EVALUATION OF NANOPARTICLES FOR ENHANCED OIL RECOVERY IN HIGH SALINITY AND HIGH TEMPERATURE CARBONATE RESERVOIRS

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

NOV 2016

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
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DEANSHIP OF GRADUATE STUDIES

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Dedication

I dedicate this effort to my parents, my wife and my brothers and sisters.

ACKNOWLEDGMENTS

I am grateful to my thesis advisor, Dr. Abdullah Sultan who gave the opportunity to work in my area of interest (EOR). I would like to thank him for his continuous contributions and support throughout my research.

I am also grateful to my manager, Dr. Wael Abdallah from Schlumberger who supported me a lot during my research and gave me the time and resources that allow me to conduct the research.

Special thanks to Dr. Safyan Khan, who helped me a lot during the stability study. He spent part of his time with me in the lab to solve some encountered problems we faced during the research work. I was glad to meet him one day.

I would like also to thank my committee members, Dr. Sidqi Abu Khamsin, Dr. Dhafer Al-Shehri for their valuable comments during my research work.

I would like to thank to my family who supported me a lot. Special thanks to my wife who encouraged me all the time, I will be always grateful to her.

I would like to thank Dr. Oki Muraza for providing us with the zeolite nanoparticles. I would like also to thank my friends and colleagues at KFUPM who supported me and offered help to train me on some instruments that I used for my research work. Special thanks to my friend Mr. Ahmad Mahboub who trained me on contact angle instruments and spent part of his time to help me conducting the measurements in the lab. I would like also to thank my friend Mr. Sulaiman Al Arifi for his supports and encouragements. Mr. Sulaiman Al Arifi trained me on zeta potential instrument.

I would like also to express my special thanks to my colleagues at Schlumberger for their help and support throughout my research work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

NPs : Nanoparticles

LHP : Lipophobic and Hydrophilic Particles

HLP : Hydrophobic and Lipophilic

PSNP :Polysilicon Nanoparticles

EOR : Enhance Oil Recover

NaCl : Sodium Chloride

PVP : Polyvinylpyrrolidone

HPHT : High Pressure High Temperature

IFT : Interfacial Tension

DIW : Deionized Water

CSC : Critical Salt Concentration

RPM : Revolution Per Minute

ABSTRACT

Full Name	:	Mohammed Fadhel Al Hamad
Thesis Title	:	Evaluation of Nanoparticles for Enhanced Oil Recovery in High Salinity and High Temperature Carbonate Reservoirs
Major Field	:	Petroleum Engineering
Date of Degree	:	May, 2016

Nanoparticles, through many studies, have proven its capability to be a potential enhanced oil recovery agent. In this study, aims to investigate the performance of natural Zeolite in nanoscale on the recovery of crude oil compared to the normal water flooding method. The natural Zeolite nanoparticles are dispersed in seawater, however nanoparticles stability in saline water have been reported to be a challenge. So, in order to investigate the performance of these natural Zeolite nanoparticles on oil recovery, one should first try to stabilize them in seawater. Natural Zeolite nanoparticles of different concentrations (0.02, 0.03, 0.05 wt%) were dispersed in seawater, where stability tests showed that precipitation of nanoparticles occurred in less than 1 hour. This problem, of nanoparticles precipitation in seawater, was investigated by studying the performance of the Zeolite nanoparticles in each electrolyte that exits in seawater. The study results showed good stability of the Zeolite nanoparticles in NaCl solution that has a concentration of 0.14 wt%, however Zeolite nanoparticles will destabilize at higher concentrations of NaCl. Divalent salts that exist in seawater (i.e. $MgCl_2$ and $CaCl_2$) were also tested by dispersing Zeolite nanoparticles in water samples that contain only these salts. The Zeolite nanoparticles were found to be destabilized even at very low concentrations of these salts. On the other hand, Zeolite nanoparticles found to have good stability in deionized water.

Therefore, addition of surfactants should be considered when Zeolite nanoparticles need to be stabilized in seawater. Different surfactants were screened by testing their performance to stabilize the Zeolite nanoparticles in seawater. Polyvinylpyrrolidone (PVP) was shown to be the best to stabilize Zeolite nanoparticles in seawater. Experiments were then carried out using Zeolite nanoparticles plus (PVP) all

dispersed in seawater. The effect of this dispersant on the interfacial tension (IFT) was investigated where the results revealed decrease in IFT values. The dispersant was shown also to change the wettability to more water wet which was due to the Zeolite nanoparticles, as a dispersant of only seawater plus (PVP) was tested and found to not alter the wettability. The efficiency of the dispersant of Zeolite nanoparticles plus (PVP) in seawater on oil recovery, was investigated where higher oil recovery compared to normal seawater injection was noted.

ملخص الرسالة

الاسم الكامل: محمد فاضل الحمد

عنوان الرسالة: تقييم الجسيمات النانوية لتعزيز أستخلاص النفط الخام في مكامن ذات درجة حرارة عاليه ونسبة ملوحه مرتفعه

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2016

جسيمات النانو، من خلال العديد من الدراسات، أثبتت قدرتها على أن تكون احد العوامل الممكنه في تعزيز استخراج النفط و هذه الدراسة، تهدف إلى دراسة أداء جسيمات الزولايت الطبيعي في مقياس النانو على تعزيز استخراج النفط الخام بالمقارنة مع الطريقة الأعتيادية وهي ضخ المياه. جسيمات النانو ،في هذه الدراسة، متناثره في ماء البحر لنتمكن بالتالي من ضخها ، ولكن العديد من الدراسات أثبتت أن استقرار جسيمات النانو في المياه المالحة يشكل تحديا كبيرا. لذلك، من أجل دراسة أداء جسيمات الزولايت النانوية على تعزيز استخراج النفط، يجب أولاً التأكد من أستقرار تلك الجسيمات في مياه البحر.

لدراسة ذلك، الجسيمات النانوية بُعثِرت بتركيزات مختلفة في مياه البحر حيث أظهرت الاختبارات المختلفة أن استقرار الجسيمات النانوية لم يدم أكثر من ساعة واحده. تم التحقق بعد ذلك من هذه المشكلة، عدم أستقرار جسيمات النانو في مياه البحر، عن طريق دراسة أستقرار الجسيمات في كلٍ من مكونات ماء البحر. أظهرت نتائج تلك الدراسة أن استقرار جسيمات الزولايت النانوية في محلول كلوريد الصوديوم ذو نسبة ملوحة تصل الى (14%) يعتبر جيد، بينما اذا زادت نسبة تلك الملوحة عن (14%) سيؤدي ذلك إلى زعزعة الاستقرار.

بعد ذلك تم اختبار أستقرار الجسيمات في محاليل تحتوي على الأملاح ثنائية التكافؤ الموجودة في ماء البحر مثل كلوريد المغنيسيوم وكلوريد الكالسيوم وذلك عن طريق تشتيت جسيمات الزولايت النانوية في تلك المحاليل. أظهرت الدراسات أن وجود تلك الأملاح ثنائية التكافؤ ولو بنسب قليله في ماء البحر، سوف يؤدي الى زعزعة الأستقرار. في جهة أخرى، شُتِت تلك الجسيمات النانوية في ماء منزوع الأيونات حيث أظهرت الجسيمات أستقرار أكثر من جيد ولِمده طويله.

لكي نتمكن من استقرار جسيمات الزولايت النانوية في ماء البحر، ينبغي أن يضاف مؤثر سطحي لماء البحر لكي يساعد في عملية الأستقرار. في هذه الدراسة تم فحص العديد من المؤثرات السطحية عن طريق اختبار أدائهم في استقرار تلك الجسيمات النانوية في ماء البحر. أظهرت نتائج تلك الدراسة أن المؤثر السطحي البوفيدون يشكل عامل استقرار جيد للجسيمات في ماء البحر.

بعد ايجاد المؤثر السطحي المناسب، تم تحضيرعينات تحتوي على ذلك المؤثر وجسيمات الزولايت النانوية في ماء البحر. تم أستخدام تلك العينه بعد ذلك في العديد من التجارب لقياس أداء جسيمات الزولايت النانوية في تعزيز أستخراج النفط. أولاً، تم دراسة تأثير تلك العينه على التوتر السطحي بين ماء البحر وزيت الخام حيث أظهرت النتائج الى تقليل في قيمة التوتر

السطحي حين أضافة تلك العينه. ثانياً، تم دراسة أثر تلك العينه على تغيير خاصية البلل للصخور الكربونية حيث أظهرت النتائج الى تغيير كبير في خاصية البلل مما قد يساعد من ثم على تعزيز أستخراج النفط.

بعد ذلك، تم ضخ تلك العينه خلال صخره كربونيه تحتوي على نفط خام حيث أظهرت نتائج تلك التجربه قدرت جسيمات الزولايت النانوية في تعزيز أستخراج النفط.

CHAPTER 1

INTRODUCTION

Large amounts of oil are left behind after primary and secondary recoveries and with the increase in the oil demand; it is important to start looking for an effective recovery method that will enable us to extract the left behind oil. Through many conducted lab experiments, nanoparticles proved its efficiency to be used as an enhance oil recovery agent. Nanoparticles defined as particles which have size of less than 100 nm. Since the pore channel throat size of the reservoir rock is in micron magnitude, nanoparticles can easily penetrate through porous medium. The nanoparticles dispersion fluid, so called nanofluid, is a fluid containing nanomaterials and the dispersing liquids. The dispersion liquids depend on the type of the nanoparticles being used. Dispersion liquid can be water for hydrophilic nanoparticles and can be oil or ethanol for hydrophobic nanoparticles.

Nanofluids can improve the oil recovery by several mechanisms (Li et al, 2013). These mechanisms include disjoining pressure, wettability alteration, emulsification, reduction of interfacial tension (IFT) and modifying fluids properties such as viscosity. Hydrophilic nanoparticles dispersed in water was found to alter the wettability from water wet to stronger water wet or from oil wet to water wet. Concentration of the nanofluids plays a role in recovery as the higher the concentration the more reduction on IFT (Hendraningrat et al, 2013). Wettability will be more altered at higher nanofluids concentration as well. However, at higher concentrations nanoparticles have the tendency to block pores network, which will decrease the oil recovery.

1.1 Statement of Problem

Nanofluids for enhanced oil recovery (EOR) in carbonates have not been studied intensively in literature. Most of the work has been done on sandstones using silica nanoparticles. Since carbonates tend to be more heterogeneous and complicated than sandstones, it will be worthy to evaluate the efficiency of nanofluids in carbonate formations. Nanofluids showed good promising results, in terms of oil recovery, in sandstones, however mechanisms behind oil recovery improvements are not fully understood.

In this study, we propose to evaluate system of nanoparticles for enhance oil recovery considering real reservoir conditions of high temperature, high pressure and high salinity. The study will investigate the impact of different nanoparticles on oil recovery through core-flooding, IFT and wettability measurements.

1.2 Thesis Objectives

The objectives of this proposal are to:

- Identify potential nanoparticles that can enhance oil recovery at high-temperature and high-salinity conditions with minimum surface adsorption.
- Investigate the effect of nanoparticles on interfacial tension between brine and oil phases.
- Investigate the impact of different nanoparticles on oil recovery using core-flooding.

CHAPTER 2

LITERATURE REVIEW

2.1 Nano Material for EOR

Miko et al, (2010) studied the ability of three different polysilicon nanoparticles (PSNP) to enhance oil recovery. The three PSNPs were lipophobic and hydrophilic PSNP (LHPN) with average particle size ranges between 20-60 nm, hydrophobic and lipophilic PSNP (HLPN) with average particle size ranges between 10-20 nm and neutrally wet PSNP (NWPN) with average particle size ranges between 10-30 nm. Ethanol was used as dispersant fluid for NWPN and HLPN, however 30 kppm brine was used for LHPN. The concentrations of LHPN, HLPN and NWPN in the dispersant fluids were 2 g/L, 3 g/L and 3 g/L respectively. Eight sandstone core samples were evaluated with two types of crude oil, low and medium grades that have API of 41 and 28 respectively. Coreflooding experiments were conducted using the eight sandstone cores, and contact angle was measured before and after nanofluids injection. In all cases, nanofluids were injected as tertiary recovery.

PSNP were able to change the wettability of the core plugs from their natural water wetting states. LHPN changed the wettability to more water-wet, while HLPN changed the wettability to more oil wet. NWPN changed the wettability to neutrally wet. NWPN and HLPN dispersed in ethanol were able to decrease the interfacial tension.

From the coreflooding experiments, it was found that LHPN is not a good EOR agent in water-wet formations because it hinders oil production but enhances water production. Permeability of the core samples was affected by LHPN as revealed from the change of the color of the effluent from cloudy to transparent; this is probably due to the larger size of particles compared to the other PSNP. A concentration of 3 g/L or less is recommended for NWPN and HLPN when to be used as nano-EOR agents.

Performance of eight nanoparticles namely oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon with particle size of 10-100 nm were investigated by another group (Ogolo et at., 2012). EOR experiments were conducted using these nanoparticles. Two set of experiments were conducted and they were run under surface conditions. Distilled water, brine, ethanol and diesel were used as the dispersing media for the nanoparticles. The first experiment involved displacement of the injected oil with nanofluids. However, in the second experiment the sands were soaked in the nanofluids for 60 days before the oil was injected and then displaced with low salinity brine.

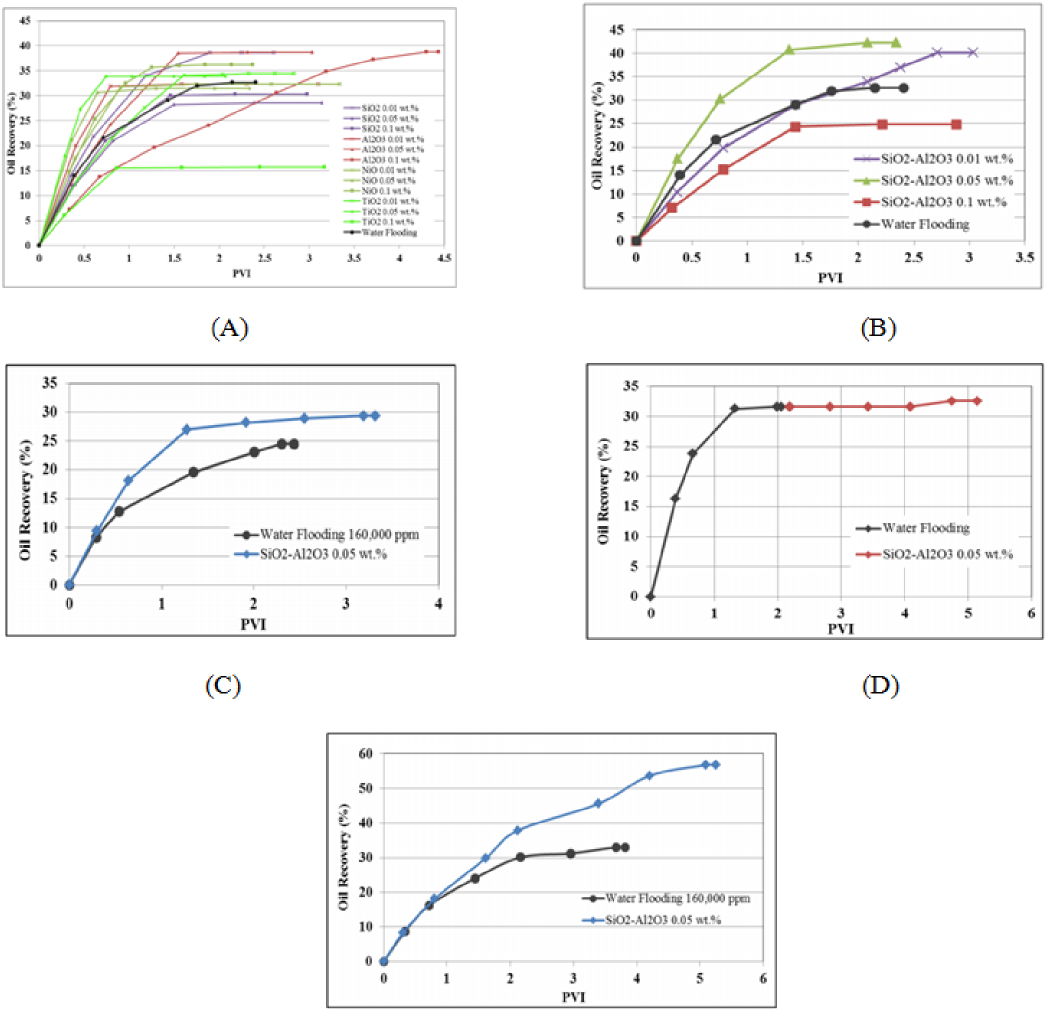
From these experiments, the use of the nanofluids as displacement for the injected oil was found to be more effective compared to the use of the nanofluids as soaking fluid. Three different coreflooding scenarios, and in all scenarios nanofluids were injected as tertiary recovery (Ogolo et al., 2012). The first scenario was conducted by injecting distilled water as secondary recovery followed by injection of the nanoparticles dispersed in distilled water. However, in the second scenario brine was used for secondary recovery followed by injection of the nanoparticles dispersed in the same brine. In the third scenario, ethanol was used for both secondary recovery and as dispersant fluid for the nanoparticles. From the coreflooding results, it is concluded that Aluminum oxide dispersed both in distilled water and brine found to be good for EOR as it reduced the oil viscosity. Silicon oxide dispersed in ethanol showed good results as it reduced the interfacial tension between oil and water and changed the surface wettability of the sand.

Copper oxide (CuO), Nickle oxide (NiO) and Iron oxide (Fe_2O_3) with average particle size of 50 nm were used to conducted several coreflooding experiments at ambient conditions to investigate the impact of three nanoparticles on oil recovery (Haroun et al, 2012). These nanoparticles dispersed in 40 kppm brine at constant concentration, 5 wt%. Nanofluids were injected as tertiary recovery through some tight carbonate samples with average permeability of 0.1 mD. CuO showed the highest recovery among the other two nanoparticles.

A new unconventional technique called EK (electrokinetics) was tested and showed a good recovery results (Haroun et al, 2012). DC voltage of about 2V/cm was applied on the oil saturated samples, after the conventional nanoflooding, to identify the increase in oil recovery due to the application of EK. Two scenarios of EK were applied, sequential and simultaneous. NiO showed the highest recovery in the sequential scenario as it has a lower conductivity and hence has more time contact with the rock surface. However, CuO in the simultaneous scenario showed the highest recovery as it has a higher density such that it will have more contact time with the rock surface.

