Wettability Alteration of Carbonate Rocks by Polyelectrolyte Complex Nanoparticles

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Abstract

More than fifty percent of oil reservoirs around the world are carbonate reservoirs. Oil recovery from carbonates requires closer attention due to the heterogeneity of the rock and its wettability system. A majority of carbonates are considered to be mixed-wet to oil-wet. Changing oil-wet systems toward more water-wet is a key factor for improving oil recovery efficiency. Recently, investigations for the optimum methods of wettability alteration, particularly in carbonates, have attracted the attention of researchers in the area of enhanced oil recovery. There are several methods for wettability alteration that have been used by the industry, including the usage of different chemicals such as surfactants or low salinity fluids. Using nanoparticles for alteration of wettability is a new and promising method that has more focus now in the industry due to its novel and unique properties. In this research, a Polyelectrolyte Complex Nanoparticle (PECNP) was synthesized in the lab in order to investigate and evaluate its ability of wettability alteration for limestone carbonate rocks. The effect of wettability alteration was investigated by measuring oil/brine interfacial tension, contact angle, and by conducting Amott test. In addition, core flooding experiments were performed using different schemes of injection by altering between nanoparticles and different brine systems. The results showed that the PECNP system could change the wettability of the rock towards a more water-wet condition. The PECNP system was able to reduce the brine/oil interfacial tension significantly to very low values reaching 2 dynes/cm. Overall, it is concluded that PECNP can be effective as an enhanced oil recovery agent.

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Chapter 1: Introduction

1.1 Chemical Enhanced Oil Recovery

More than half of the oil reserves in the world lie in carbonate reservoirs with a potential of high gas reserves [2]. The heterogeneity of carbonate reservoirs is known to the industry. It can exhibit varying properties (e.g., porosity and permeability) and as a result flow mechanism variations would occur within small sections of the reservoir, making them difficult to characterize. Understanding the heterogeneity of a reservoir is an essential key to productivity enhancement, beginning from exploration and up to production phase. Another important key for production enhancement is by applying chemical injection methods, which are known as enhanced oil recovery (EOR). EOR is defined as oil recovery by injecting materials that are not normally present in the reservoir, which alter the petrophysical properties of the reservoir in order to lengthen its life and ensure a continuous oil supply.

EOR can initiate during secondary recovery when pressure maintenance is initiated through gas or water injection, or even at the tertiary stage. The injection of different chemicals as dilute solutions has been used for mobility control and to reduce oil/water interfacial tension (IFT). These techniques are recognized as chemical EOR (cEOR), a challenging method that involves various scientific disciplines [3].

1.2 Production Challenges of Carbonate Rocks

In carbonate rocks, secondary water flooding is not favorable due to the existence of fractures, where water flows through the easiest path leaving most of the oil behind. Majority of carbonate rocks are of oil-wet state, which makes the recovery even more complex. Spontaneous imbibition is a proven method to achieve the highest recovery under these conditions. Therefore, to achieve high recoveries from carbonate rocks, wettability of the rock surface can be modified towards a less oil-wet state [4]. As for capillary number, it has shown to have a direct correlation with the desaturation of residual oil after water flooding.

1.3 Wettability Alteration Using Nanoparticles

Wettability alteration has received many attentions recently due to economic benefits and simplicity of operation. There are several ways to alter the wettability of the rock, either physically such as injecting steam to increase reservoir temperature, or chemically such as surfactants, low salinity fluids, or nanofluids [5]. The latest literature has reported the usage of nanoparticles for wettability alteration due to many facts that are explained in detail in the literature review chapter. Nanoparticles can be used along with other chemicals as additives or modifiers to improve the effectiveness of wettability alteration [6].

Different nanoparticles have been investigated for their ability in wettability alteration by different researchers verifying the capability of nanostructured materials in enhancing oil recovery. The main objective of this research is to study the effect of wettability alteration on a limestone rock by using Polyelectrolyte Complex Nanoparticles (PECNP) without adding any additives such as surface acting-agents (Surfactants). A variety of methods was used to evaluate and measure the effect of wettability alteration on a rock surface. In this study, the performance of the PECNP system was evaluated by conducting IFT measurements, contact angle, spontaneous imbibition (Amott index), and core flooding experiments.

