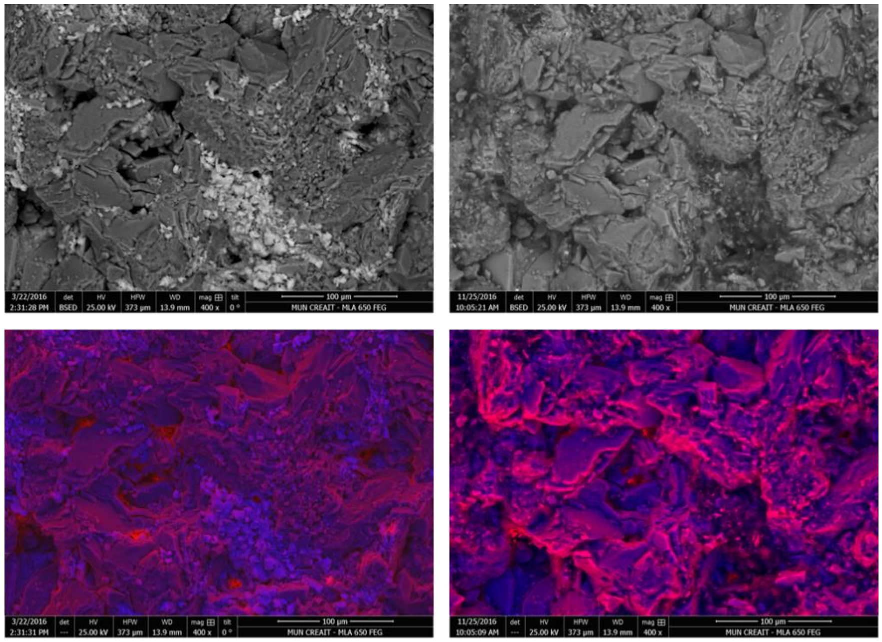
Initial Conditions After Aging in Nanofluid

Appendix R SEM Images of Bandera Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 200X – 200μm (Analysed by SEM-MLA)



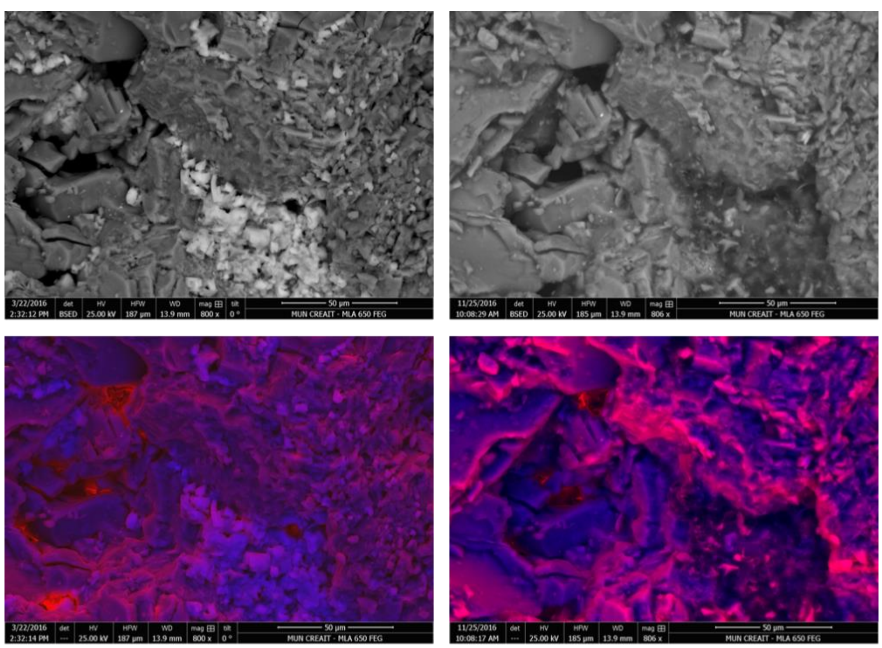
Initial Conditions After Aging in Nanofluid

Appendix S SEM Images of Bandera Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 400X – 100µm (Analysed by SEM-MLA)