Osamah et al, (2014) studied the effect of different nanofluids on the recovery of heavy oil compared to water flooding in 21 Brea sandstone samples that have average water permeability of 70 mD. Silicon Oxides (SiO_2), Aluminum Oxides (Al_2O_3), Titanium Oxides (TiO_2) and Nickel Oxides (NiO) have been used in this study with average particle sizes from 15-50 nm. 30 kppm brine was used as dispersant for all four nanoparticles. Three different concentrations, (0.01, 0.05 and 0.1 wt%) of nanofluids were prepared. Five stages of coreflooding experiments were conducted. In stage 1, all four nanofluids at different concentrations were used as secondary recovery and compared to water flooding. In stage 2, the best two performance nanofluids in stage 1 were mixed together and used as secondary recovery and compared to water flooding. In stage 3, the mixture in stage 2 was used as tertiary recovery. In stage 4, the mixture is stage 2&3 is studied in high saline environment. In last stage, 5, the mixture was carried out for HPHT experiment. Figure 2.1 summarizes the coreflooding results for all the stages.

IFT measurements were also conducted. It was difficult to perform IFT tests due to the clarity of the solution, so lower concentrations (0.005 and 0.0075 wt%) were used to study the IFT. Results showed that IFT decreased exponentially with increasing the nanofluid concentrations. Reason behind IFT reduction was suggested to be the effect of specific surface area (SSA) of nanoparticles. SiO_2, which has SSA of 650 m^2/g, caused the highest reduction in IFT. However, NiO, which has SSA of 6 m^2/g, caused the lowest effect on IFT. Particle size also has a role in IFT reduction. For Al_2O_3 and TiO_2, where they have the same SSA, TiO_2 caused more reduction in IFT. This is probably because TiO_2 has a bigger particle size than Al_2O_3.



(A)

(B)

(C)

(D)

(E)

Figure 2-1 (A) nanofluids oil recovery (stage1), (B) SiO2-Al2O3 nanofluids oil recovery (stage2), (C) SiO2-Al2O3 nanofluids oil recovery as tertiary recovery (stage3), (D) SiO2-Al2O3 nanofluids oil recovery under high salinity (stage4), (E) SiO2-Al2O3 nanofluids oil recovery at reservoir condition (stage5)

Different nanofluids at various concentrations behaved differently in terms of affecting the emulsion viscosity for low concentration (<0.05wt%) Al_2O_3 decreased the emulsion viscosity. However, further increase in the concentration will increase the viscosity. NiO found to have no effect on the viscosity; however TiO_2 had the tendency to decrease the emulsion viscosity at high nanofluids concentrations. Introducing SiO_2, will increase the viscosity of the emulsion even at low nanoparticle concentrations.

From coreflooding experiments, all nanofluids with different concentrations were investigated and results revealed that Al_2O_3 (0.05 wt%) and SiO_2 (0.01 wt%) are the best among all the others. So, the mixture of both nanofluids was used for all other stages. Al_2O_3 (0.05 wt%) and SiO_2 (0.01 wt%) mixture showed good recovery results when it was used as secondary recovery. The mixture was tested at various salinity of the dispersant fluid, and found to perform better in low saline. The mixture was also tested at reservoir conditions and found to perform well. It showed an incremental oil recovery factor of 23.724%.

Effect of the mixture in asphaltene precipitation was studied, where it can be observed that as the nanofluid concentration increases, asphaltene precipitation will be delayed further (Osamah et al, 2014).

2.2 Silica Nano Particles EOR

Shahrabadi et al. (2012) investigated a special type of polysilicon nanoparticle which is the Hydrophobic and Lipophilic Polysilicon, HLP, as an EOR agent during different water injection scenarios. For his work, he used water-wet sandstones with permeability ranges from 27-35 md and porosity ranges from 17-18%. HLP nanoparticles cannot be dispersed in water or brine as they are Hydrophobic. Therefore, an organic solvent will be used, ethanol. Contact angle and interfacial tension measurement experiments were conducted to understand the rule of HLP in improving the oil recovery. HLP nanofluid was found to lower the oil-water interfacial tension by a factor of ten, from 26.5 dyne/cm to 3 dyne/cm, and change the rock wettability to less water wet condition, reduces the contact angle from 123^o to 99^o.

Three different injection scenarios of HLP dispersed in ethanol were applied. In one scenario, the nanofluid was injected after water flooding. In another scenario, sequence of water/HLP nanofluid injections was applied followed by an injection of 3 PV of water. In the last scenario, HLP nanofluid was injected from the beginning. From these experiments, it was found that the last scenario which is injecting the nanofluid from the beginning gave the highest oil recovery. Most of the oil was recovered during the first pore volume injection of the HLP nanofluid, however pores plugging was trigger when three pore volumes of the HLP nanofluid was injected.

Roustaei et al. (2012) studied three special types of nanoparticles namely hydrophobic and lipophilic polysilicon (HLP) and naturally wet polysilicon (NWP) in water-wet sandstone rocks with average permeability of 186md and average porosity of17%. These nanoparticles were dispersed in ethanol. Contact angle and interfacial tension tests were conducted to study the impact of these nanofluids on the water-wet sandstone rocks. Coreflooding experiments were run under ambient conditions. First, the rocks were flooded with two pore volumes of 30 kppm brine to mimic the primary and secondary recovery. Then, two pore volumes of the nanofluids were injected followed by injection of two pore volumes of brine to recover the nanofluids.

From the experimental results, NWP found to have a stronger impact on the rock wettability, contact angle reduced from 135.5^o to 81.88^o. However, HLP reduced the interfacial tension, from 26.3 dyne/cm to 1.75 dyne/cm between oil-water. Therefore, HLP nanofluid showed higher amount of incremental oil produced. Higher pressure drop was observed when injecting two and three pore volumes of NWP and HLP respectively.

Hendraningrat et al. (2012) studied the impact of LHP silica nanoparticles of single particle size of 7nm on oil recovery of Brea sandstone rocks samples that have average permeability of 375 mD. Brine with salinity of 30 kppm was used as dispersant for the nanoparticles. Two concentrations of nanofluids were studied, 0.01 and 0.05 wt%.

IFT measurements were conducted, as it might be the displacement mechanism of oil, followed by coreflooding experiments at ambient conditions. Three scenarios of coreflooding experiments were studied, nanofluids injection as secondary recovery, followed by water as tertiary recovery and nanofluids injected as tertiary recovery. IFT measurements showed a decrease in the IFT value, when nano fluid was introduce. The IFT of brine/oil was 14.7 nM/m and got reduced to 9.3 nM/m, when 0.01 wt% nanofluid was introduced. Further reduction of IFT to 5.2 nM/m was noted, when nanofluid concentration increased to 0.05 wt%. Results of coreflooding showed that, nanofluids as secondary recovery performed stronger than brine as it reported more oil recovery compared to brine. However, oil recovery when nanofluids were used as tertiary recovery was not significant (less than 2%). Nanofluids in all scenarios were able to reduce the residual oil saturation.

Hendraningrat et al, (2012) initiated a test study, investigation of nanoparticles injection into glass micro-model and study the impact of nanoparticles in IFT reduction and permeability impairment. Two hydrophilic silica nanoparticles from two different companies were selected for this study, HNP-A with single particle size ranges from 15-40 nm and HNP-B with single particle size ranges from 20-50 nm. Brine with salinity of 30 kppm was used as dispersant for these nanoparticles. Nanoparticles were made with various concentrations range from 0.1-1 wt%.

Results of IFT measurement showed a decrease in the IFT (from 65 mN/m to 28 mN/m) when nanoparticles were added. The higher the concentration of nanofluids, the more IFT reduction was encountered. Entrapping of nanoparticles was observed, as the permeability of the glass micro model decreased significantly specially at high nanofluids concentrations. The pH for the two nanofluids was in the range of 3-5. Increasing the concentrations of the nanofluids will decrease the pH. Measurement of pH is very important especially if the porous medium is sensitive to its alteration such as carbonate rocks. In this particular study, there was no change in pH and this is probably due to the stability of the nanofluids at various concentrations.

Hendraningrat et al. (2013) studied the effect of different concentrations of hydrophilic silica nanoparticles (with single particle size of 7 nm) on improving oil recovery. Concentrations range from 0.01 – 0.1 wt% were investigated on low permeability Brea sandstones (K= 5-20 mD). Nanoparticles were dispersed in 30 kppm brine. Contact angle measurements were conducted followed by coreflooding experiments. All nanofluids were injected as tertiary recovery.

Contact angle was decreased with the increase of the concentration of nanofluids. Causing the rock samples surface to be more water wet, where the nanofluids will then probably get adsorbed by the rock surface and mobilized the trapped oil. Coreflooding tests showed up to 10% incremental increase in the oil recovery in the case of concentration = 0.05 wt%. From these tests, it was found that the nanofluids may plug pores, reduce the permeability and therefore reduce the oil recovery. This was for the case of high concentration nanofluids (>0.06 wt%).

Different concentrations of Hydrophilic silica nanoparticles with average particle size of 7 nm were investigated by (Li et al, 2013). And since the nanoparticles are hydrophilic, 30 kppm brine was used as dispersed fluid. Nanofluids were prepared at different concentrations (0.01, 0.05 and 0.1 wt%). (Li et al, 2013) used two kind of porous medium, Brea sandstones rock with permeability ranges from 300-400 md and porosity ranges from 20-23% and a water- wet transparent glass micromodel. Contact angle and interfacial tension measurements were conducted to study the impact of these nanofluids with different concentrations on the water-wet porous mediums. Interfacial tension was found to reduce as the nanofluids concentration increased. IFT of brine/crude oil was 19.2 dyne/cm, however when 0.01% wt nanofluids introduced IFT was reduced almost to half. Contact angle was also reduced from 54^o which is the case of brine to 40^o when 0.01 wt% of nanofluids was introduced. As the concentrations of the nanofluids increased, the contact angle reduced to stronger water-wet.

Then, two coreflooding experiments were conducted at ambient conditions to study the impact of the nanofluid with different concentrations on oil recovery. First experiment was conducted using the transparent glass micromodel and the other experiment was conducted using the Brea sandstones cores.

In both experiments, nanofluids were used as tertiary recovery and they showed good recovery. Oil recovery was increased as the concentration of nanofluids increased. However, higher concentration (>0.05 wt %) of nanofluids may plug the medium pores and therefore reduce the oil recovery.

Hendraningrat et al, (2013) investigated the performance of Litho hydrophilic nanoparticles with particle size ranges between 21-40 nm (LHP) on oil recovery of low-medium permeability Brea Sandstones. Different concentrations of nanoparticles (0.01, 0.05 and 0.1 wt %) dispersed in 30 kppm brine were investigated. Contact angle measurements were conducted to investigate the disjoining pressure as displacement mechanism duo to nanoparticles.

IFT measurements were also conducted to understand the role of LHP at different concentrations in improving the oil recovery followed by coreflooding experiments. The results showed that IFT reduced when nanofluids were introduced. And as the concentration increases, the IFT will reduce more and more. Results from the contact angle measurements showed a change in wettability to more water wet. In all coreflooding tests, nanofluids were injected as tertiary recovery. Results revealed that additional oil recovery from low-medium permeability Brea sandstone was not significant at high nanofluids concentration, as it may plug the pores and reduce the permeability. Therefore, a lower concentration of 0.05 wt% seems to be good candidate for nano-EOR for both low-medium permeability and high permeability formations.

Hendraningrat et al, (2013) investigated the effect of some parameters/factors on the oil recovery from silica nanoparticles. These factors were the particle size, rock permeability, initial rock wettability, injection rate and temperature. Three different sizes of LHP silica nanoparticles were used with single particle size ranges from 7-40 nm. Nanofluids with concentration of 0.05 wt% were synthesized using 30 kppm NaCl. Contact angle measurements were conducted for studying the effect of the initial rock wettability followed by coreflooding tests to study the impact on oil recovery due to Nano-EOR. 26 Brea sandstone samples with permeability ranges from 5-450 mD were used for these experiments. Nanofluids were injected as tertiary recovery.

From these different measurements conducted, the following conclusion can be drawn:

1. The smaller the size of the nanoparticles, the higher the oil recovery is. Also, contact angle decreased as the size of the nanoparticles was decreased.
2. For small size nanoparticles, 7 nm, the oil recovery is not affected by the permeability of the core sample being used.
3. Initial rock wettability affected the incremental oil recovery. Intermediate oil-wet samples reported the highest incremental recovery. This is probably due to disconnection and trapping of oil phase.
4. Nanofluids injection rate had a strong impact on the oil recovery. As the flow rate was increased, the incremental oil recovery decreased. A flow rate of 0.2 cc/min or low is recommended.
5. Increasing temperature will increase the incremental oil recovery; however the mechanism is not well addressed.

Hendraningrat et al, (2014) investigated the effect of two metal oxides, aluminum and titanium oxides, with average particle sizes of 17-40 nm on oil recovery and compared them to silica nanoparticles. Polyvinylpyrrolidone (PVP) with average size of 50-250nm at different concentrations, 0.1, 0.5 and 1 wt%, was used as dispersant to stabilize the nanoparticles and avoid early aggregation. PVP was found to alter the fluid behavior, such as pH and surface conductivity, and successfully provide better stability at particular concentration.

Berra sandstones with permeability range from 118-330 md and porosity ranges from 14-16 %. Contact angle measurements were conducted to investigate the effect of these metal oxides. Results for these measurements indicated that metal oxides nanoparticles can change the wettability of the rock to more water-wet.

Then, coreflooding experiments were conducted using metal oxides dispersed in PVP, SiO2 nanoparticles dispersed in brine, brine only and PVP only. In all cases, nanofluids were used as tertiary recovery. Metallic oxides with PVP as dispersant showed higher recovery compared to SiO2, brine and PVP only with titanium oxide showing the higher recovery. From the results, it is concluded that metal oxides can be used for nano-EOR as an alternative to silica nanoparticles.

Hendraningrat et al, (2014) studied saline water in the presence of hydrophilic silica nanoparticles at different conditions such as temperature, concentration, various salt ions and nanoparticle size and initial rock wettability. Also, he ran fluid properties measurement such as density, viscosity, pH and surface conductivity. IFT and contact angle were studied as they might be the mechanism in improving oil recovery by nanofluids. Three different hydrophilic silica nanoparticles, that have different particle size, 7, 16 and 40 nm, were used for these studies. Brines with different salinity and compositions were used as dispersant for the nanoparticles. PVP with a size of approximately 1 µm to 250 µm was added to stabilize the nanoparticles in the solutions. Quartz plate and Bera core specimen were used to conduct the rock-fluid interactions.

From fluid-fluid interaction results, the effect of addition of PVP on the density or the viscosity of the dispersed fluid is very low. However, it adjusted the pH and surface conductivity of the nanofluids and reduced the IFT as well. PVP was found to reduce its efficiency at high temperature (>50 ^{o}C). Nanofluids reduced the IFT and altered the wettability of the rock surface. PVP alone was shown to not affect the wettability, however once hydrophilic NPs were introduced the contact angle reduced to towards more water-wetting. Increasing the concentration of nanofluids further decreased the contact angle of the aqueous phase.

The results from this particular study demonstrate that the wettability alteration plays a more dominant role in the oil displacement mechanism using nano-EOR.

Katherine et al, (2014) studied two kinds of nanoparticles Fumed Hydrophilic silica nanoparticle and Hydrophilic silica colloidal nanoparticle with average particle sizes of 7-75 nm. The objective of this study was to determine the optimum nanoparticle morphology and particle size for EOR while gaining insight into the mechanisms driving the system. Interfacial tension and contact angle measurements were conducted to understand the mechanisms behind nanoparticles followed by coreflooding experiments. The tests were conducted at ambient conditions using water wet, high permeability (avg.

K ≈ 362 mD) Berea sandstone cores. The nano flooding was conducted as a tertiary EOR method after secondary water flooding. A brine of salinity of 35 kppm was used as dispersant fluid and a stabilizer was used. All of the concentrated nanofluids contained a sodium hydroxide stabilizer with the exception of the large colloidal nanofluid which contained a potassium based stabilizer.

From the experiments, the IFT results showed that the addition of NPs to the brine decreases the IFT. The fumed NPs have a greater IFT reduction than the colloidal NPs, but there is no clear trend correlating with the core flooding results. The contact angle measurements also have no clear trend correlating with the core flooding results. From the coreflooding results, the fumed silica dispersions are a better choice for EOR applications than the colloidal silica. For both the fumed and colloidal NPs, there was a positive correlation between particle size and oil recovery. The larger the particle size, the larger the additional oil recovery.

Katherine et al, (2014) concluded that the IFT reduction mechanism likely plays a small role in the increase in oil recovery, but it cannot be the dominant mechanism. The log-jamming mechanism is likely the dominant mechanism in the system.

2.3 Retention and Transport of nano silica particles

Rodriguez et al, (2009) studied the retention and migration of silica nanoparticles with particle size ranges 5-20 nm. Nanoparticles were injected at different concentrations (up to 20 wt %), and in all cases nanoparticle breakthroughs occurred later than 1 PV. To properly understand the retention of nanoparticles in reservoir rock whose surface generally carries ionic charges, the electrostatic forces need to be fully understood. The electrostatic forces between the nanoparticles, and between the nanoparticles and the rock surface, govern the conditions under which nanoparticles aggregate or attach to the reservoir rock surfaces. Electrostatic forces are highly dependent on ionic strength. High ionic strengths reduce the size of the double layer, which then reduce or decrease the repulsive forces between the nanoparticles. Since the repulsive force decreases, aggregation of nanoparticles will increase.

In all experiments, nano silica particles were coated with polymer to allow the nanoparticles to stay dispersed in water without aggregation.

Six coreflooding experiments were conducted on two different rock types, limestone and sandstones. In all experiments nanoparticles coated with polymer were dispersed in water of different salinity. For the nanoparticles used for limestone, they were dispersed in DI water. However, for these used in sandstone, they were dispersed in 30 Kppm brine. Nanofluids were injected first and then followed by water injection to examine the retention. From the experiments, it is concluded that concentrated dispersion of suitably surface treated nanoparticles can be transported through sedimentary rocks, even those of low permeability. Two factors seem to be leading the ease transportation of these nanoparticles, the small size of them and the surface coating of these nanoparticles that ensures the ability of these nanoparticles to stay individually dispersed in water.