1.4 A Brief Review of the Thesis Structure

In the first chapter, a brief introduction of cEOR and production challenges of carbonate rocks is provided with a scope on the wettability alteration as a mechanism for oil recovery enhancement. In Chapter 2, a literature review introduces the fundamentals of rock wettability, and showing examples of nanoparticle systems by describing the main mechanism of how it can alter the wettability of a rock surface. Chapter 3 summarizes the materials used for this research followed by methods and procedures for all experiments. Chapter 4 presents the results obtained from experiments and discuss them in detail. The fifth chapter provides a summary and conclusion of the thesis.

Chapter 2: Literature Review

This chapter consists of two main sections. The first section briefly introduces fundamentals of wettability and the effects of wettability alteration on production enhancement, precisely in carbonate rocks. In addition, methods of wettability alteration and ways of measurement are explained at the end of the section. The second section provides applications of nanoparticles in oil industry particularly in EOR. The literature focuses mainly on wettability alteration using nanoparticles, and its impact on oil production enhancement.

2.1 Rock Wettability

Wettability is a measure of the contact forces between fluids and solid surfaces [7]. In reservoir rock, the fluid could be oil, gas or water and the solid surface is the rock. Therefore, in a rock/oil/water system, if oil is more favorable to the rock then it is categorized as oil-wet. In contrast, if water is more favorable to the rock then it is considered as water-wet. Figure 1 shows a system of oil and water on a rock surface were θ indicates the contact angle of water. When $\theta < 90^o$, water is the spreading fluid and the system is considered as water-wet. In the same way, the system is oil-wet when $\theta > 90^o$ and the spreading fluid is oil. Moreover, a neutral-wet condition is referred to a system that is neither oil-wet nor water-wet. The contact angle for neutral-wet system is equal to 90^o. In addition, a mixed-wet condition is defined when inhomogeneous wetting phases exist in the same rock system [8].

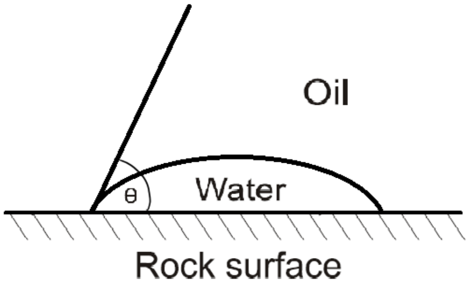


Figure 1 Rock wettability in oil/rock/water system

2.1.1 Wettability of Carbonate Rocks

Originally, all reservoir rocks were assumed to be water-wet. A change in wettability is then occurred by the deposition of organic components that exist in crude oil. The polar compounds in crude oil are adsorbed onto the rock surface, and thus alters the surface to oil-wet [7]. There is a large volume of published studies describing the wettability of carbonate rocks and confirming that majority of them to be oil-wet. Treiber et al. (1972) have investigated wettability for more than fifty oil producing wells from different areas around the world. The data indicated that most of carbonates were to be moderately oil-wet [9]. The heterogeneity of carbonates unlocked the desires for a better understanding of the rock petrophysical properties to find the optimum methods for production enhancement.

2.1.2 Effect of Wettability Alteration

The porous media in carbonate rocks consist of matrix and fracture systems. Fractures contain a smaller amount of oil compared to the matrix due to its lower storage capacity (porosity). However, the rock matrix is less permeable to fluid movement, but it holds most of the oil due to its higher porosity. In conclusion, water flooding is less effective in this case because water follows the path of least resistant by only displacing oil in the fractures. The oil in the matrix is typically displaced by spontaneous imbibition towards the fracture and high permeable systems. However, if wettability is neutral to oil-wet, oil recovery by spontaneous imbibition is limited due to low capillary pressure. The capillary pressure is affected by wettability interaction and therefore is a function of interfacial tension forces. Therefore, in order to attain a high oil recovery from carbonate reservoirs, the capillary pressure should be increased through wettability alteration. In summary, altering wettability to a less oil-wet state tends to expel more oil by spontaneous imbibition of water [4]. Several studies that include laboratory results have shown that wettability alteration can have a remarkable effect on the efficiency of oil displacement by water. It has also shown that neutral to oil-wet carbonate reservoirs point toward poor spontaneous imbibition of oil by water [10].