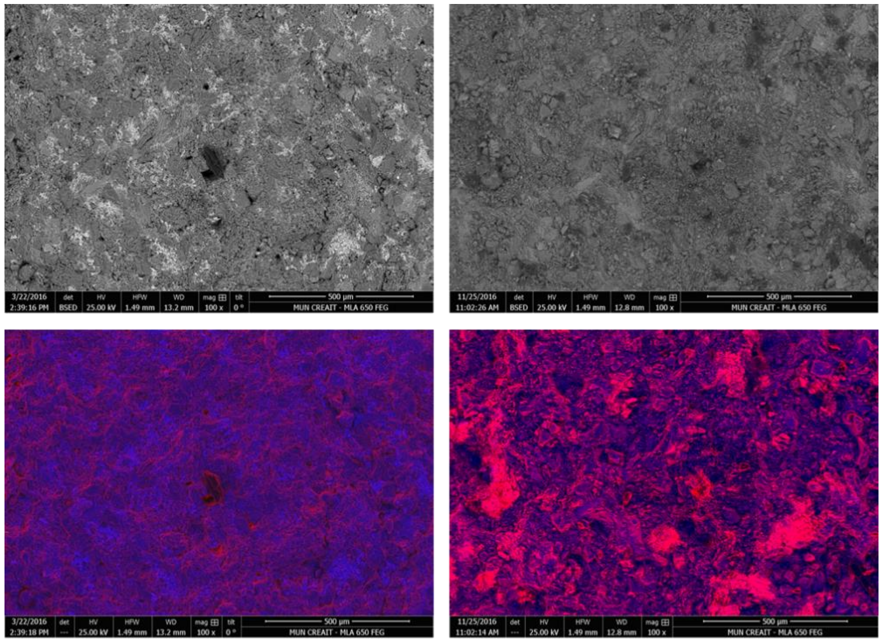
Initial Conditions After Aging in Nanofluid

Appendix T SEM Images of Bandera Before and After Aging in 0.03 wt% SiO_2 Nanofluid at Magnification of 800X – 50µm (Analysed by SEM-MLA)



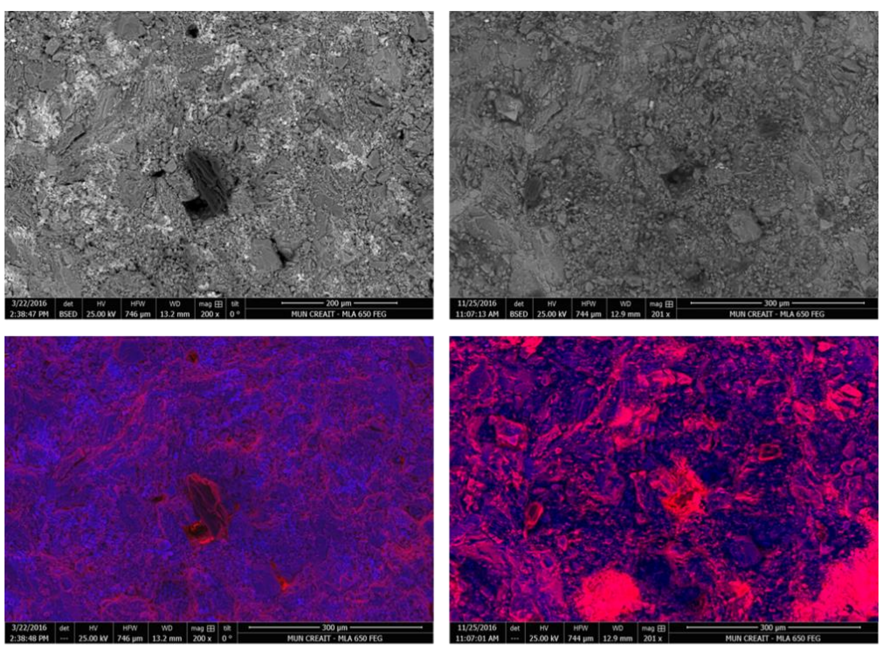
Initial Conditions After Aging in Nanofluid

Appendix U SEM Images of Bandera Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 100X – 500μm (Analysed by SEM-MLA)