Jianjia et al, (2012) investigated the adsorption, retention and transpose of nano silica particles, with particle size of 11 nm, in three different rock types, limestone, sandstone and dolomite under conditions of high salinity. Nanoparticle dispersions are diluted to 5000 ppm with (2%NaCl).

The results of the adsorption tests showed that limestone has the highest adsorption equilibrium which could be due to the electrostatic forces between the nanosilica and the limestone surface. Sandstone showed low adsorption equilibrium and this is due to the composition of sandstone as SiO_2 is the dominant mineral. And since SiO_2 nanoparticles were injected, this result is expected. However, dolomite showed no adsorption equilibrium.

Then, three coreflooding experiments were conducted to study the transpose and retention of the silica nano particles in the three different rock samples. The first experiment was conducted using the sandstone sample, which has a moderate permeability. Nanoparticles were easily transported and had no effect on the rock permeability. The second experiment was conducted in the limestone sample. Although there was little adsorption, the permeability was not affected. In the third experiment, a dolomite of low permeability was used. Although dolomite was the highest in terms of particles recovery, core plugging occurred and the permeability was changed as observed from the pressure drop data. Small pore sizes of the dolomite could be the reason behind plugging.

Li et al, (2015) conducted a series of wettability measurement experiments for aged intermediate-wet Bera sandstones that have average permeability of 186 mD. Two kinds of hydrophilic silica nanoparticles, Nano-Structure Nanoparticles (NSP) and Colloidal Nanoparticles (CNP), were utilized for this experimental study. NSP hydrophilic silica nanoparticle has average particle size of 7 nm but it can aggregate to form bigger particle. However, CNP hydrophilic silica nanoparticle has average particle size of 18 nm and this kind of nanoparticles can't aggregate.

Three different concentrations of nanoparticles (0.05, 0.2 and 0.5 wt%) were used for this study with 30 kppm brine as the dispersed fluid. Wettability index measurements experiments and nanoparticles transport experiments were performed to evaluate the effect of nanoparticles adsorption and transport on wettability alteration.

From the wettability index measurements it was found that NSP altered the rock wettability to more water-wet with 0.2 wt% concentration showing the best result. Generally, the more the concentration of nanoparticles the more change in wettability is. However, it was not the case here as at high concentration the pores were plugged by the nanoparticles. Therefore, the wettability was shown to be less water-wet. CNP nanoparticles showed insignificant alteration of wettability at low concentration. However, the alteration was quite obvious at high concentration. Transport experiments revealed that NCP adsorption inside the core is very fast and strong and this adsorption is multilayer and almost irreversible. However, adsorption of CNP is weak especially for low concentration case. The more the concentration of NCP, the more the damage by the pore plugging is. However, high concentration of CNP makes the core more permeable.

2.4 Nanomaterial Improving Relative Permeability

Parvazdavani et al, (2012) studied one kind of poly silicon with particle sizes ranging from 10-500 nm. This nanoparticle was dispersed in brine of 10Kppm. In his study, he used one sandstone rock sample supplied from one of the Iranian fields that has a permeability of 10 md and porosity of 13.5%. Interfacial tension test was conducted between oil/brine and oil/nanofluid to study the impact of the nanofluid in the oil recovery. Relative permeability using unsteady-state test was conducted for both cases oil/brine and oil/nanofluid. Experimental results showed improvement of the non-wetting phase, oil phase.

2.5 Nanoparticles Stability

Paul Mc et al, (2012) used three types of nanoparticles dispersions (NPDs) and tested them for stability in both sandstones and carbonates. He used soft particle microemulsion with a basic silica nanoparticles, surfactant package with colloidal silica nanoparticles and surfactant package with surface modified silica nanoparticles. Generally, nanoparticles dispersions will become unstable and agglomerate in harsh environment, i.e. at high temperature and high salinity. NPDs can be stabilized in harsh environment by altering charge density, hydrodynamic diameter and the zeta potential of the particles. These can be accomplished by surface modification or by the addition of stabilizing chemistry. The performance of these nanoparticles was investigated through SP imbibition tests and coreflooding test.

The results revealed that the soft particle microemulsion with basic silica nanoparticles failed to stabilize in harsh environment due to their exposed surface charge. Surfactant package with colloidal silica nanoparticles was stabilized by acidic pH manipulation; however it was unstable at the extremes of salinity and temperature. Also being an acidic fluid, it will react with carbonate reservoir which could be undesirable. Surfactant package with surface modified silica nanoparticles showed the best stability in harsh environment. Once the surfactant package with surface modified silica nanoparticles showed its good efficiency, it is been carried out for a coreflooding test in both sandstone and limestone. Coreflooding results showed good performance of this nanoparticle to improve the oil recovery.

2.6 Mechanisms of Improving Oil Recovery by Nanoparticles

Hendraningrat et al, (2014) concluded that wettability alteration and IFT reduction are the main mechanisms behind the additional oil recovery by nanoparticles. However, different conclusions were drawn on wettability alteration by nanoparticles. Hendraningrat et al, (2013) concluded that wettability alteration to less water wet will enhance the oil recovery by nanoparticles, but Hendraningrat et al, (2014) observed that wettability alteration to more water-wet will increase the oil recovery. Different parameters were investigated by (Hendraningrat et al, 2014) on oil recovery by nanoparticles such as nanoparticles size, core samples permeability, flow rate and applied temperature. He concluded the following:

- The larger the size of nanoparticles, the better the oil recovery.
- Permeability of the core samples has no effect.
- The lower the flow rate, the better the oil recovery.
- And nanoparticles seemed to perform better at higher temperature.

Katherine et al, (2014) observed that mechanical mechanism is the dominant mechanism and IFT reduction and wettability alteration were not having a clear trend. Log-jamming due to higher particles size was the mechanism behind the additional oil recovery.

2.7 Ionic Content

Cigdem et al, (2011) and his colleagues studied the effect of electrolytes that exist in reservoir brines on the stability of silica nanoparticle dispersions. They started with dispersing the silica nanoparticles in water that has different concentrations of NaCl. The test results showed that NaCl concentration up to 1.5 wt% does not destabilize the silica nanoparticles. However, increasing the concentration of NaCl to more than 1.5 wt% will destabilize the silica nanoparticles, they will aggregate and then sediment. The explanation to this phenomenon is that NaCl will reach its critical salts concentration (CSC) at a concentration of 1.5 wt%. After that, they studied the effect of divalent cations that present in reservoir brines such as Mg2+, Ca2+, and Ba2+. The test results showed that divalent cations are more effective in destabilizing the silica nanoparticles, even at a very low concentration, than the monovalent cation. A divalent cation of concentration of 0.04 wt% can destabilize the silica nanoparticles. The reason is that divalent cations will reach its CSC at a very low concentration.

CHAPTER 3

Experimental & Materials

A brief description of all the used materials and equipment in this thesis will be described below.

3.1 Materials

3.1.1 Rock Samples and Rock Chips

Indiana limestone core samples of 2” length and 1.5” diameter were used in coreflooding experiments. Three core samples (LS1, LS2, LS3) that are shown in (Figure 3.1) were used that have porosity of 16.03%, 16.84% and 17.5% respectively. They have gas permeability of 328.6 mD, 410.6 mD and 210 mD respectively. Thin limestone chips of 1mm (Figure 3.2) were prepared for contact angle measurements.

Figure 3-1 Indiana limestone core samples

Figure 3-2 Indiana limestone chips

3.1.2 Brines and Crude Oil

Synthetic seawater that has a salinity of 67 kppm and density of 1.0411 at 25°C was used for most of the experiments in this study. Its salts composition for 1 liter is shown in (Table 3.1). NaCl brines of different salinities (i.e 1, 6.5, 12.5, 30, 50 kppm) were also prepared and used in this study in the nanofluid stability test. A crude oil that has a density of 0.8651 at 25°C was used. Some tests in this study required seawater and crude oil densities at elevated temperatures and pressures. The measured densities of seawater and crude oil at different pressures and temperatures are presented in (Figure 3.3 and 3.4), respectively.

Table 3-1 Seawater salts composition

Salt	Weight (g)
$NaHCO_3$	0.24
Na_2SO_4	6.58
NaCl	40.29
$CaCl_2*2H_2O$	2.39
$MgCl_2*6H_2O$	18.06

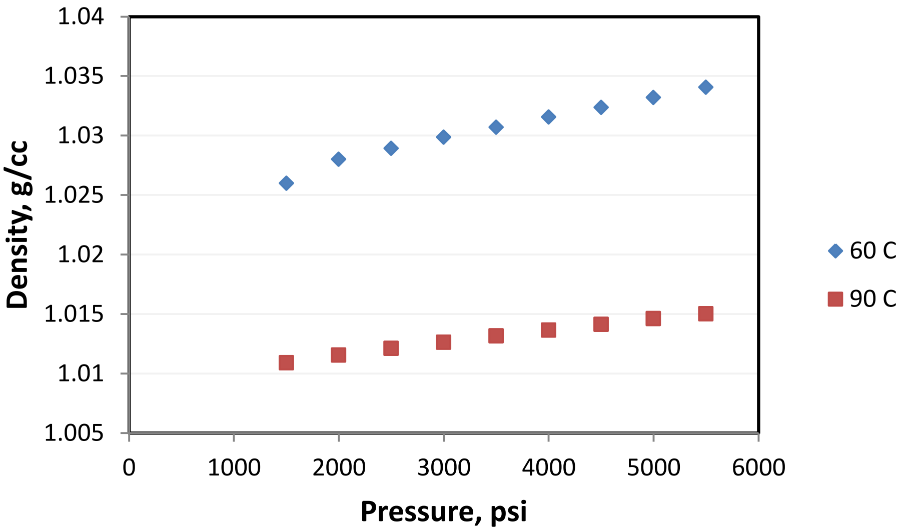


Figure 3-3 Seawater densities at elevated pressures and temperatures

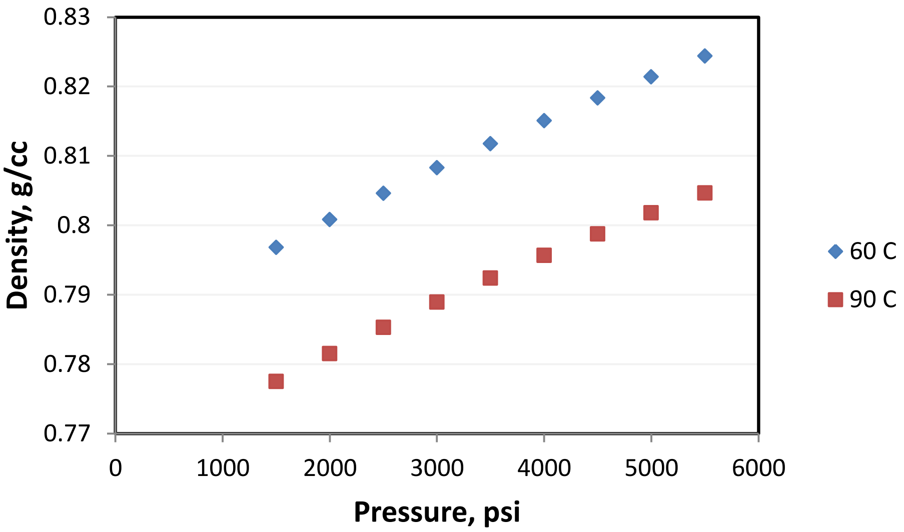


Figure 3-4 Crude oil densities at elevated pressures and temperatures

3.1.3 Nanoparticles

Natural zeolite materials that are abundant in nature were used throughout this study. These natural zeolite materials were analyzed using X-ray Powder Diffraction (XRD) and found to be composed of the minerals that are shown in Table 3.2.

Table 3-2 Natural zeolite composition

Symbol	Concentration, wt%
Al_2O_3	6.61
SiO_2	44.38
P_2O_5	0.62
K_2O	0.99
CaO	3.44
TiO_2	0.34
Fe_2O_3	1.99

3.1.4 Surfactants

Different surfactants as shown in Table 3.3 were used in this study for the purpose to stabilize nanoparticles in seawater. All the surfactants were at 1% concentrations from the total dispersant solution which has seawater and nanofluid.

Table 3-3 Surfactants

Surfactant	Concentration
Polyethylene glycol (PEG)	1%
Tergitol	1%
Triton surfactant	1%
(Cetyl trimethylammonium bromide) CTAB	1%
Solsperse	1%
Pluronic	1%
Synperonic	1%
Polyvinylpyrrolidone (PVP)	1%

3.2 Equipment

3.2.1 Natural Zeolite Crushing to Microscale

A sample of 50 g from the natural zeolite was first crushed using Jaw Crusher BB50, Figure 3.5. This machine can only take maximum feed size of 40 mm and the final fineness that can be achieved can be up to 0.5 mm or below depending on the feed material.

The crushed zeolite materials that have particle sizes range from 0.5 mm and below were then taken for further crushing to micro scale using Oscillating Mill MM400 (Figure 3.6). Final fineness of down to 1 µm can be achieved, depending on the milling time and the specific properties of the sample material.

Figure 3-5 Jaw Crusher B50

Figure 3-6 Oscillating Mill MM400

3.2.2 Natural Zeolite Crushing to Nanoscale

All crushed zeolite materials to microscale were taken to one more crushing step to bring them down to nanoscale. HD-01/HDDM-01 Lab Attritor equipment as shown in (Figure 3.7) was used for this purpose. This equipment has a tank, where the material to be crushed is placed, and this tank is made of zirconium oxide. It also has an agitator disk that is made of zirconium, too.

The nanoparticles that are in microscale were first dispersed in deionized water (DIW) to create what is called nanofluid, Figure 3.8. Then the dispersant was put in the tank and crushing was taking place for 12 hours at a speed of 2000 RPM.

Figure 3-7 HD-01/HDDM-01 Lab Attritor

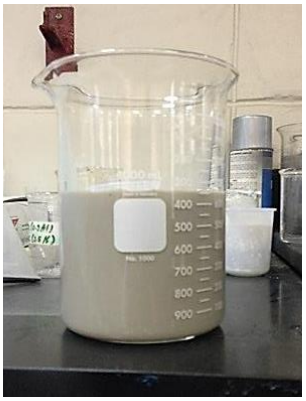


Figure 3-8 Zeolite nanoparticles dispersed in DIW

3.2.3 Zeolite Nanoparticles Size Determination

After crushing the particles to nanoscale, it is required to know their sizes range. Scanning Electron Microscopy (SEM) instrument (Figure 3.9) was used for this purpose. (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

In this study, different samples of the prepared nanofluids were analyzed to know the nanoparticles size distributions.

Figure 3-9 Scanning electron microscopy (SEM) instrument

3.2.4 Centrifuge

Centrifugation of nanofluid was needed to separate some large size nanoparticles using a centrifuge instrument, Figure 3.10.

Figure 3-10 Centrifuge for fluid separation

3.2.5 Turbiscan

A turbiscan instrument (Figure 3.11) is used in order to characterize the dispersion state of emulsions, suspensions and foams. Changes in terms of size and concentration (such as creaming, sedimentation, flocculation or coalescence...) are directly monitored, in realistic conditions enabling faster and more relevant characterization compared to common methods such as visual observation or centrifugation, which are time-consuming or non-realistic. In this study, the turbiscan instrument was used to observe the stability of some nanofluids dispersants.

Figure 3-11 Turbiscan instrument

3.2.6 Automated Permeameter-Porosimeter

Porosity and permeability for the core samples used were measured using AP-608 Automated Permeameter-Porosimeter, Figure 3.12.

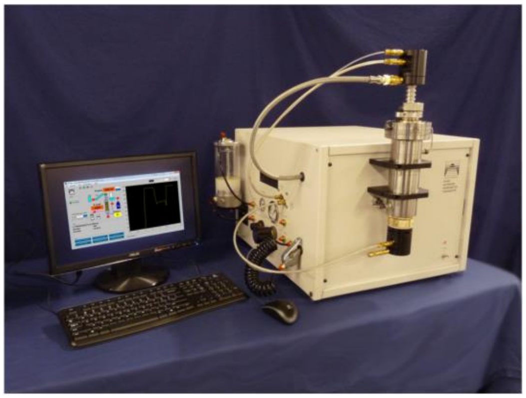


Figure 3-12 AP-608 Automated Permeameter-Porosimeter

3.2.7 Interfacial Tension

Interfacial tension (IFT) exists when two phases are present. In our case these phases are oil/brine and oil/brine plus nanoparticles. Interfacial tension is the force that holds the surface of a particular phase together and is normally measured in dynes/cm. It is a function of pressure, temperature, and the composition of each phase. Capillary pressure caused by IFT between reservoir fluids is the most basic rock-fluid property in multiphase flow. Capillary forces resist externally applied viscous forces and hence, to large extent govern the mobility of the reservoir. Capillary forces can cause large quantities of oil to be left behind. Therefore, the applied EOR should be capable to lower the IFT by several orders of magnitude to recover more oil. For this study, KRUSS Drop Shape Analyzer as shown in (Figure 3.13) was used to measure the (IFT).

Figure 3-13 KRUSS drop shape analyzer

3.2.8 Contact Angle

The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface. Contact angles, measured for crude oil against brine on smooth mineral surfaces, have been used to characterize wettability. Treiber et al (1971), developed the classification for the contact angle in a three phase system (oil, water and surface). A contact angle in the range of 0^o – 75^o indicates water-wet conditions, a contact angle in the range of 75^o – 105^o indicates intermediate-wet conditions and a contact angle in the range of 105^o – 180^o indicates oil-wet conditions. VINCI IFT 700 equipment was used in this study for measuring the contact angle on carbonate surfaces, Figure 3.14.