2.1.3 Wettability Alteration Methods

Many factors are involved in rock wettability alteration such as temperature, injected fluid properties, and oil composition. This study is mainly focused on the effect of injected fluid properties on wettability alteration by water flooding mechanism. There are different approaches that have been used in the industry to alter the wettability, particularly in carbonate rocks. One approach is by modifying the ionic composition of the injected brine such as Ca^{2+} and SO_4^{2-}. Carbonates adsorb high Ca^{2+} ions that exists in formation brine, thus it creates the positive surface charge in the range of $pH<9$ [10]. On the other hand, adding sulfate to the injected water is proven to be able to change the surface charge of carbonates from positive to negatively charged [11]. Because wettability of carbonates is heavily linked to its surface charge, sulfates react as wettability modifier agents in this case and alter the wettability based on its reaction with the rock surface.

Another method for altering wettability is by using surfactants. Surfactants are well known for their ability in reducing oil/water interfacial tension. With respect of surfactant application in EOR, researchers are focusing mainly on the effect of lowering the IFT between oil and water. At lower IFT values, the mobility of oil improves, and a higher recovery is going to be achieved.

2.1.4 Measurement Techniques of Wettability

Various methods have been proposed to evaluate the wettability of a system in both qualitative and quantitative terms. Quantitative methods include contact angle, imbibition and forced displacement (Amott), and USBM wettability method. Whereas the qualitative methods are imbibition rates, flotation, microscopic examination, and some other methods [12]. In this study, only contact angle and Amott test were used as a wettability indicator.

2.2 Nanoparticles Applications in Enhanced Oil Recovery

Recently, nanoparticles have gained more attention as a promising wettability modifying agent to enhance oil recovery. Several studies have reported the effectiveness of nanoparticles in oil industry application, not only in production enhancement, but also in other petroleum aspects. Many factors are involved in nanoparticle applications in terms of efficiency. The particle size, surface charge, particle concentration and stability of the nanoparticle system are considered to have a vital impact on oil recovery. The novel properties of nanoparticles have attracted scientists to test this new technology for a bigger development of EOR in the oil industry. Different studies showed that nanoparticles can improve wettability of the rock and they are more stable than surfactants and polymers at certain reservoir conditions [13]. Surfactants are well known for their ability to reduce IFT, but as for nanoparticles, the studies proved that they are involved in oil recovery by two mechanisms (1) reducing IFT and (2) altering rock wettability [14]. Moreover, recent studies demonstrated a third line mechanism for improving oil recovery by forming a layered structure on the rock surface, which is responsible for detaching oil from rock surface by spreading the nanofluid over it [13].

2.2.1 Silica Nanoparticles

Among the existing nanoparticles, silica nanoparticles (SNPs) have gained more interest in oil industry due to its outstanding properties. A comparative study using different types of nanoparticles, polyelectrolyte complex nanoparticles being studied in this work not being among them, showed that SNPs had the highest performance in enhancing oil recovery [6]. In addition, SNPs have low cost of fabrication and a surface that can be easily modified using chemical methods [13].

Several studies indicated successful results of using SNPs for wettability alteration purposes. SNPs also showed exciting effects in improving oil recovery by surfactant flooding. One of the limitations of surfactants is the high chemical consumption during oil recovery operations due to surface adsorption. Zargartalebi et al. (2015) explored the capability of using silica nanoparticles in improving the performance of surfactants. In his study, he concluded that surfactant adsorption on rock surface was reduced in the presence of silica nanoparticles [15].

Another study by Al-Anssari et al. (2016) have investigated the effects of nanoparticle concentration and brine salinity on wettability alteration of oil-wet calcite surfaces. In his research, he found that formulations of nanoparticle are very effective in enhanced oil recovery. The aim was to find optimum condition for each parameter in terms of wettability alteration efficiency. Figure 2 shows the effect of salinity on nanoparticle properties. A calcite surface was immersed into silica nanofluid with different NaCl concentration, then contact angle is measured for each concentration. Surprisingly, nanoparticles did not show any impact at 0% brine concentration, which indicates the importance of salinity as a function for these systems. As the salinity increases, it starts to react and alter the wettability which confirmed by contact angle measurements in Figure 2. However, it can be clearly seen that there is an optimum value for salinity were the efficiency of wettability alteration starts to decrease [16]. Similar scenario applies for the other parameters such as particle concentrations, size and surface charge.