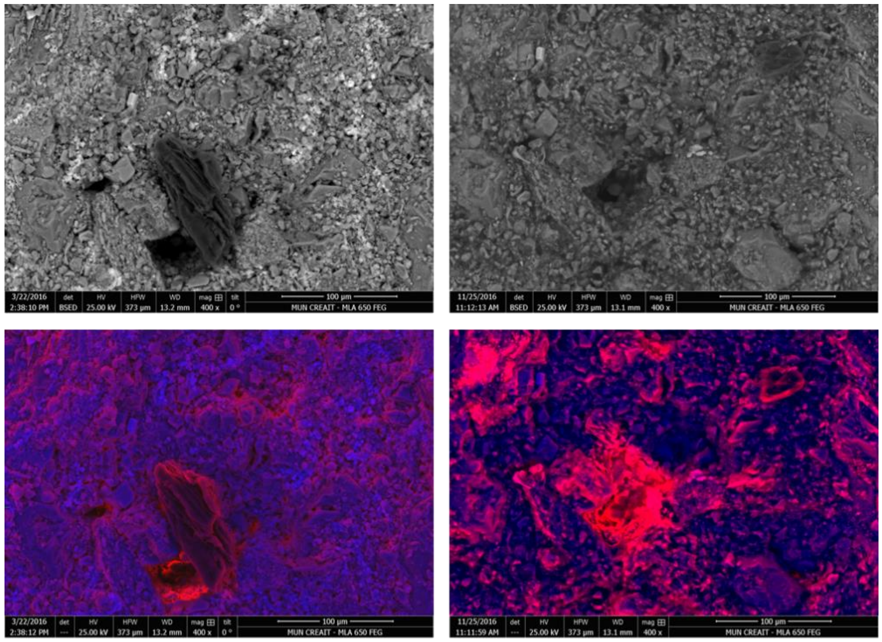
Initial Conditions | After Aging in Nanofluid

Appendix V SEM Images of Bandera Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 200X – 200μm (Analysed by SEM-MLA)



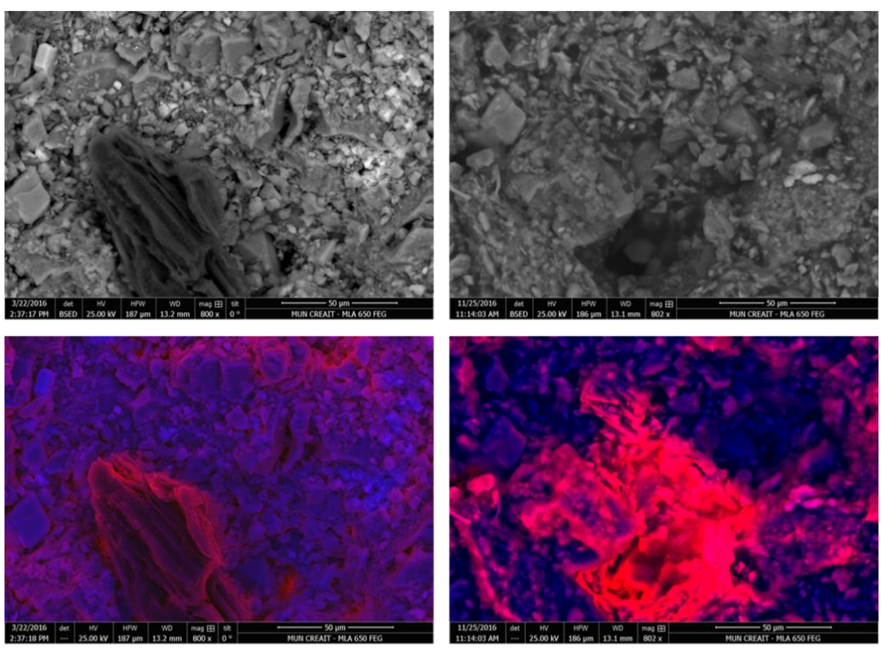
Initial Conditions | After Aging in Nanofluid

Appendix W SEM Images of Bandera Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 400X – 100µm (Analysed by SEM-MLA)



Initial Conditions | After Aging in Nanofluid

Appendix X SEM Images of Bandera Before and After Aging in 0.05 wt% SiO_2 Nanofluid at Magnification of 800X – 50µm (Analysed by SEM-MLA)



Initial Conditions | After Aging in Nanofluid