Figure 3-14 VINCI IFT 700

3.2.9 Zeta Potential

Zeta potential is the measured point between two separate particles and the strength of electrostatic attraction/repulsion between them. The charge of the particle, positive or negative, corresponds to positive and negative zeta potential. It is one of the fundamental parameters known to affect stability. Its measurement brings detailed insight into the causes of dispersion and/or aggregation, thus it can be applied to improve the formulation of dispersions. Zeta potential of different nanofluids was measured to find the most stable nanofluid dispersion using Zetapals instrument, Figure 3.15. Zetapals instrument uses a phase-analysis light-scattering (PALS) technique to determine the electrophoretic mobility (speed measurement) of charged colloidal suspensions, and calculates the ζ – Potential (in mV) with the Smoluchowsky and Huckel model. The model equation is given as follows:

$$\zeta = 113000\, EM\, \frac{v_t}{D_t} \tag{3.1}$$

Where ζ = zeta potential (mV); v_t=viscosity of the suspending liquid in poises at temperature t; D_t= dielectric constant of the suspending liquid at temperature t; and *EM*=electrophoretic mobility at actual temperature.

Figure 3-15 Zeta potential instrument

3.2.10 Coreflooding Setup

Coreflooding experiments will be conducted to study the performance of the nanofluids in oil recovery compared to normal seawater flooding. A schematic of the coreflooding setup is shown in, Figure 3.16. The system consists of two vessels that have brine and nanofluids. A pump is used to flow a “pump fluid” to push the piston plate inside the vessels. The piston plate is useful to separate different fluids without mixing. The reason for this is that injection of nanofluids by pump directly harmful for the pump. The rock sample used in this study is placed inside a core holder in a rubber sleeve. This rubber sleeve will be confined with a pressure of around 1000 psig using an overburden pump. Then to mimic the reservoir conditions, the core holder will be placed inside an oven and high temperature will be applied. Once reservoir conditions are established, seawater that has a salinity of 57 kppm will be injected at a rate of 0.1 cc/min as a secondary recovery until no more oil production by this brine is seen.

Then, the flooding will be switched to a tertiary recovery using nanofluids at optimum concentration. Nanofluids will be injected at a rate of 0.1 cc/min to allow sometime for the nanoparticles to interact with the rock surface and fluids in the pores. The oil recovery performance, expressed as the percentage of initial oil in place, for each flooding scenario will be then evaluated.

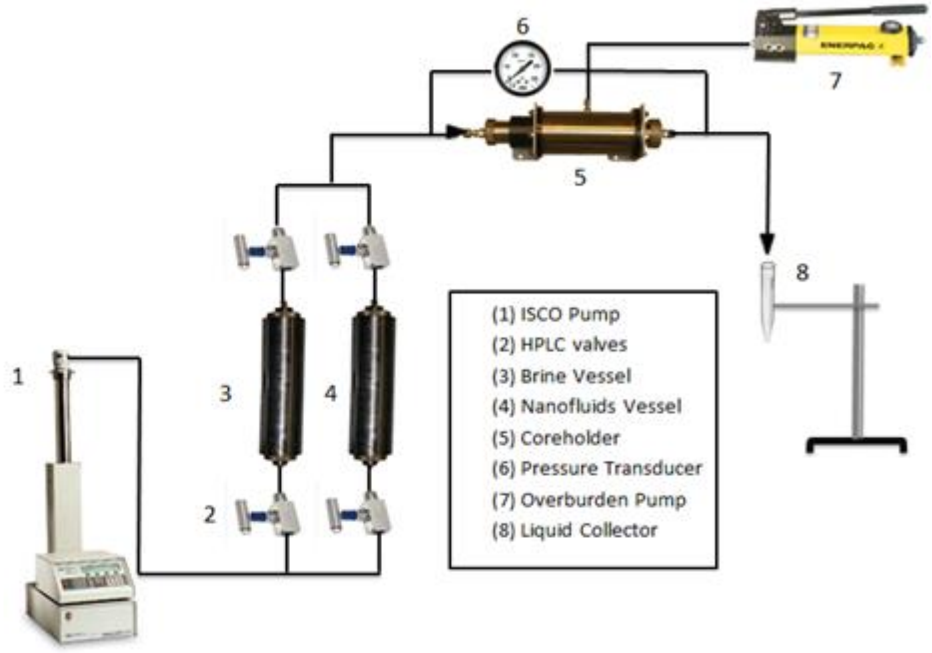


Figure 3-16 Schematic diagram of coreflooding setup

3.2.11 High Shear Mixer

A high shear mixing instrument (Figure 3.17) that is suitable for the widest range of applications mixing, emulsifying, homogenizing, disintegrating and dissolving was used in this study to mix some nanofluids dispersants. The used instrument has a capacity from 1ml up to 12 liters and the ability to mix in-line with flow rates up to 20 liters/minute.

Figure 3-17 Shear mixer instrument

3.3 Experimental Methodology

3.3.1 Size Analyses of Zeolite Nanoparticles

The first step before doing any experiment using the prepared nanoparticles is to make sure that they are of right size. After finishing all the crushing phases of the nanoparticles, nanoparticles sample will be sent for (SEM) to have a basic idea of particles size distributions. When the crushed sample was analyzed under (SEM) instrument, different ranges of bigger particles were noticed as shown in the (SEM) image below (Figure 3.18). Some particles have sizes range from 250 nm to 500 nm. Such particles may cause a lot of problems when it comes to real application, as bigger particles tend to attach smaller particles to them. Therefore, they will be getting heavier enough which could result in precipitation of these particles. Also, bigger particles can result in plugging of some pore channels when they are injected in the reservoir for example.

Therefore, it is very important to have nanoparticles that are smaller in sizes (i.e. 100 nm or below). In order to get rid of bigger particles, centrifugation was done using a centrifuge instrument for fluid separation where bigger particles were separated from smaller once. Multiple tests were performed at different centrifugation times and at fixed centrifugation speed of 3000 RPM. After each test, a sample was sent to (SEM) lab to check the particles sizes. Three tests were done at different centrifugation times (i.e. 5, 20, 35 minutes) and the results of (SEM) analyses are as shown in (Figure 3.19-3.21). As seen from the (SEM) images that a centrifugation of 35 minutes is good enough to have a small size range of particles. Particles are ranging from 50-70 nm.

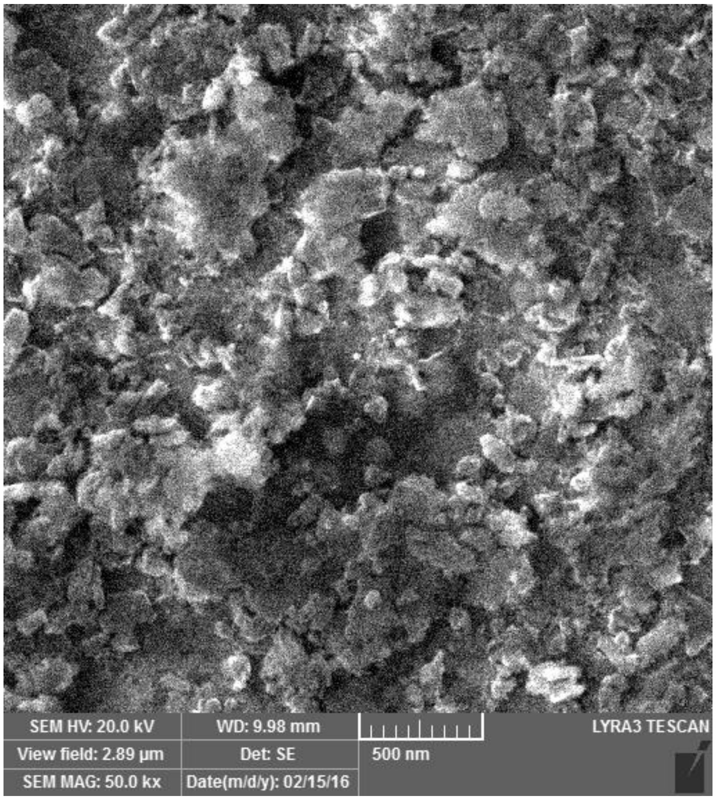


Figure 3-18 (SEM) Image for crushed zeolite nanoparticles

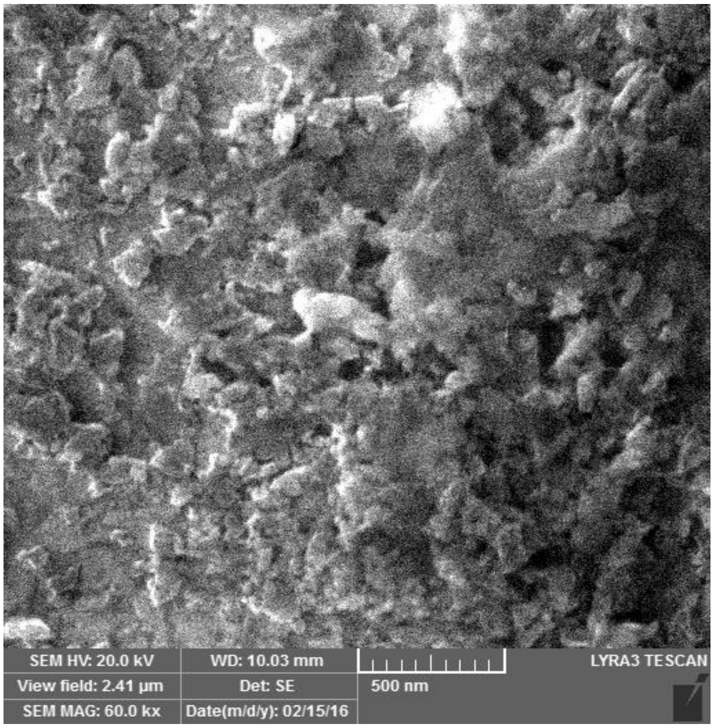


Figure 3-19 (SEM) Image of nanoparticles after centrifugation of 5 min

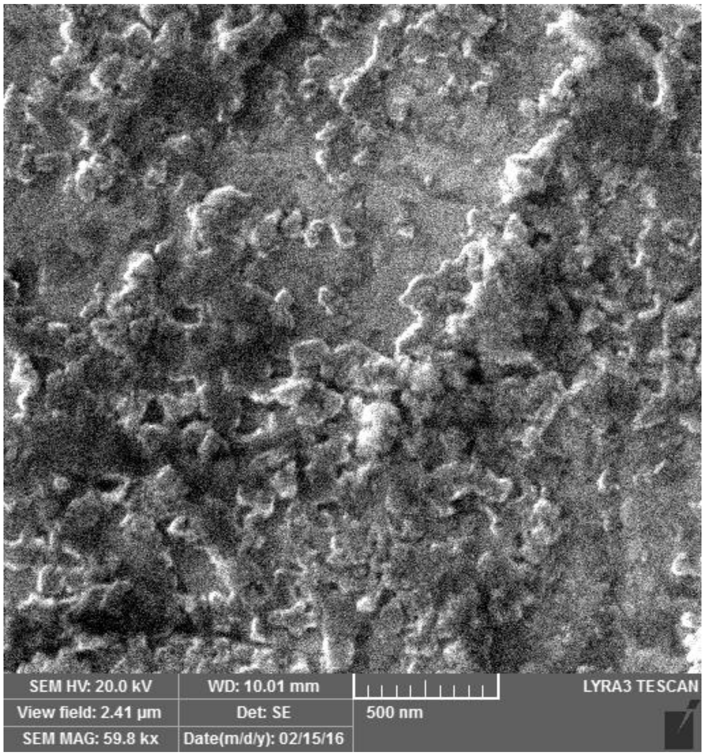


Figure 3-20 (SEM) Image of nanoparticles after centrifugation of 20 min

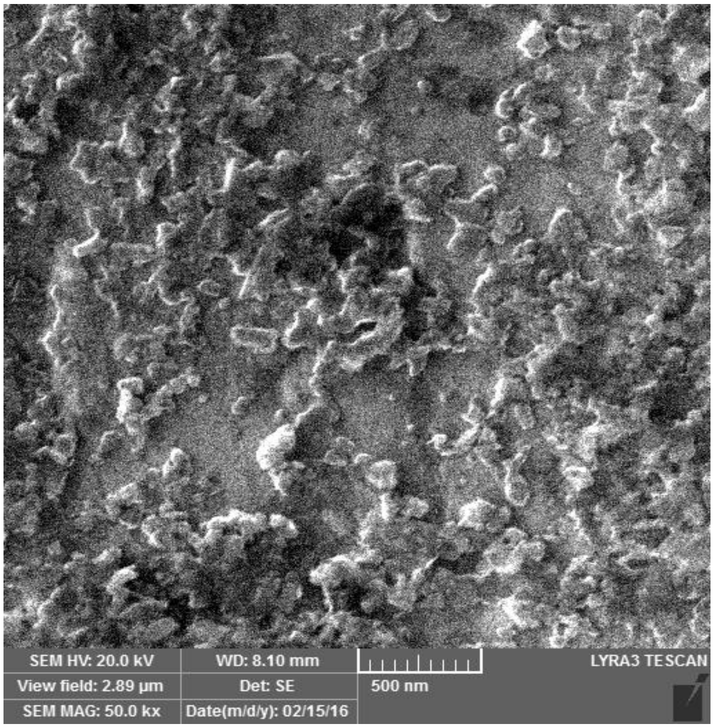


Figure 3-21 (SEM) Image of nanoparticles after centrifugation of 35 min

CHAPTER 4

Results and Discussion

4.1 Stability of Zeolite Nanoparticles

4.1.1 Stability of Zeolite Nanoparticles in Aqueous Solutions

After getting the right size of nanoparticles, it is very important to check their stability in the planned fluids (i.e. synthetic seawater and NaCl brines). Their degree of stability or dispersant in the fluids will help to answer the question whether these nanoparticles is good as a promising EOR agent.

Zeolite nanoparticles were found to show good stability in deionized water and precipitation started to take place only after 5 days. However, when synthetic seawater was used as a dispersant fluid for these nanoparticles, the precipitation of the nanoparticles took place in less than 1 hour. Different concentrations of the nanoparticles were tried and the conclusion was the same, precipitation in less than 1 hour, as shown in (Figure 4.1) where at the bottom of the vails clearly seen precipitated nanoparticles.

Figure 4-1 Nanoparticles dispersed in seawater after 1 hour

After that, it was very important to know what drive precipitation and why it is taking place. To help to understand that, all salts that exist in sweater were analyzed; nanoparticles were dispersed in each salt separately. Each salt was taken and dissolved in deionized water, and then nanoparticles were dispersed in that solution. NaCl was analyzed first at that dissolved in deionized water at different concentrations (i.e. 1, 6.5, 12.5, 30, 50 kppm). The tests were showing that at NaCl concentration of 6.5 kppm or less, the nanoparticles will stay stable in solution for almost 3 days. However, at higher NaCl concentrations it was easy to destabilize the nanoparticles. At a concentration of 12.5 kppm, it took 1 day to have full nanoparticles precipitation, while for other higher concentrations almost 6 hours was enough to have full precipitations of the nanoparticles.

Figure 4.2 showed the tested nanoparticles samples at different NaCl concentrations. This observation of nanoparticles precipitation in NaCl solutions was also noted by Metin *et al* (2011), where they concluded that NaCl at concentration higher than 15 kppm will result in destabilization of silica nanoparticles as NaCl will reach its critical salt concentration (CSC) at a concentration of 15 kppm. During their experiments, they observe three stages of particles aggregations (1) an early stage where the dispersant is a single clear phase, (2) precipitation stage with a single turbid phase, and (3) a sedimentation stage with two separate phases. Then, the other different salts in seawater were checked. Sodium Sulfate (Na_2SO_4) and Sodium bicarbonate ($NaHCO_3$) were showing good stability, at least for 3-4 days, for the nanoparticles dispersed in them (Figure 4.3). However, when the divalent cation salts were checked (i.e. Calcium Chloride ($CaCl_2$) and Magnesium Chloride ($MgCl_2$)) at different concentrations, precipitation of nanoparticles took place in less than 1 hour, regardless of the salts concentrations (Figure 4.4 and Figure 4.5). This was also explained by Metin *et al* (2011) as $MgCl_2$ and $CaCl_2$ will reach their (CSC) at 0.125 kppm and 0.25 kppm, respectively, which are 50-100 times less than that for NaCl.

Figure 4-2 Nanoparticles dispersed in NaCl solutions of different concentrations

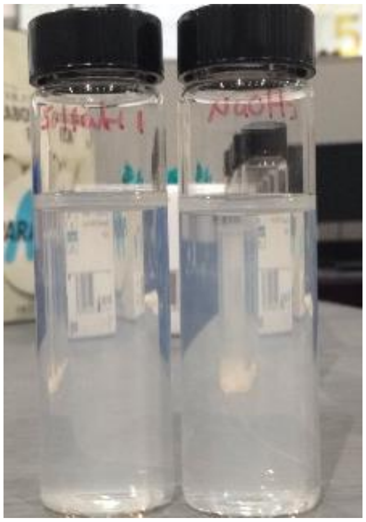


Figure 4-3 Nanoparticles dispersed in Na_2SO_4 and $NaHCO_3$ solutions after 3 days

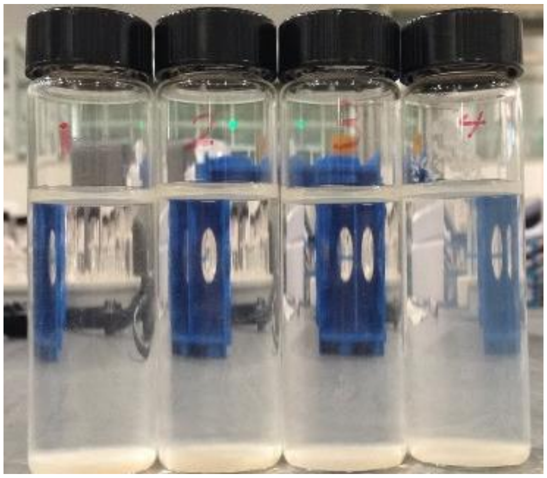


Figure 4-4 Nanoparticles dispersed in different concentrations of $MgCl_2$ after 1 hr

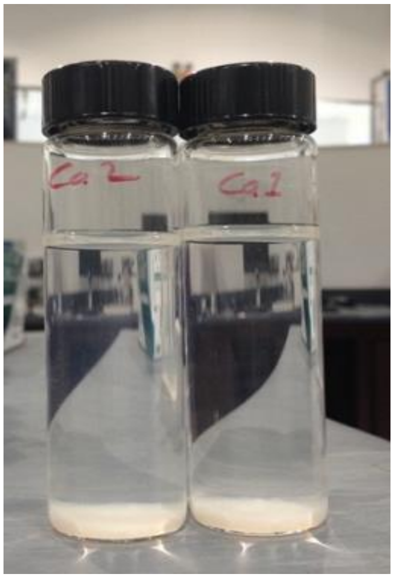


Figure 4-5 Nanoparticles dispersed in different concentrations of $CaCl_2$ after 1 hr

4.1.2 Zeta Potential to Check Stability of Zeolite Nanoparticles in Aqueous Solutions

The stability of the different nanofluids dispersants was also checked by the mean of measuring zeta potential which is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles. Zeta potential is one of the fundamental parameters known to affect stability and its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation. The zeta potential is also known as the electric potential in the interfacial double layer at the location of the slipping plane relative to a point in the bulk fluid away from the interface which described by Greenwood and Kendall (1999), in (Figure 4.6) . It can be also described as the potential difference between the dispersion medium and the stationary layer (Stern layer) that is attached to the dispersed particle. It is measured in unit of millivolt (mV), and its magnitude as described by Greenwood and Kendall (1999), indicates the stability behavior as shown in (Table 4.1). All measured zeta potential values for the different dispersant are listed in (Table 4.2) along with their pH.