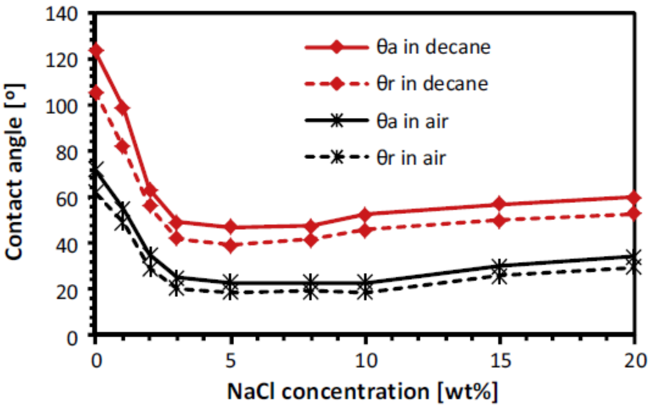


Figure 2 Water contact angle on nano-modified calcite surface as a function of brine salinity [16]

2.2.2 Zirconium Oxide Nanoparticles

Another example of nanoparticle application that have been tested for their ability of wettability alteration is ZrO_2 nanoparticles. A study by Karimi et al. (2012) showed that a significant amount of oil can be quickly recovered using nanoparticles, which was verified using spontaneous imbibition technique for wettability measurement [17]. They used nanoparticle as an additive to surfactants and created different nanoparticle systems. Contact angle measurement was performed for different mixtures of nanoparticle, in which the top two of these fluid mixtures were picked for spontaneous imbibition test. Figure 3 shows the result of imbibition test using these two nanoparticle fluids as a comparison with distilled water [17] . The result implies that the interaction between rock/nanoparticle system/oil has been introduced which initiated an improvement in oil displacement.

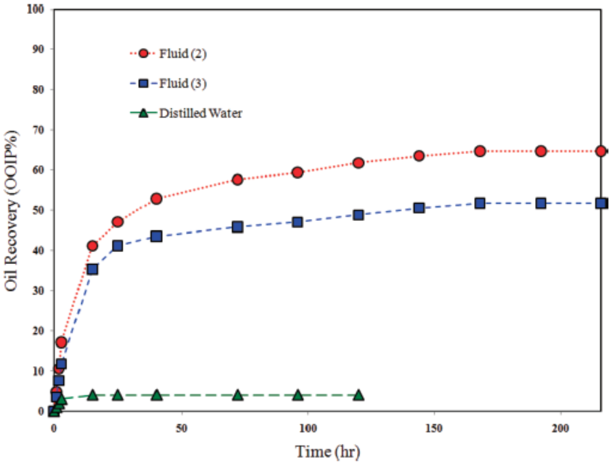


Figure 3 Spontaneous imbibition of two different nanoparticle mixtures (Fluid 2&3) into oil-wet core plug at 70 °C [17]

2.2.3 Polyelectrolyte Complex Nanoparticles

Polyelectrolyte complex nanoparticles were introduced by Tiyaboonchai [18] in order to be used as drug delivery carriers. Polyelectrolyte (PEI) are polymers with dissociating groups of ions that can be classified into natural, modified natural and synthetic polymers [19]. With respect to surface charges, they can be divided into polyanions, polycations, and polyampholytes, see Figure 4.

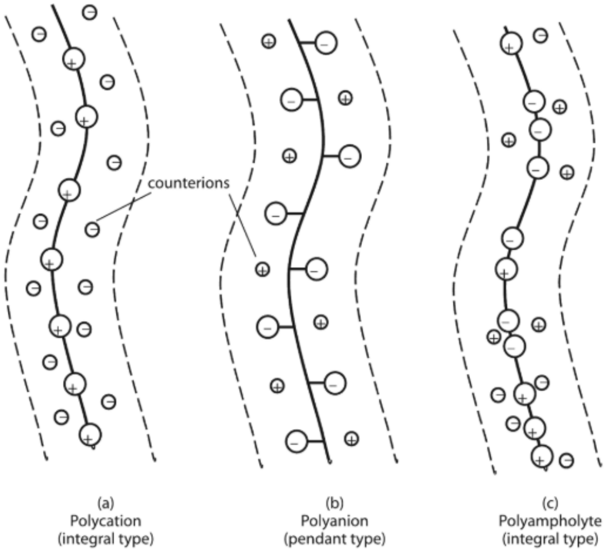


Figure 4 Classification of polyelectrolytes [19]