Table 4-1 Zeta potential magnitudes and their stability behavior indications

Zeta potential (mV)	Stability behavior of the colloid
from 0 to ±5	Rapid coagulation or flocculation
from 10 to ±30	Incipient instability
from 30 to ±40	Moderate stability
from 40 to ±60	Good stability
more than ±61	Excellent stability

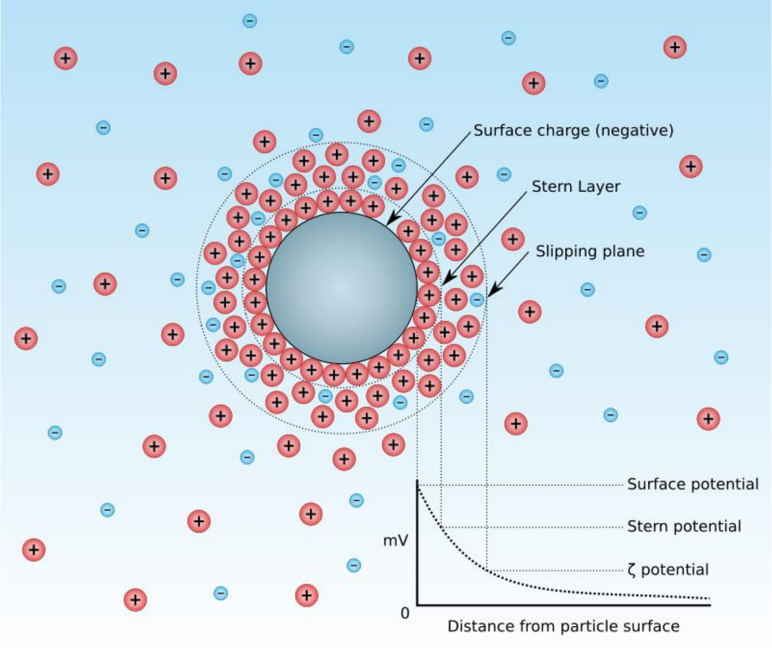


Figure 4-6 Diagram showing the ionic concentration and potential difference as a function of distance from the charged surface of a particle suspended in a dispersion medium.

Table 4-2 Zeta potential of different nanofluids dispersants

Solution	pH	Zeta Potential, mV
Deionized Water + 0.05 wt% nanoparticles	6.52	-30.97
Sodium Sulfate + 0.05 wt% nanoparticles	7.03	-26.62
Sodium Bicarbonate + 0.05 wt% nanoparticles	8.29	-26.82
Magnesium Chloride + 0.05 wt% nanoparticles	6.66	-7.23
0.1 wt% Sodium Chloride + 0.05 wt% nanoparticles	7.01	-24.08
0.65 wt% Sodium Chloride + 0.05 wt% nanoparticles	6.89	-20.30
1.25 wt% Sodium Chloride + 0.05 wt% nanoparticles	6.83	-13.50
3 wt% Sodium Chloride + 0.05 wt% nanoparticles	6.71	-6.90
5 wt% Sodium Chloride + 0.05 wt% nanoparticles	6.54	…
Seawater (5.7 wt%) + 0.05 wt% nanoparticles	8.08	…

Form the results presented in (Table 4.2), it is confirmed that nanoparticles have moderate stability in deionized water as the zeta potential showed a value of -30.97 mV according to the study done by. Divalent cations salt such as $MgCl_2$ was confirmed to cause rapid coagulation or flocculation as the reported zeta potential value is -7.23 mV. Other monovalent cations salts that are presented in seawater, such as Na_2SO_4 and $NaHCO_3$ were shown to have incipient to almost moderate stability of the nanoparticles as the zeta potential values were -26.62 mV and -26.82 mV, respectively. It was also concluded that nanoparticles will have incipient stability in low concentrated NaCl solutions.

Nanoparticles dispersed in a 0.1 wt% NaCl solution showed to have a zeta potential value of -24.08 mV, whereas nanoparticles dispersed in a 0.65 wt% NaCl solution showed to have a zeta potential value of -20.30 mV. For nanoparticles dispersed in a 1.2 wt% NaCl solution, the zeta potential value was -13.50 mV which is almost near the zone of rapid coagulation or flocculation. However, at higher NaCl concentrations (i.e. 3 wt%) the nanoparticles will be easily destabilized as the zeta potential value is-6.90 mV. When the NaCl concentration was furtherly increased to 5 wt%, it was very difficult to get a reliable zeta potential measurement. The zeta potential values were fluctuating between negative and positive zeta values which indicate non-stability of nanoparticles. Similar behavior was noted when measured the zeta potential of the nanoparticles dispersed in seawater.

The aggregation and therefore the precipitation of nanoparticles at high ionic concentrations can be explained by the DVLO theory. The theory explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through a liquid medium. In the case of the nanoparticles dispersants aqueous solutions, the nanoparticles are having double layers or what so called electrical double layer. The first layer is related to the surface charge of these nanoparticles either positive or negative depending on the type of the nanoparticles used. The second layer, which is parallel to the first layer, is associated with dispersed fluid under the influence of electric attraction between the nanoparticle surface and the ions in the fluid. The second layer is called a diffuse layer. The nanoparticles will repel each other when dispersed in a fluid preventing themselves from aggregation and then precipitation due to gravity. However, at high ionic fluid concentrations such as brines, the repulsive forces or energies between the nanoparticles will be reduced as a result of collapsing of the electrical double layers. The repulsion energy, that is a function of the thickness of the electrical double layer, decreases as electrolyte concentration increases. Therefore, the total interaction energy that was described by Reerink and Overbeek (1954), changes as a function of electrolyte concentration. They showed that the aggregation rate is proportional to the maximum interaction energy. Equation (4.1) is best described the theory of aggregations. They divided the aggregations into two regimes, a fast regime and a slow regime.

At high ionic concentrations, fast aggregations regime of the nanoparticles will occur as a result of absence of the maximum interaction energy at high ionic salts concentrations. This should explain the aggregation behavior of the nanoparticles dispersed in the different aqueous solutions used. Metin *et al* (2011), studied the effect of different solutions that have different NaCl concentrations on the aggregation of silica nanoparticles. The results showed that an increase in the aggregation effective size as a function of NaCl concentrations.

$$W \approx \frac{1}{2\kappa a} e^{\left(\frac{V_{T\max}}{k_B T}\right)} = \frac{k_{fast}}{k_s} \tag{4.1}$$

Where:

W: Stability ratio

a: Particle Radius

K_B: Boltzmann constant

T: Temperature

$V_{T\max}$: The maximum total interaction energy

K_{fas}: The aggregation rate constant

K_s: The actual aggregation rate constant

4.1.3 Surfactants to Stabilize the Nanoparticles in Seawater

From the above discussions, it can be concluded that it is very hard to make the nanoparticles suspended in seawater for a longer period of time and since seawater is an available source that is widely used, easy to get and doesn't need a lot of investments. Therefore, it would be more economically to suspend the nanoparticles in seawater in order to be injected in the reservoirs.

Surfactants can be used in this regard to act as a dispersant agent that can be added to the nanoparticles suspensions, to improve the separation of these particles and avoid early aggregation that will result then in nanoparticles precipitation. Eight different surfactants were tried to help dispersed the nanoparticles in seawater. Polythylene (PEG), Tergitol, Triton, Cetyl trimethylammonium bromide (CTAB), Solsperse, Pluronic, Synperonic and Polyvinylpyrrolidone (PVP) surfactants were all tested. These surfactants were added at optimum concentrations of 1 wt% to seawater solutions contain a fixed nanoparticles concentration of 0.05 wt%. Each seawater solution that contains a surfactant of 1 wt% and nanoparticles of 0.05 wt% was stirred for 25 minutes at a rotation speed of 5000 revolution per minute (RPM) using a high shear mixer. Then, all the dispersants were observed by naked eye. The observation results for all the dispersants are presented in (Table 4.3). The results showed that (PVP) is best in dispersing the nanoparticles of 0.05 wt% for a longer period of time, almost 9 hours. Therefore, (PVP) surfactant was considered for further measurements and tests.

Table 4-3 Observation results of surfactants used for nanoparticles dispersion

Surfactant	Concentration, wt%	Test Conditions	Observations
Polyethylene glycol (PEG)	1.0	Stirring for 25 min @ 5000 rpm	Precipitation in 1 hr 20 min
Tergitol			Precipitation in 2 hr
Triton surfactant			Precipitation in 1 hr 30 min
(Cetyl trimethylammonium bromide) CTAB			Precipitation in 4 hr
Solsperse			Precipitation in 2-3 hr
Pluronic			Precipitation in 2-3 hr
Synperonic			Precipitation in 2-3 hr
Polyvinylpyrrolidone (PVP)			Precipitation in 8-9 hr

4.1.4 Polyvinylpyrrolidone (PVP) Surfactant to Disperse the Nanoparticles in Seawater

Since (PVP) surfactant showed the best to disperse nanoparticles in seawater, it was considered for all upcoming tests and measurements. First of all, different dispersants were prepared that contain (PVP) of 1% and different concentrations of nanoparticles (i.e. 0.02 wt%, 0.03 wt%, 0.05 wt%, 0.075 wt% and 0.1wt%) and there were observed for stability. Zeta potential measurements were conducted for the three dispersants and results are presented in (Table 4.4) and (Figure 4.7). From the results, it can be clearly seen that at nanoparticles concentrations of 0.02 wt%, 0.03 wt% and 0.05 wt% the three dispersants have incipient stability and almost the same zeta potential values were reported. However, at higher nanoparticles concentration (i.e. 0.075 wt% and 0.1 wt%) the dispersants have rapid aggregations and therefore rapid precipitations. So, it can be concluded that for a (PVP) concentration of 1%, the maximum nanoparticles concentration to be used is 0.05 wt%. For higher nanoparticles concentrations, higher concentration of (PVP) is needed.

Table 4-4 Zeta potential of nanoparticles dispersed in seawater with 1 wt% of (PVP)

Solution	pH	Zeta Potential, mV
Seawater (5.7 wt%) + 0.02 wt% nanoparticles + 1.0 wt% PVP	7.79	-15.04
Seawater (5.7 wt%) + 0.03 wt% nanoparticles + 1.0 wt% PVP	7.83	-14.39
Seawater (5.7 wt%) + 0.05 wt% nanoparticles + 1.0 wt% PVP	7.86	-16.82
Seawater (5.7 wt%) + 0.075 wt% nanoparticles + 1.0 wt% PVP	7.57	-7.80
Seawater (5.7 wt%) + 0.1 wt% nanoparticles + 1.0 wt% PVP	7.51	-2.78

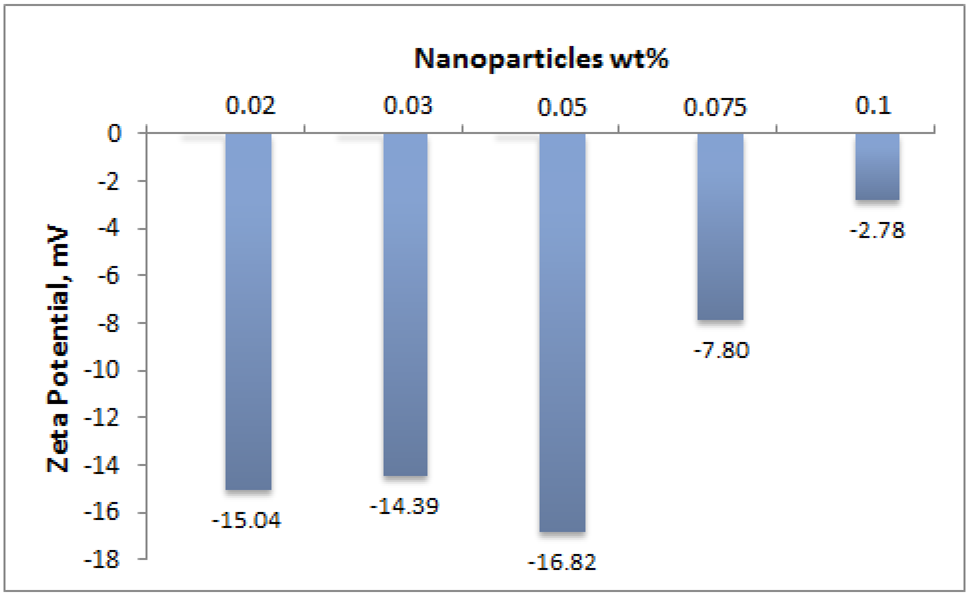


Figure 4-7 Zeta potential of nanoparticles dispersed in seawater with 1 wt% of (PVP)

From the above results, 0.05 wt% nanopartciles concentration was considered as the optimum concentration and was used for all the different measurements conducted forward.

The next step was to lower the concentration of PVP and check whether a lower concnetration can still help in dispersing the 0.05 wt% nanoparticles for a longer period of time in seawater. Different concentrations of (PVP) were tested (i.e. 0.3 wt%, 0.5wt%, 0.7 wt% and 1 wt%). The zeta potentail measurements were taken and the results are presented in (Table 4.5) and (Figure 4.8). From the results, it was concluded that (PVP) of concenration of 1 wt% was best in dispersing the nanopartilces of 0.05 wt% concentration for a longer period of time as the reported zeta potentail value was the highest.

Table 4-5 Zeta potential of nanoparticles dispersed in seawater with different (PVP) concentrations

Solution	pH	Zeta Potential, mV
Seawater (5.7 wt%) + 0.05 wt% nanoparticles + 0.3 wt% PVP	8.01	-4.66
Seawater (5.7 wt%) + 0.05 wt% nanoparticles + 0.5 wt% PVP	7.79	-10.03
Seawater (5.7 wt%) + 0.05 wt% nanoparticles + 0.7 wt% PVP	7.80	-12.07
Seawater (5.7 wt%) + 0.05 wt% nanoparticles + 1 wt% PVP	7.86	-16.82

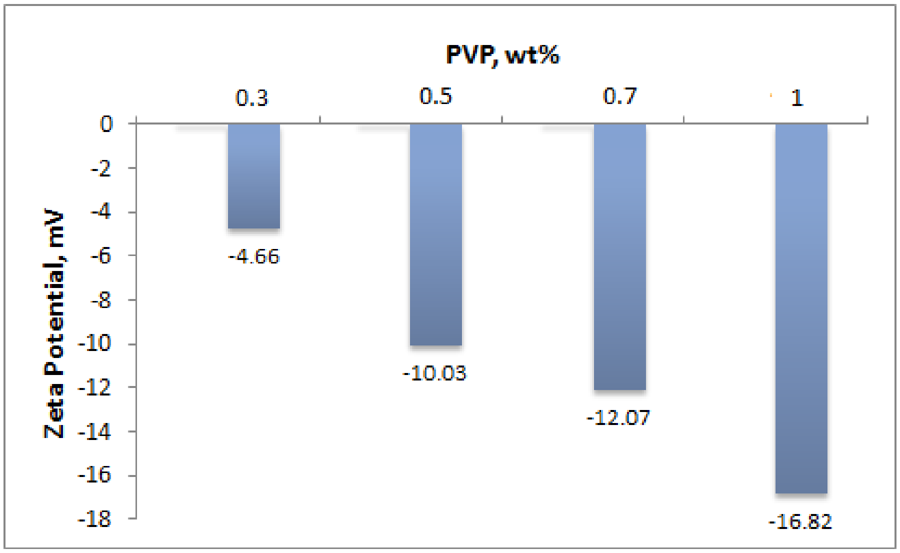


Figure 4-8 Zeta potential of nanoparticles dispersed in seawater with different (PVP) concentrations

4.2 Precipitation Phenomena of the Nanofluids Dispersants

To help understand the precipitation phenomenon of the different nanofluids dispersants, the four samples of the nanofluids dispersants of different (PVP) concentrations were sent for turbidity scan measurements. The scan measurements are shown in (Figure 4.9 – Figure 4.12). The figures show both the transmission and back scattering along the length of the scanned tubes that contain the nanofluids dispersants. Clearly from the figures, the transmission percentage, which is increasing with time, it is almost the same across the length of the scanned sample at any particular time. Therefore, the interpretation from these figures is that the dispersed nanoparticles will first agglomerate forming larger foam of particles. Then, sedimentation/precipitations of nanoparticles will start to happen, which is faster at low (PVP) concentrations. Figure 4.13 better explain the precipitation process. Looking to the transmission curves for all the scanned samples, (PVP) of 1 wt% showed the latest to start the agglomeration of nanoparticles.