The charge density and solution acidity of polyelectrolyte are key factors for creating strong or weak polyelectrolyte complexes. In addition, solid colloids with nano-sized particles are the most important additives to polyelectrolyte solutions in order to initiate the interaction forces between particles. The interactions generate electrostatic forces that are considered as the fundamental mechanism for generation of nanoparticles. As for system stability, there are many factors that are involved in nanoparticle in terms of particles suspension stability. Particle size and density, along with surface charge of particle, could have impact on the suspension stability of the nanoparticle solution [20]. Moreover, adsorption of nanoparticles to rock surface is also an important factor that plays a big role in applications targets. Particles adsorption can occur during transportation in rock porous media, although their size is much less than typical pore throat. The capacity of adsorption not only depends on nanoparticle type and porous media, but also on injection concentrations and flow rate [21].

In terms of application and feasibility of the system, the polyelectrolyte complex nanoparticles have been studied and reviewed recently in many areas in the petroleum industry. It has a wide range of application particularly in EOR projects such as CO_2 injection, which is known for improving the mobility control of hydrocarbon flooding. One of the forms of CO_2 injection is using a CO_2 foam, generated by surfactants, in order to enhance the sweep efficiency by addressing the mobility control problems of the conventional CO2 system. However, instability occurs in foam system in some cases like the presence of high temperature and high salinity environment [22]. Adding nanoparticle is a new method to stabilize the CO_2 foam system. Polyelectrolyte complex nanoparticles have been tested using high salinity brine under reservoir condition and it has successfully improved oil recovery. It was able to reduce the interfacial tension further even in the presence of surfactant and this is one of the important factors of the recovery improvement.

Furthermore, it generated a very stable system that showed a more efficient oil recovery as per the core flooding tests [1].

Another area of application is using this nanoparticle system in fracturing operations. It is been tested as fluid loss additive and breaker carrier in the hydraulic fracturing operations of tight formations in particular [23]. After each fracturing job, because of using high viscous gel to achieve effecient fractures in the formation, it creates a filter cake that needs to be degraded in order to recover the conductivity of the reservoir [20]. Enzymes are most commenly used in the industry for the cleaning and degredation processes but they usually lose their effeciency against pH and temperature condition of the reservoir. The polyelcrtolyte complex nanoparticles found capable to be as feasable carrier to the enzyme breaker. They can delay the release of the ezymes and protect them against the changes in reservoir conditions [20].

In this study, the main purpose is to explore and evaluate the feasibility of employing polyelcrtolyte complex nanoparticle solutions in EOR applications by focusing on the results of wettability and IFT measurements without further analysis.

Chapter 3: Material and Experimental Procedures

This chapter consists of two main sections. The first one describes the type of materials used for this research including their properties. Equipment and experimental procedures are provided in the next section.

3.1 Materials

3.1.1 Brine

Brine was prepared by adding 2 wt% ratio of sodium chloride (Fisher Scientific, Lot No. 177409) to reverse osmosis water (R.O. water). The brine had a density of 1.006 g/cm^3 and viscosity of 0.69 cp at 25 degree Celsius.

3.1.2 Polyethylenimine

Polyethylenimine (PEI) branched polycation with an average M_w =25kDa from SIGMA, Lot No. MKCB1222V was obtained from Sigma-Aldrich. Figure 5 shows the chemical structure for PEI obtained from the same manufacturer.

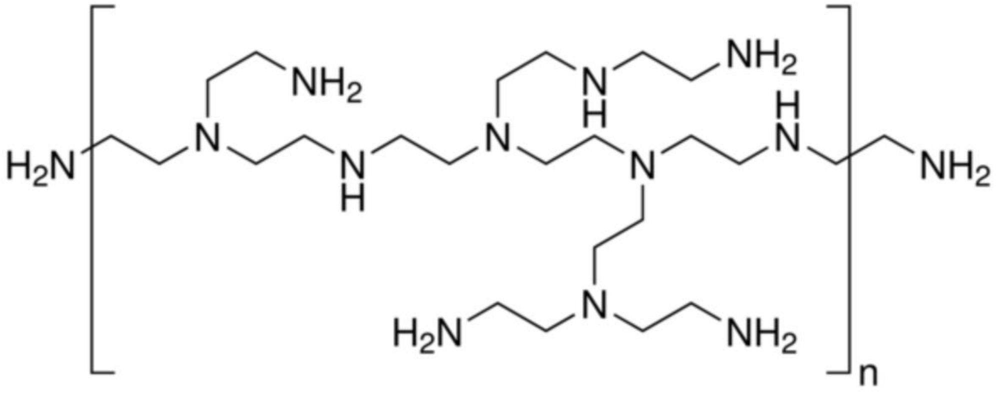


Figure 5 Chemical structure of PEI (sigma-aldrich.com)

3.1.3 Dextran Sulfate

Dextran sulfate sodium salt (DS) (Fisher Scientific, Lot No. 173138) is a polyanion that was used for nanoparticles preparation. The chemical structure of DS is shown in Figure 6.

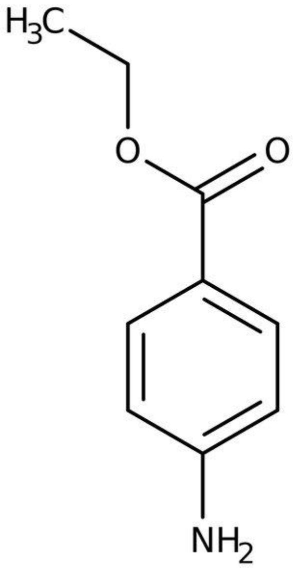


Figure 6 Chemical structure of Dextran Sulfate Sodium Salt (White to off-white powder), Fisher BioReagents

3.1.4 PH Modifiers

Hydrochloric acid (HCl) was used as pH modifier and it was obtained from Fisher Scientific (Pittsburgh, PA). The pH was adjusted only for PEI to the desired value using HCl, then it was mixed with other chemicals to prepare the nanoparticle system.

3.1.5 Core Materials

Indiana limestone (IL) cores within permeability ranges of 40-90 mD and porosity range of 17% were cut from larger plugs into three inch length each. Based on permeability and oil saturation, the cores were divided into three groups; group one has the highest permeability while group two has the intermediate values and finally group three has the lowest permeability.

Application of each group is described in the experimental chapter. Properties and characterization of cores are listed in Table 1.

Table 1 Calculation related to porosity measurement for IL cores before the experiments

Core #	Length (cm)	Diameter (cm)	Dry Weight (g)	Saturated Weight (g)	PV (mL)	Porosity, %
1	7.60	2.55	84.50	91.23	6.69	17.24
2	7.46	2.55	82.54	89.08	6.50	17.06
3	7.61	2.55	85.23	91.88	6.61	17.01
4	7.24	2.55	80.77	86.92	6.11	16.53
5	7.55	2.55	84.14	90.71	6.53	16.94
6	7.40	2.55	81.31	87.79	6.44	17.04
7	7.41	2.55	83.09	89.16	6.03	15.94
8	7.52	2.56	83.70	90.38	6.64	17.16
9	7.61	2.56	86.39	92.39	5.96	15.23
10	7.53	2.55	85.02	90.97	5.91	15.38
11	7.42	2.55	83.14	89.10	5.92	15.63
12	7.30	2.56	81.17	87.38	6.17	16.43
13	7.60	2.55	85.09	91.45	6.32	16.29
14	7.59	2.54	84.63	91.12	6.45	16.77

3.1.6 Crude Oil

Mississippian limestone play (MLP) crude oil was used for all experiments. First, it was used for primary drainage to initially saturate the cores with oil before aging. Then it was used for IFT measurements including contact angle test. The density for the crude oil was measured to be 0.8073 g/cc at 40 degree Celsius.