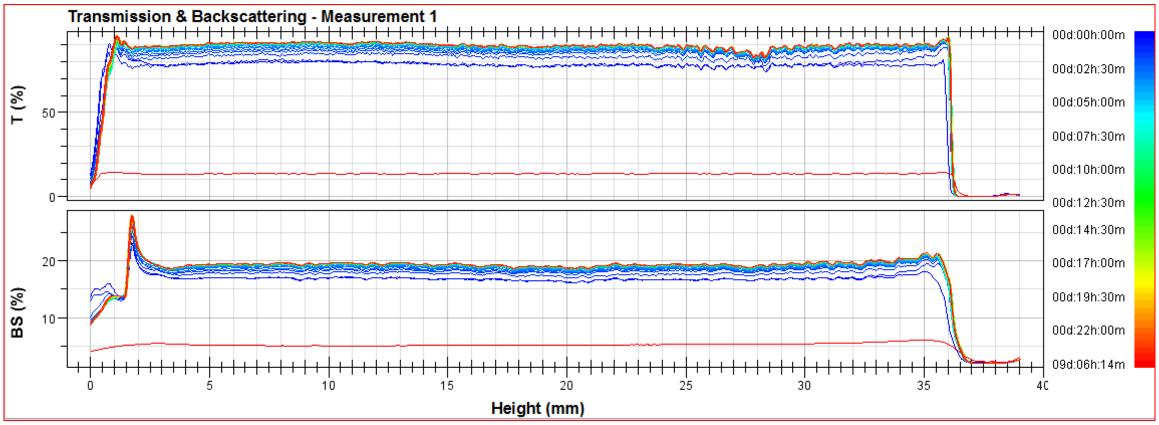


Figure 4-9 Turbidity scan results for seawater plus 0.3 wt% (PVP) plus 0.05 wt% nanoparticles

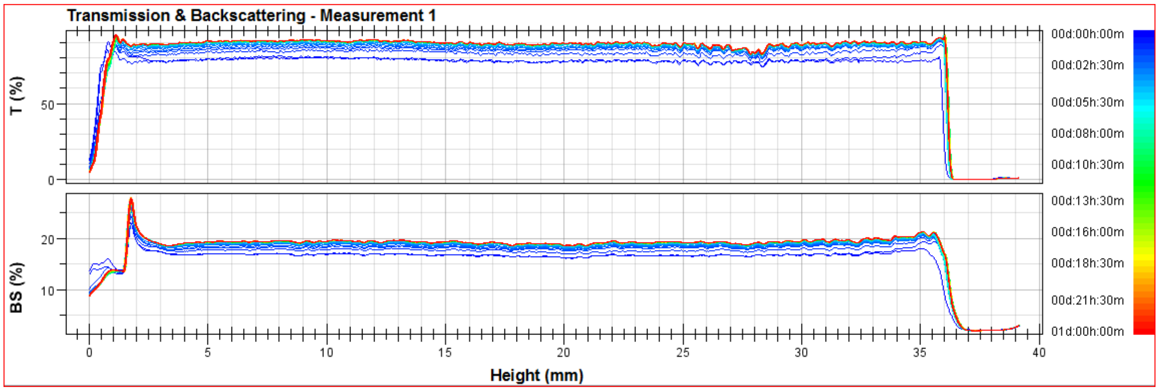


Figure 4-10 Turbidity scan results for seawater plus 0.5 wt% (PVP) plus 0.05 wt% nanoparticles

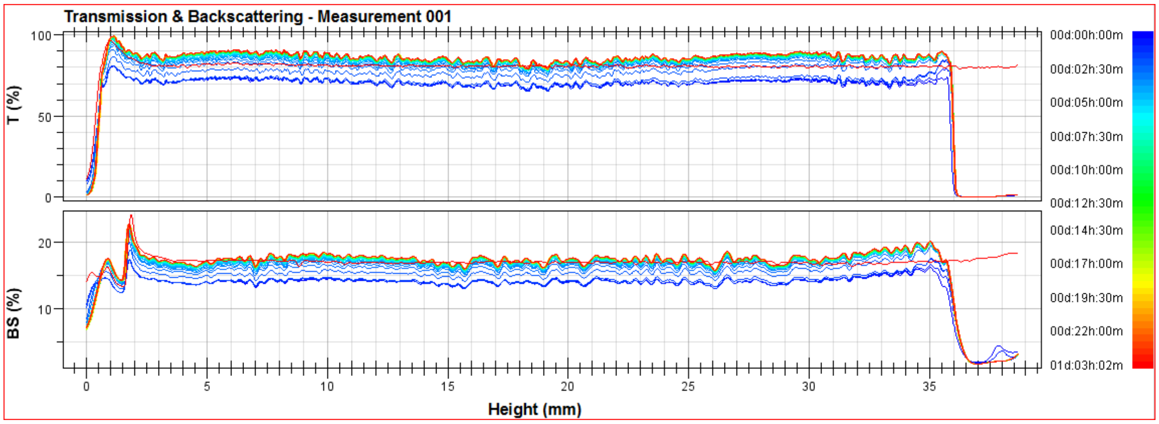


Figure 4-11 Turbidity scan results for seawater plus 0.7 wt% (PVP) plus 0.05 wt% nanoparticles

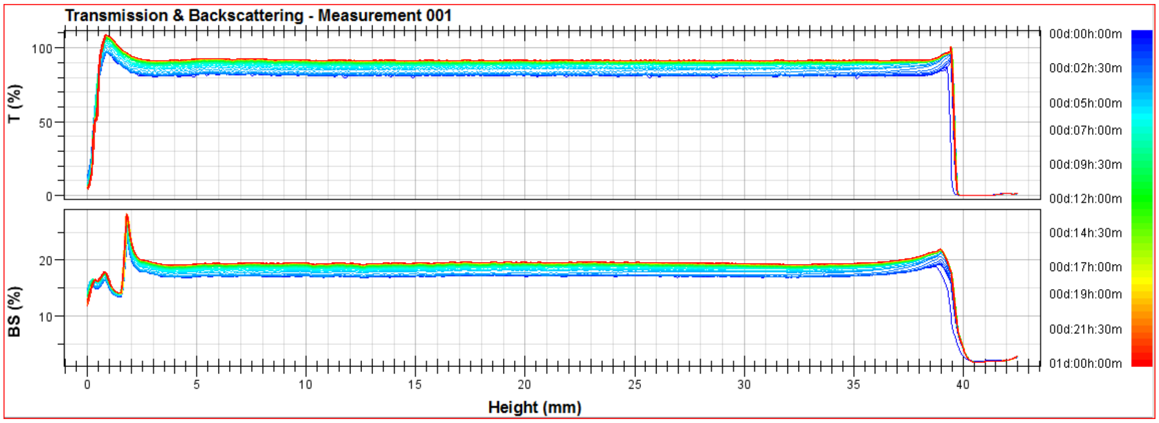


Figure 4-12 Turbidity scan results for seawater plus 1.0 wt% (PVP) plus 0.05 wt% nanoparticles

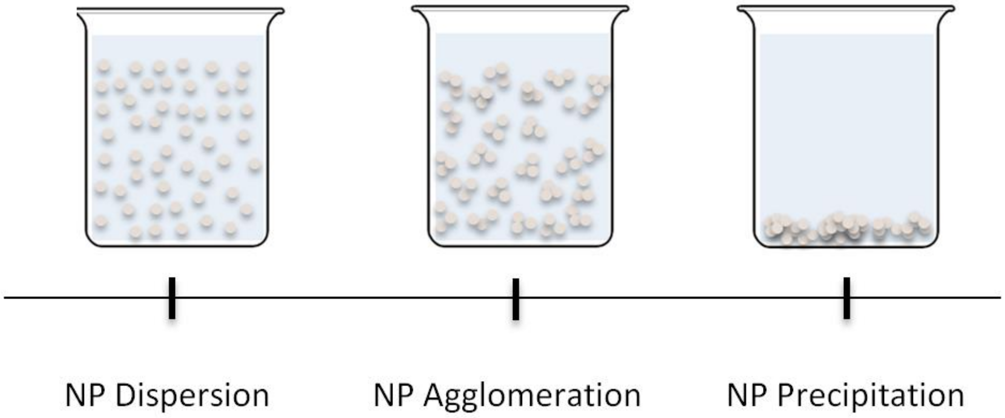


Figure 4-13 Precipitation process of dispersed nanoparticles

4.3 Interfacial Tension (IFT) Measurement Results

The interfacial tensions (IFTs) of the three most stable nanoparticles dispersants (i.e. 0.02 wt%, 0.03 wt% and 0.05 wt%) in seawater that has 1 wt% of (PVP) were measured. The dispersants were used as bulk phase and crude oil was used as a drop phase. First of all, IFT of crude oil in seawater was measured and (Figure 4.14) shows the oil droplet in the bulk seawater, whereas the result is shown in (Figure 4.15). This measurement was considered as a base line or a reference to the next measurement. Then, IFT of seawater that has only 1 wt% of (PVP) was measured to know the exact effect of adding this surfactant on IFT before adding the nanoparticles. Figure 4.16 shows the oil drop in the bulk of seawater plus 1 wt% of PVP and (Figure 4.17) shows the IFT results in comparison to the reference, IFT of crude oil in seawater. From the results, it can be seen that (PVP) lowered the IFT by 10% and that what surfactants will normally do. They will lower the IFT to different degrees depending on the type of surfactant used. This IFT result, for seawater plus 1 wt% of (PVP), was considered as a base line or a reference to all other measurements.

After that, the zeolite nanoparticles of different concentrations (i.e. 0.02 wt%, 0.03 wt% and 0.05 wt%) were added to the bulk phase of seawater plus 1 wt% (PVP) surfactant and

IFT were measured for each concentration. Figure 4.18 shows the oil droplet in bulk phase of seawater plus 1 wt% of PVP plus 0.02 wt% of the zeolite nanoparticles and (Figure 4.19) shows the IFT result in comparison to previous cases. From the reported results, the nanoparticles of concentration of 0.02 wt% did not help much to lower the IFT. It only reduced the IFT by 3.7% in comparison to the case of only 1 wt% (PVP). As the concentrations of the zeolite nanoparticles increased, more reductions to (IFT) were noticed. IFT of bulk phases, that contain 0.03 wt% and 0.05 wt% of nanoparticles concentrations, reduced by 6.7 % and 9% respectively in comparison to the case of only 1 wt% of PVP. Results are presented in (Figure 4.20 – 4.23). IFT results revealed that the nanoparticles at higher concentrations tend to affect the oil/water interface and therefore result in lower IFT values. Among all the results, it is clearly seen that a bulk phase of seawater plus 1 wt% (PVP) plus 0.05 wt% nanoparticles was best in lowering the IFT; it reduced the IFT by 19% compared to the bulk of only seawater. Figure 24 showed a summary of the IFT results as a function of the nanoparticles concentration.

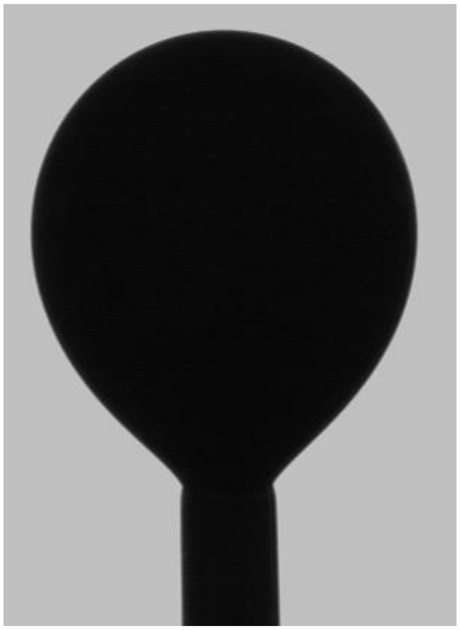


Figure 4-14 Oil droplet in seawater

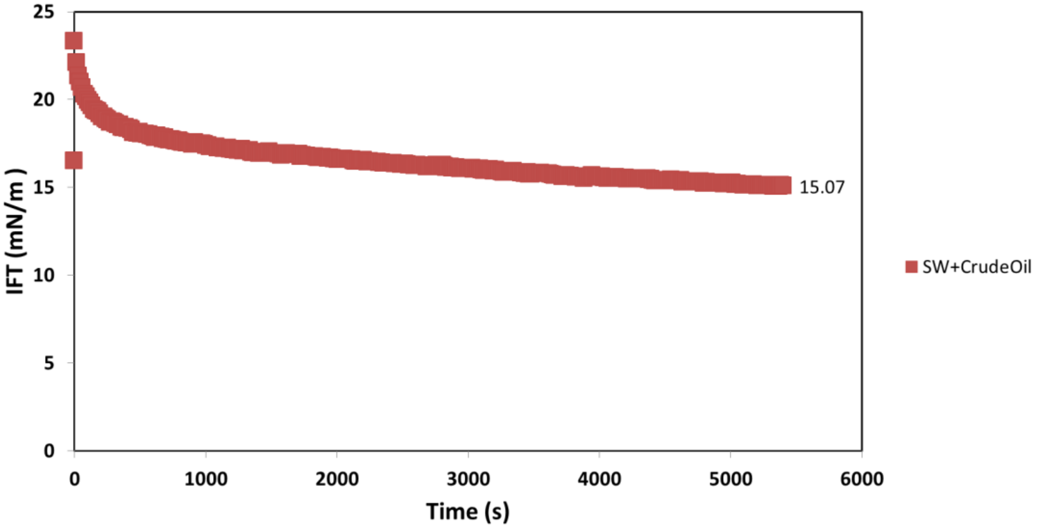


Figure 4-15 (IFT) of crude oil in seawater

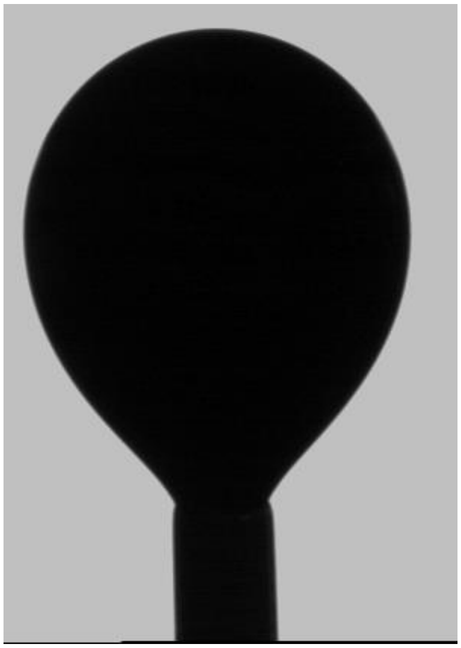


Figure 4-16 Oil droplet in seawater plus 1 wt% (PVP)

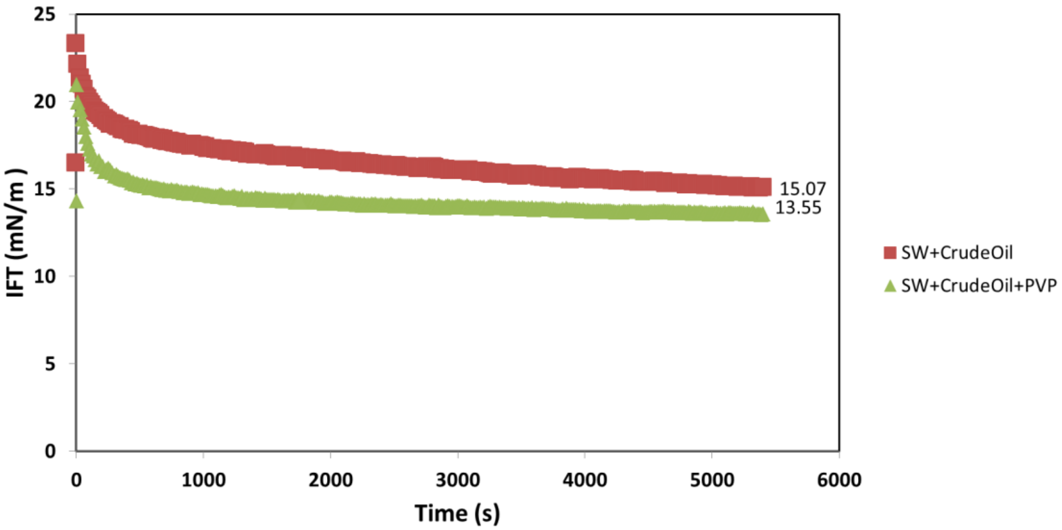


Figure 4-17 (IFT) of crude oil in seawater plus 1 wt% of (PVP)

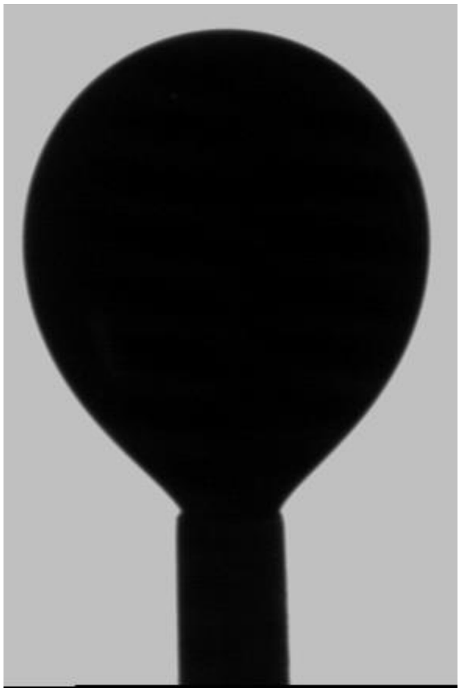


Figure 4-18 oil droplet in seawater plus 1 wt% (PVP) plus 0.02 wt% nanoparticles

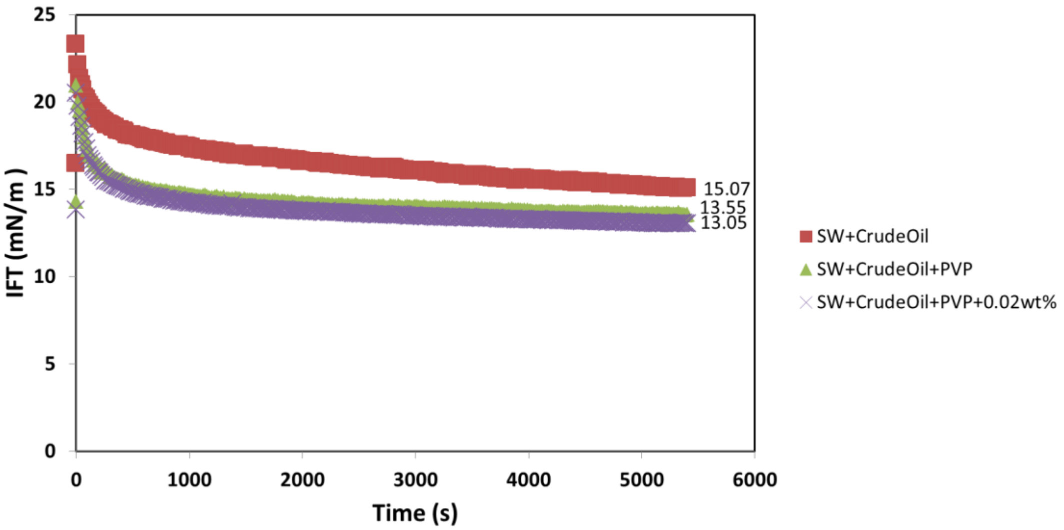


Figure 4-19 (IFT) of crude oil in seawater plus 1 wt% of (PVP) plus 0.02 wt% nanoparticles