3.2 Experimental Procedures

In this section, all equipment and procedures used during the research are presented in detail. The results and conclusions are explained in different chapter.

3.2.1 Preparation of Polyelectrolyte Complex Nanoparticles

Polyelectrolyte Complex Nanoparticles (PECNP) is prepared by mixing two different types of polyelectrolyte, PEI and DS. Initially, each of these polyelectrolyte solutions is prepared separately using the main brine (2% NaCl). A concentration of 1 wt% of PEI and DS is dissolved separately into the 2% NaCl brine separately and each allowed to stir at a 600 revolutions per minute (RPM) for about an hour [18]. Then, the PECNP is self-synthesized in the laboratory before each experiment. PEI was mixed with DS and brine at different ratios based on volumetric basis as follow (PEI : DS : brine). The 1% DS solution should be released in a beaker containing 1% PEI solution instantaneously, at the desired ratio, to avoid precipitation. The batch of PECNP which is a mixture of PEI/DS is prepared/diluted with brine (2% NaCl) as per the required ratio for the experiment.

Different ratios along with different pH values for PEI were used to prepare PECNP as shown in Table 2. The main concept was to determine the optimum system for research experiments. Stability of PECNP system is an essential and important part for the success of the research and experiments. These systems can be either positively or negatively charged based on the ratio of PEI to DS. PEI is a polycation which is positively charged while DS is a polyanion with negative charge. When PEI volume is higher than DS it creates a positively charged PECNP system, which was used for this study. Stability of PECNP can be evaluated by measuring the size and zeta potential, and that is presented in next section. All the PECNP solutions used during this study were diluted 8 times in 2% NaCl brine.

Table 2 PECNP batches prepared at different PEI/DS mixture ratios and pH

Batch #	Ratio	pH
1	PECNP (3:1:0.1)	9
2	PECNP (3:1:0.1)	8
3	PECNP (4:1:0.1)	9
4	PECNP (4:1:0.1)	8
5	PECNP (2:1:0.1)	9
6	PECNP (2:1:0.1)	8

3.2.2 Size and Zeta potential of Polyelectrolyte Complex Nanoparticles

A particle size and zeta potential analyzer (Brookhaven's NanoBrook Omni instrument) as shown in Figure 7 was used for the purpose of particle size and charge measurements. The scope was to measure the mean size of particle and the electrical surface charge as well. Dilute suspensions (DLS) method was used for particle sizing measurements in which samples of nanoparticle were diluted in R.O. water by 40 times. Using the same instrument, zeta potential was measured by utilizing phase analysis light scattering (PALS) to determine the electrophoretic mobility. The sample for PALS test were diluted 20 times in 10 mM NaCl solution. The results that were obtained from DLS and PALS for all the PECNP batches was the main source for choosing the optimum batch to be used for the rest of the study.

Figure 7 NanoBrook ZetaPALS Potential Analyzer

3.2.3 Core Characterization

Core Saturation

First, the cores were cut to the desired length and diameter then dried in oven at 40 degree Celsius for two days, this is to ensure that it is completely dry and free from any liquid. After drying process was completed, the dry weight was measured for all cores and recorded. The cores then are vacuumed using a vacuum pump till a pressure reading of -30 psi is reached and is allowed to stay for one hour. Following this step without releasing the vacuum pressure, brine is allowed to saturate the cores through suction line. The cores remain under saturation for one hour approximately.

Porosity Measurement

After saturation process is completed, the wet weight for each core is measured. Given the weights of cores both wet and dry, the pore volume (PV) of the core can be calculated using Equation 1. Porosity is then calculated using Equation 2.

$$PV = \frac{W_{wet}-W_{dry}}{\rho} \text{ ………………………………………………………………Equation 1}$$

$$Porosity\ \emptyset = \frac{PV}{BV} \text{………………………………………………………………Equation 2}$$

PV = pore volume, cc

W_{wet} = Saturated weight of core, g

W_{dry} = Dry weight of core, g

ρ = Density of saturation fluid (brine), g/cc

Permeability Measurement with Brine

Permeability was measured using a core flooding system. The whole setup was at 40 degree Celsius temperature and at atmospheric pressure. The cores that were vacuumed and saturated with brine, as explained in core saturation section, are placed in a Hassler-type core holder. An overburden pressure is applied using an external hydraulic pump in order to apply 600 psi confining pressure. A simple core flooding experiment is performed for each core using brine as the injection fluid. The test was run for each core at three different flow rates of 1, 2, and 3 ml per minute (ml/min). Switching to higher rate was based on the pressure stability. A pressure transmitter (Honeywell) was connected to the inlet and outlet of the core holder to measure the differential pressure. All the pressure lines connected to the transmitter were initially flushed with SOLTROL-130 and trapped up to the pressure reading node. A diagram for the core flooding setup is shown in core flooding section 3.2.8.