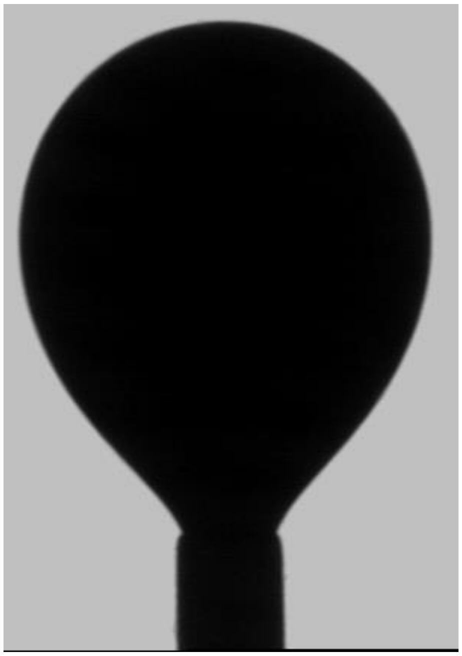


Figure 4-20 Oil droplet in seawater plus 1 wt% (PVP) plus 0.03 wt% nanoparticles

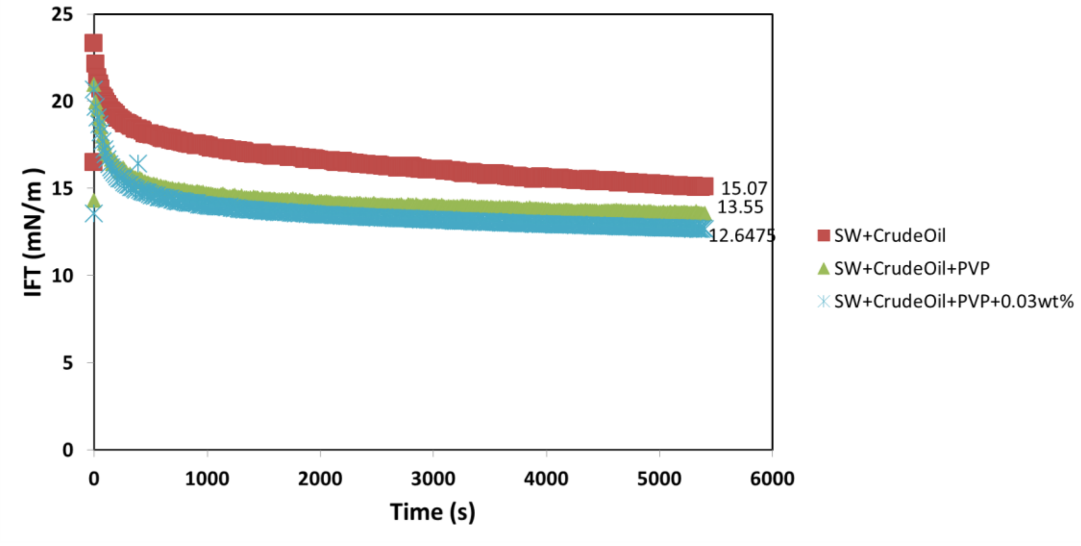


Figure 4-21 (IFT) of crude oil in seawater plus 1 wt% of (PVP) plus 0.03 wt% nanoparticles

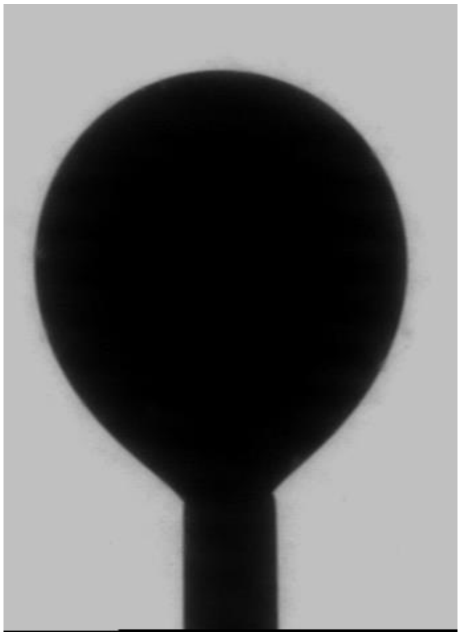


Figure 4-22 Oil droplet in seawater plus 1 wt% (PVP) plus 0.05 wt% nanoparticles

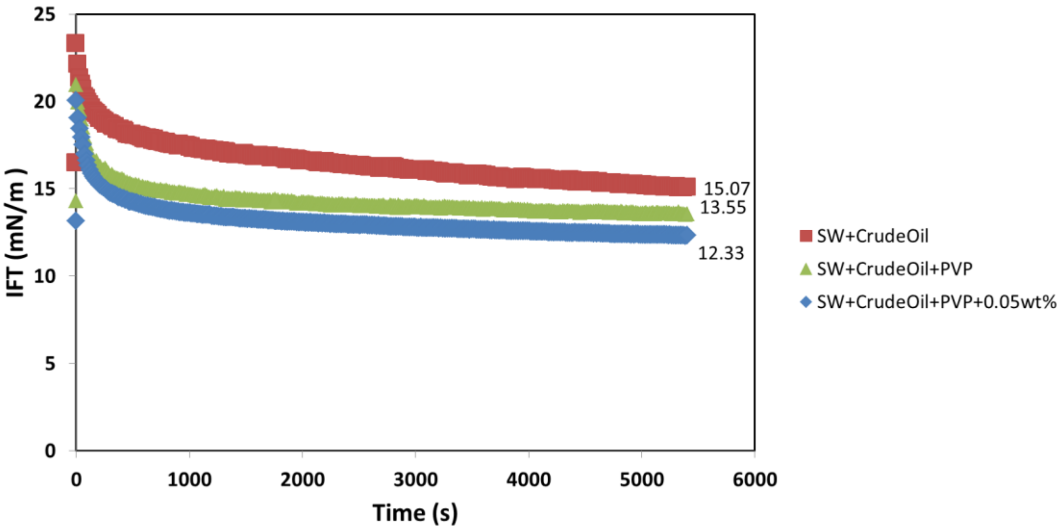


Figure 4-23 (IFT) of crude oil in seawater plus 1 wt% of (PVP) plus 0.05 wt% nanoparticles

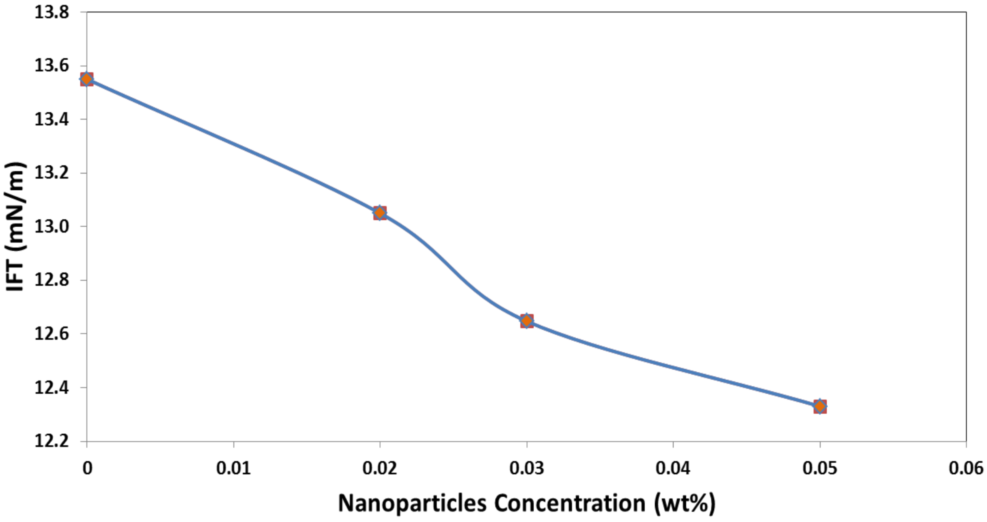


Figure 4-24 (IFT) results as function of nanoparticles concentrations

4.4 Contact Angle Measurement Results

The contact angle of oil droplets in different bulk phases, were measured on carbonates disks. Many carbonate disks from a whole core carbonate were prepared for this study. For each bulk phase, three to four oil droplets were generated and then the average value was taken and reported. Equilibrium for 12 minutes was allowed for each measurement. The first measurement was done with seawater as a bulk phase, and the second measurement was done on different disk with seawater plus 1 wt% (PVP) as a bulk phase. In the third measurement, 0.02 wt% nanoparticles were added to the bulk phase of seawater plus 1 wt% (PVP) and contact angle measurement was performed. For fourth and fifth measurements, the nanoparticles concentrations were increased to 0.03 wt% and 0.05 wt%, respectively.

There were three batches of experiments: 1) at ambient conditions, 2) at temperature of 60^{o}C and pressure of 1500 psi, and 3) at temperature of 60^{o}C and pressure of 3000 psi. All the measurements were done at ambient conditions. Then, the optimum nanoparticles concentration was considered for the other two different conditions.

The first measurement, with only seawater as a bulk phase and oil as a droplet phase, should identify the wettability status of the carbonate disks, and it should be considered then as a reference to the all other measurements. The contact angle measurement for the first bulk phase gave a value of 69.0^{o} and according to Treiber *et al* (1971), this is a water-wet condition. Then, I wt% of (PVP) was added to the seawater bulk phase and contact angle measurement was taken on different carbonate disk. The contact angle value was 73.0^{o} which is slightly higher than the case of only seawater. Hendraningrat *et al* (2014), observed similar behavior in his study that (PVP) has the tendency to alter the wettability to weaker water-wet condition. After that, nanoparticles of different concentrations were added to the bulk phase of seawater and 1 wt% (PVP) and contact angle were also measured. The reported contact angle measurements were 63.5^{o}, 49.3^{o} and 36.5^{o} for nanoparticles concentrations of 0.02 wt%, 0.03 wt% and 0.05 wt%, respectively. From the results, it can be seen that nanoparticles have the tendency to alter the rock wettability to more water wet. The nanoparticles of concentration of 0.05 wt% were the best in altering the rock wettability to stronger water-wet condition, which is an important factor to increase the oil recovery.

All the contact angle images for the different measurements done at ambient condition case are shown in (Figure 4.25).

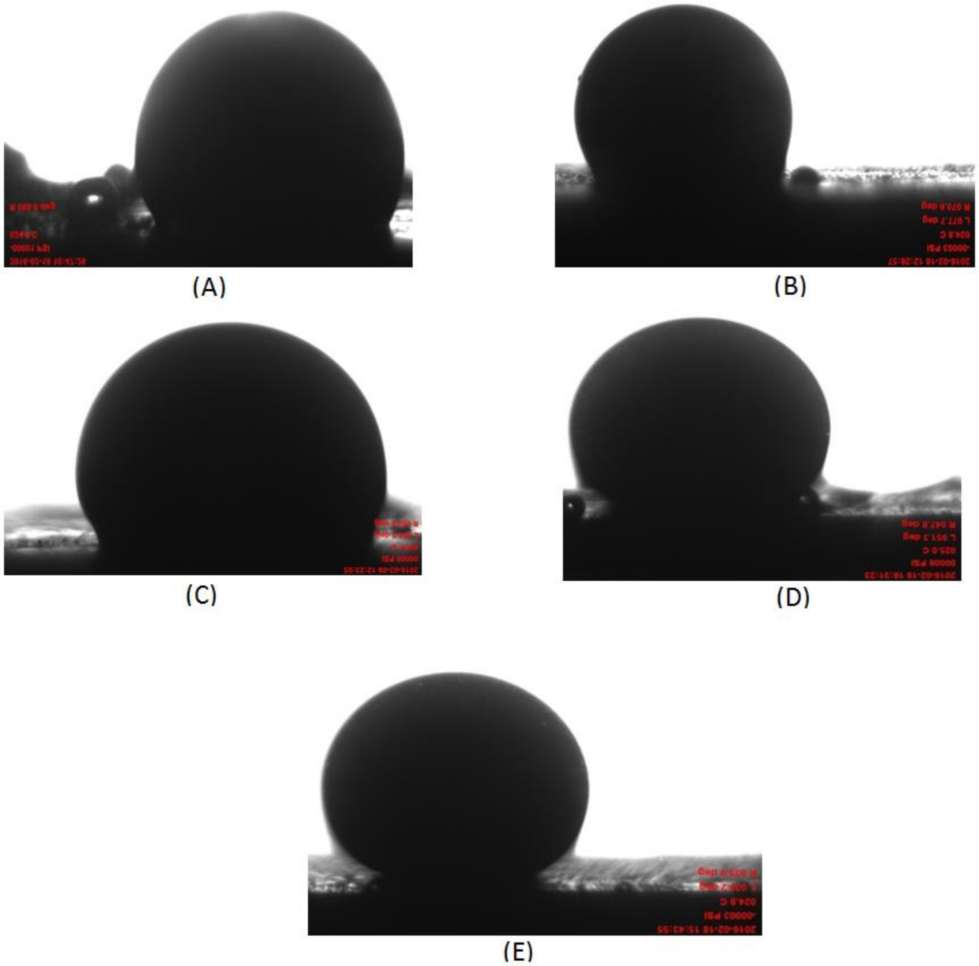

(A) (B) (C) (D) (E)

Figure 4-25 (A) Oil droplet in a bulk phase of seawater (B) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) (C) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) plus 0.02 wt% nanoparticles (D) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) plus 0.03 wt% nanoparticles (E) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) plus 0.05 wt% nanoparticles

The bulk phase of seawater plus 1 wt% of (PVP) plus 0.05 wt% of nanoparticles was chosen as the optimum phase since it showed the maximum alteration of contact angle towards stronger water-wet. Therefore, it was considered for batches 2 and 3 high pressure high temperature (HPHT) experiments. First of all, it is important to establish a base line for (HPHT) condition, which is contact angle of oil droplets in seawater at the (HPHT) test conditions.

Prior to that, it was essential to measure the contact angle of oil droplet in seawater at ambient condition as there was a time gap between the two experiments, at ambient condition and at (HPHT) conditions. The carbonate disks were soaked in oil during that time gap, which could result in a change in the wettability status. The contact angle measurement was conducted and reported a value of 73.4^o which is slightly higher than the one previously reported. After that, one carbonate disk was taken to perform (HPHT) at temperature of 60^o and two pressures of 1500 psi and 3000 psi for the same bulk phase of only seawater. The measurements at 60^o reported contact angle values of 69.3^o and 67.5^o for pressures 1500 psi and 3000 psi, respectively. The oil droplets images for the three above conditions are shown in (Figure 4.26). From the reported results, slight reduction in contact angle was observed at (HPHT) conditions when the bulk phase is seawater. This reduction of contact angles is due to the reduction of interfacial tension between crude oil and brine at high temperature and pressure. These results were considered as base line for the next measurements. Once the base line was established, a bulk phase of seawater plus 1 wt% of (PVP) plus 0.05 wt% of nanoparticles was taken for contact angle measurements at (HPHT) conditions. A new disk was loaded to the contact angle setup and temperature and pressure was applied. For the first condition, pressure of 1500 psi and temperature of 60^oC, the measurements revealed a contact angle value of $39.5\ ^o$. This result is consistent with the measurement at ambient condition, that nanoparticles have the tendency to alter the rock wettability to more water-wet condition. Moreover, when the pressure was increased further to 3000 psi, for the second test condition, the contact angle reduced slightly more to a value of 33^o.Figure 4.27 showed the oil droplets in the bulk of seawater plus 1 wt% of (PVP) plus 0.05 wt% of nanoparticles at the two tests conditions. These results proved that zeolite nanoparticles can alter the wettability at the tested (HPHT) conditions, and this alteration may be considered as the main drive mechanism for (EOR) by nanoparticles.

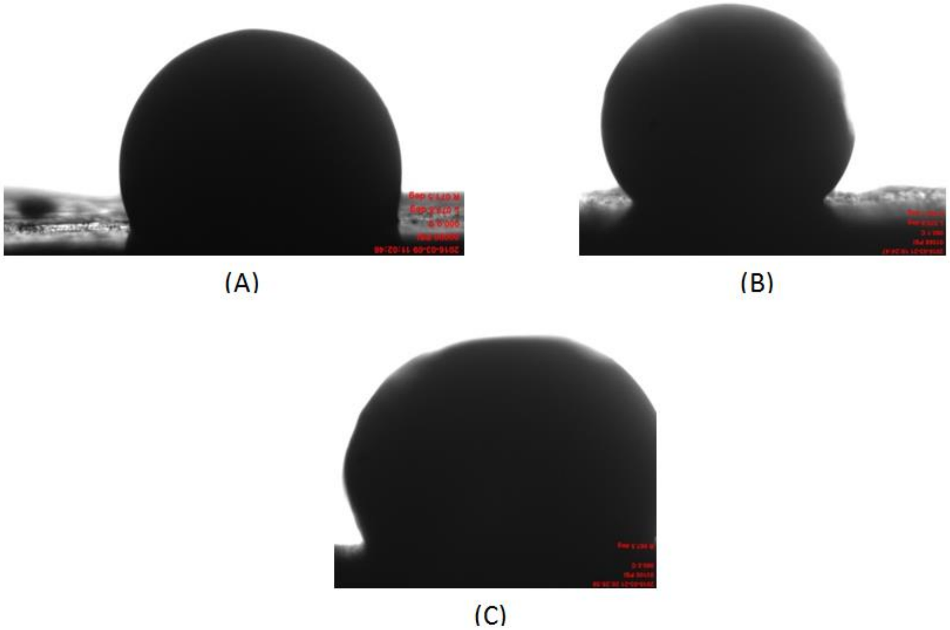

(A)
(B)
(C)

Figure 4-26 (A) Oil droplet in a bulk phase of seawater, (B) Oil droplet in a bulk phase of seawater at P=1500 psi and T= 60 C, (C) Oil droplet in a bulk phase of seawater at P=3000 psi and T= 60 C


(A)
(B)

Figure 4-27 (A) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) plus 0.05 wt% nanoparticles at P=1500 psi and T= 60 C, (B) Oil droplet in a bulk phase of seawater plus 1 wt% (PVP) plus 0.05 wt% nanoparticles at P=3000 psi and T= 60 C

4.5 Core Flooding

Three rock samples were designated for coreflooding experiments. First, the dry weights of the rock samples were measured. After that, these three rock samples were fully saturated with formation brine that has a salinity of 213 kppm and density of 1.1791 g/cc and the wet weight or saturated weights were measured. Then, the rock samples were centrifuged with crude oil to bring their status to irreducible water saturation. Rock samples measurements data and results after centrifugations are in (Table 4.6).

Table 4-6 Rock samples measurements data

Sample	Length (cm)	Diameter (cm)	Porosity (%)	Pore Volume, cc	Dry Weight, g	Saturated Weight, g	Weight After Centrifugation, g
LS1	4.765	3.767	16.03	8.51	118.9443	127.7554	126.0699
LS2	4.817	3.762	16.84	9.01	118.9836	128.2696	126.4137
LS3	4.005	3.765	17.5	7.80	98.6768	106.9525	106.9154

The calculations of the water saturations for the two samples are as the following:

Oil Density = 0.866 g/cc

Formation Brine Density = 1.1791 g/cc

Density Difference = 1.1791 – 0.866 = 0.3131g/cc

For sample LS1:

<u>To calculate the amount of irreducible water saturations:</u>

1. Saturated Weight – Weight after Centrifugation = 127.7554-126.0699 = 1.6855 g
2. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Centrifugation}}{Density\ Difference}$

$$= \frac{1.6855}{0.3131} = 5.38\ cc$$

3. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$= \frac{8.51-5.38}{8.51} * 100 = 36.83\ \%$$

For sample LS2:

To calculate the amount of irreducible water saturations:

1. Saturated Weight – Weight after Centrifugation = 128.2696-126.4137 = 1.8559 g
2. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Centrifugation}}{Density\ Difference}$

$$= \frac{1.8559}{0.3131} = 5.92\ cc$$

3. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$= \frac{9.01-5.92}{9.01} * 100 = 34.29\ \%$$

For sample LS3:

To calculate the amount of irreducible water saturations:

1. Saturated Weight – Weight after Centrifugation = 106.9525-105.4154 = 1.5371 g
2. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Centrifugation}}{Density\ Difference}$

$$= \frac{1.5371}{0.3131} = 4.91\ cc$$

3. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$= \frac{7.80-4.91}{7.80} * 100 = 37.05\ \%$$

Once irreducible water saturations were established, the three rock samples were sent for aging in crude oil using the aging setup, Figure 4.28. Aging will help to change the wettability of these rocks close to reservoir wettability conditions (i.e. oil-wet). Aging was taken place for one week and was done at temperature of 60^o and pressure of 500 psi was applied to not lose significant amount of the irreducible waters.

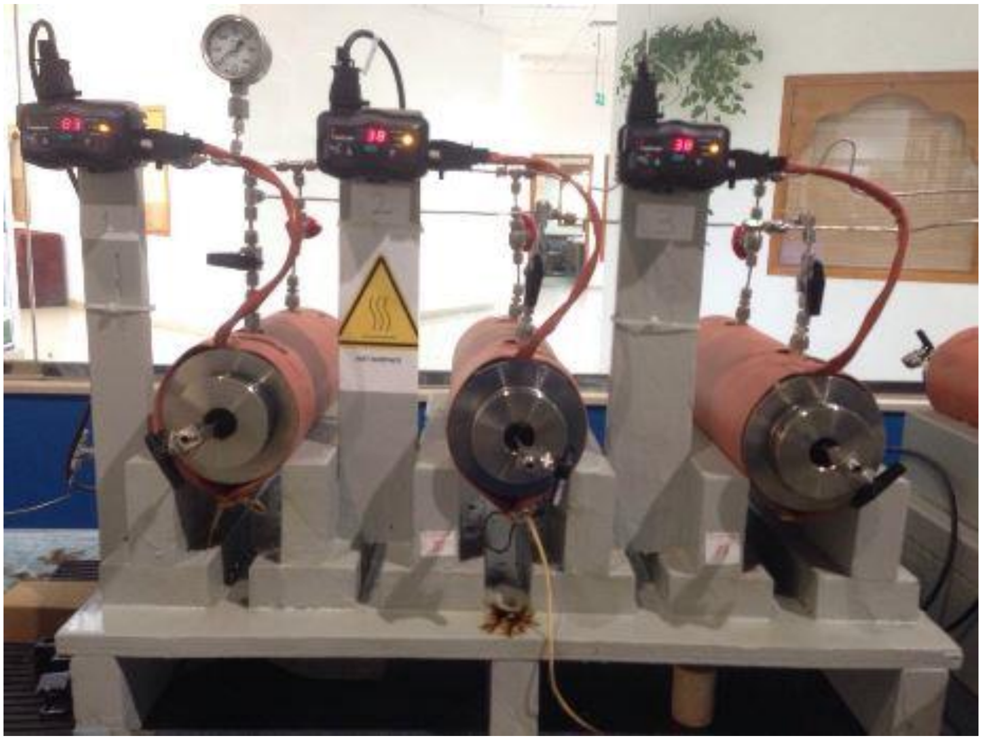


Figure 4-28 Aging setup

Once aging was done, the weight of the three rock samples were measured again to know if irreducible saturations have been changed. The measured weights for the three rock samples were slightly reduced which is normal after aging process. Calculations of the new irreducible water saturation after the change due to aging are as the following.

For sample LS1:

Weight after Aging = 125.8915g

1. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Aging}}{Density\ Difference}$

$$= \frac{128.2696 - 125.8915}{0.3131} = 5.95\ cc$$

2. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$=\frac{8.51-5.95}{8.51} * 100 = 30.15\ \%$$

For sample LS2:

Weight after Aging = 126.3265 g

3. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Aging}}{Density\ Difference}$

$$= \frac{128.2696 - 126.3265}{0.3131} = 6.2\ cc$$

4. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$=\frac{9.01-6.2}{9.01} * 100 = 31.20\ \%$$

For sample LS3:

Weight after Aging = 105.2887 g

1. Displace Volume of Formation Brine = $\frac{\text{Saturated Weight – Weight after Aging}}{Density\ Difference}$

$$= \frac{106.9525 - 105.2887}{0.3131} = 5.31\ cc$$

2. Irreducible Water Saturation = $\frac{\text{Pore Volume}-\text{Displace Volume}}{\text{Pore Volum}} * 100$

$$=\frac{7.80-5.31}{7.80} * 100 = 31.87\ \%$$

After that, the rock samples were loaded in the coreflooding setup and temperature of 60^{o}C, confining pressure of 1000 psi and pore pressure of 80 psi were applied. The samples were kept under these conditions for almost 24 hours in order to make sure that the samples are heated to the required temperature. Once the temperature stabilized, the flooding started at a flow rate of 0.25 cc/min. There were three scenarios, one for each sample. For sample LS1, the sample was first flooded with seawater until a recovery Pluto was achieved, which indicates no more oil recovery by seawater injection. Then, a nanofluid that contains zeolite nanoparticles of 0.05 wt% dispersed in deionized water was flooded. Flooding was in a slug mode, where seawater was alternating nanofluid. The nanofluid was injected for two-three pore volumes followed by seawater injection of two-three pore volumes followed by nanofluid injection of two-three pore volumes. After that, the sample was soaked overnight in with nanofluid to see whether soaking has an effect on the oil recovery. The recovery results along with the pressure profile are presented in (Figure 4.29). From the results, it can be seen that this nanofluid helped to recover more oil, the recovery enhanced by 12%. Moreover, soaking has also shown to be a good factor in enhancing the oil recovery, where nanoparticles will be allowed to interact with the rock surface for a longer time. This will change the rock wettability to more water-wet such that the oil will be then released from the pores and it will be as a bulk, where it can be easily produced. In this case, soaking enhanced the recovery by 5%. The pressure profile however, was consistent with the injected phase. The moment where nanoparticles were injected, the pressure was increased as some of these nanoparticles will be adsorbed to the rock surface and some will trapped at the pore channels causing the pressure to increase.

For sample LS2, the sample was first flooded by seawater until a recovery Pluto was achieved. Then, a nanofluid that contains zeolite nanoparticles of 0.05 wt% plus 1 wt% of (PVP) dispersed in seawater was injected. The injections were also in sequence mode similar to sample LS1, where seawater was alternating nanofluid. The recovery results a long with the pressure profile are shown in (Figure 4.30). From the results, the sequence injection of the nanofluid and seawater enhanced the recovery by 13.7%. Soaking of the nanofluid was also shown to enhance the recovery of oil. In this case, the recovery was enhanced by 5.3%. Similar behavior of the pressure profile was noted.

The last flooding scenario was done utilizing sample LS3. The sample was first flooded by seawater followed by the nanofluid. Unlike the flooding scenarios of LS1 and LS2, in this scenario continuous injection of nanofluid was in the tertiary recovery, no slug injection. The nanofluid showed to increase the oil recovery by 7.7%. Soaking was also done in this scenario but showed to not result in additional oil recovery. The recovery results for this scenario along with the pressure profile are presented in (Figure 4.31). In the three cases, it was not possible to get out all the nanoparticles. This can be clearly seen from the pressure profile at the late stage of seawater injection after soaking. The pressure was high in all cases.

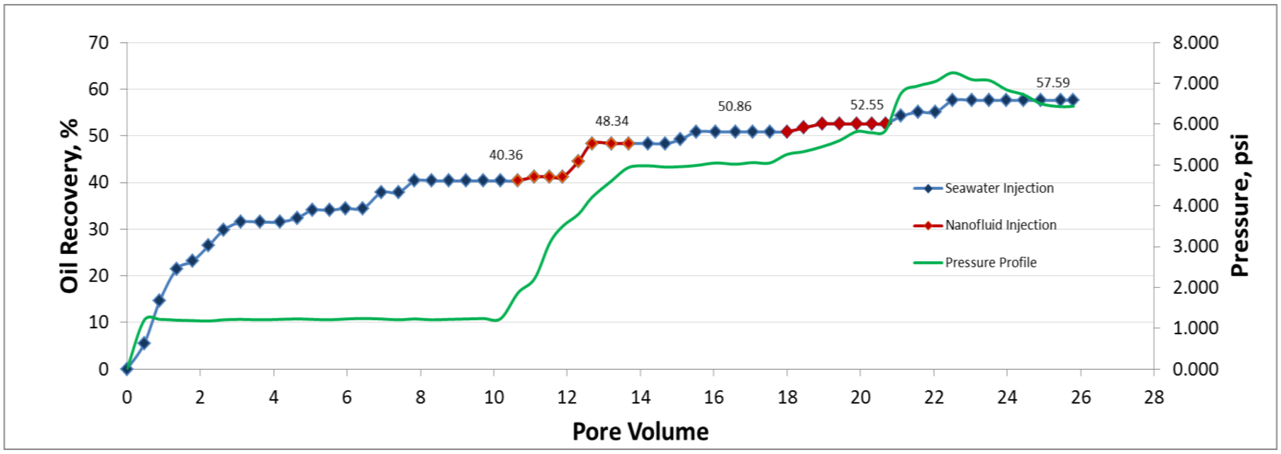


Figure 4-29 Flooding results for sample LS1

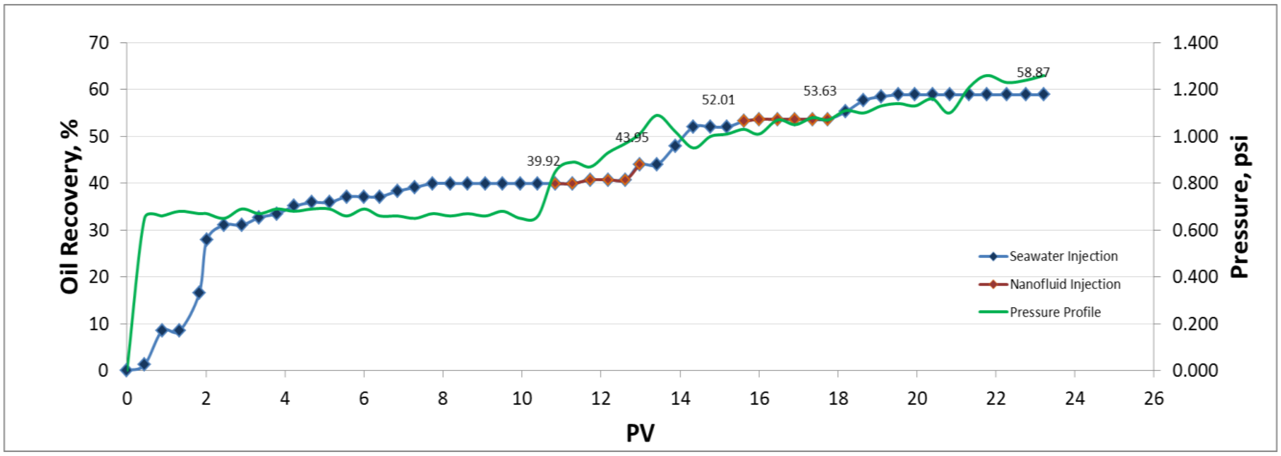


Figure 4-30 Flooding results for sample LS2

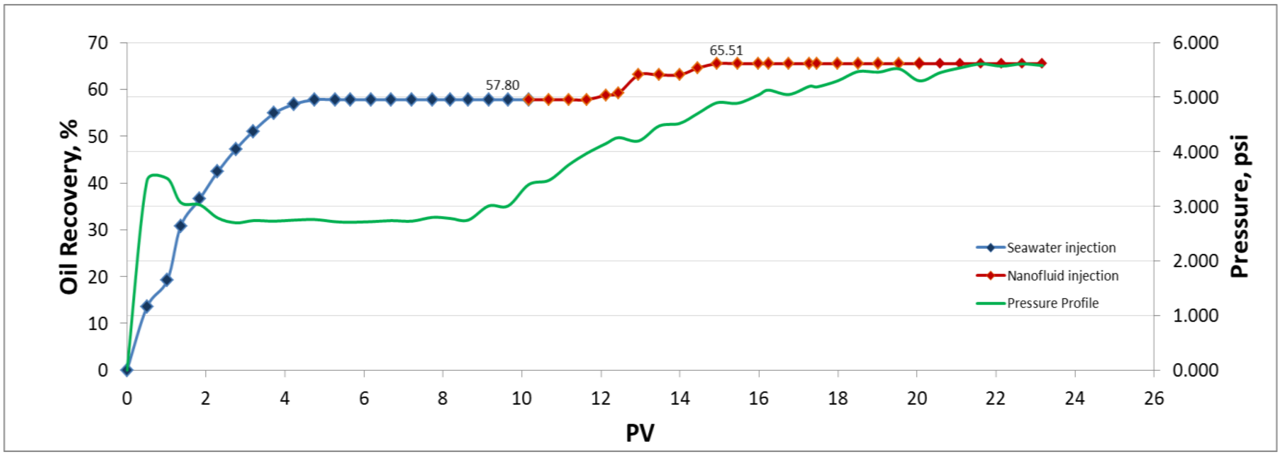


Figure 4-31 Flooding results for sample LS3

CHAPTER 5

Conclusions and Recommendations

5.1 Conclusion

Through comprehensive analysis measurements for the nanoparticles zeolite, the following can be concluded:

- It is mandatory to analyze the nanoparticles size at the beginning. Nanoparticles sizes will play a very important rule and particles size of below 100 nm is preferable for EOR application as bigger particles may cause problem. The bigger particles tend to attach smaller particles to them. Therefore, they will be getting heavier enough which could result in precipitation of these particles. Also, bigger particles can result in plugging of some pore channels when they are injected in the reservoir for example.

- Zeolite nanoparticles were found to show good stability in deionized water and precipitation started to take place only after 5 days.

- When synthetic seawater was used as a dispersant fluid for these nanoparticles, the precipitation of the nanoparticles took place in less than 1 hour. Different concentrations of the nanoparticles were tried and the conclusion was the same, precipitation in less than 1 hour.

- The nanoparticles were dispersed in different solutions that have different salts compositions. These salts are the one exist in seawater. The divalent salts ($CaCl_2$) and ($MgCl_2$) were found to be the reason behind faster nanoparticles precipitation.

- The nanoparticles precipitation phenomenon was also investigated by zeta-potential measurements and tubed scan measurements. The two measurements confirmed what was observed earlier, quick precipitation when seawater is used as a dispersant agent.

- Different surfactants were then used to help dispersing the nanoparticles in seawater for longer time. PVP was found to be the best in extending the dispersion time of the nanoparticles in seawater. Therefore, in all the experiments PVP was used with nanoparticles dispersions.

- IFT measurement results revealed that the nanoparticles at higher concentrations tend to affect the oil/water interface and therefore result in lower IFT values. Among the three tested nanoparticles concentrations, the 0.05 wt% concentration of the zeolite nanoparticles was best in lowering the IFT.

- From the ambient contact angel measurements, it was concluded that the nanoparticles have the tendency to alter the rock wettability to more water wet. The nanoparticles of concentration of 0.05 wt% were the best in altering the rock wettability to stronger water-wet condition, which is an important factor to increase the oil recovery afterword.

- Contact angle measurements were also done at HPHT and similar observations to the ambient condition measurements were noticed, which prove that these nanoparticles can actually work at HPHT conditions.

- Coreflooding experiments showed that the nanoparticles helped to recover more oil where the recovery was enhanced by 12% in one experiment and by 13.7% in another experiment.

5.2 Recommendations

- Functionalization of nanoparticles should be considered which can help to extend the dispersion time in seawater solution.

- HPHT IFT experiments should be considered to help in understanding the fluid to fluid interaction at reservoir conditions. In other words, how the nanoparticles will help in advancing the mobility ratio between seawater and oil.

- More coreflooding experiments should be run in different scenarios to understand the behavior of nanoparticles in porous media.

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