Given pressure drop data and flow rate along with core specification and property, the permeability was calculated using Darcy's law by substituting in Equation 3.

$$q = \frac{k\ A\ \Delta P}{\mu\ L} \quad \text{………………………………………………………..………………...Equation 3}$$

q = Injection flow rate, cm^3/s

k = Permeability, Darcy

ΔP = Differential pressure, atm

μ = Viscosity of injection fluid, cp

A = Cross-section are of core, cm^2

L = Length of core, cm

Primary Drainage with MLP crude oil

MLP crude oil was pumped into the saturated cores at an injection rate of 2 ml/min till no more brine is produced through the outlet. The outlet of the core was connected to a tube line that is ended in a graduated glass cylinder, in order to measure the amount of brine that was displaced by crude oil. This volume of produced brine is considered as the initial oil volume in the core. Oil saturation is calculated by dividing produced brine volume to the total pore volume of the core, this method is known as volumetric method. In addition, mass balance is a different approach to calculate oil saturation by measuring the mass of the core before and after each experiment. The oil saturation then can be calculated by substituting into equation 4.

$$S_o = \frac{W_B - W_A}{PV\ (\rho_b - \rho_o)} \quad \text{…… Equation 4}$$

S_o = Oil Saturation

W_B = Weight of core before injection, g

W_A = Weight of core after injection, g

PV = pore volume, cm^3

ρ_b = Density of Brine, g/cm^3

ρ_o = Density of Crude Oil, g/cm^3

The injected crude oil for each core was approximately 10-12 PV. The core system setup was similar to the permeability measurement experiment. Ambient pressure, and confining pressure of 600 psi was applied. The temperature of the system was at 40 degree Celsius.

Aging of Cores

The principal of core aging is to restore the rock to its initial reservoir condition, wettability in particular. After the core is displaced with crude oil (Primary Drainage), it was placed in an oven at 90 degree Celsius for 4-5 weeks. All the 14 cores have been aged after the primary drainage experiment.

3.2.4 Viscosity and Density Measurements

A Brookfield viscometer was used to measure the viscosity of all fluids used in this research including crude oil. Viscosity was measured at 40 degree Celsius temperature to simulate reservoir condition. The final recorded viscosity for each material was an average of three reading at the highest rotation speed.

An Anton Paar density meter was used to measure the density of the samples that were used in this study. Similarly, all the density measurements were at 40 degree Celsius temperature.

3.2.5 Interfacial Tension Measurements

Interfacial tension (IFT) is a measure of the forces between two immiscible fluids, it is normally measured in dynes/cm. A pendant drop technique was used in this experiment to determine the dynamic IFT between two liquid phases as shown in Figure 8. The setup consists of two main chambers, one is filled with MLP crude oil which was injected through the needle using a hand pump. The second chamber contains the aqueous solution that need to be tested, which is pumped using the same hand pump in order to fill the cylindrical view cell. In this experiment, all the fluid materials were used, starting with brine (2 wt% NaCl) as a base case, then moving to the next solutions, which are 1% DS, 1% PEI, and PECNP in order to compare their result with the base line brine. However, as part of investigation and screening, PEI and PECNP were tested on two different pH levels (pH=8 and 9) to have better evaluation on the effect of pH on IFT, and to choose the most efficient system for the next experiments. Overall, a total of six fluid materials were tested in this experiment as shown in Table 3.

Table 3 Materials prepared for the IFT experiments

No.	Sample
1	2% NaCl
2	1% DS
3	1% PEI (pH=8)
4	1% PEI (pH=9)
5	PECNP (pH=8)
6	PECNP (pH=9)

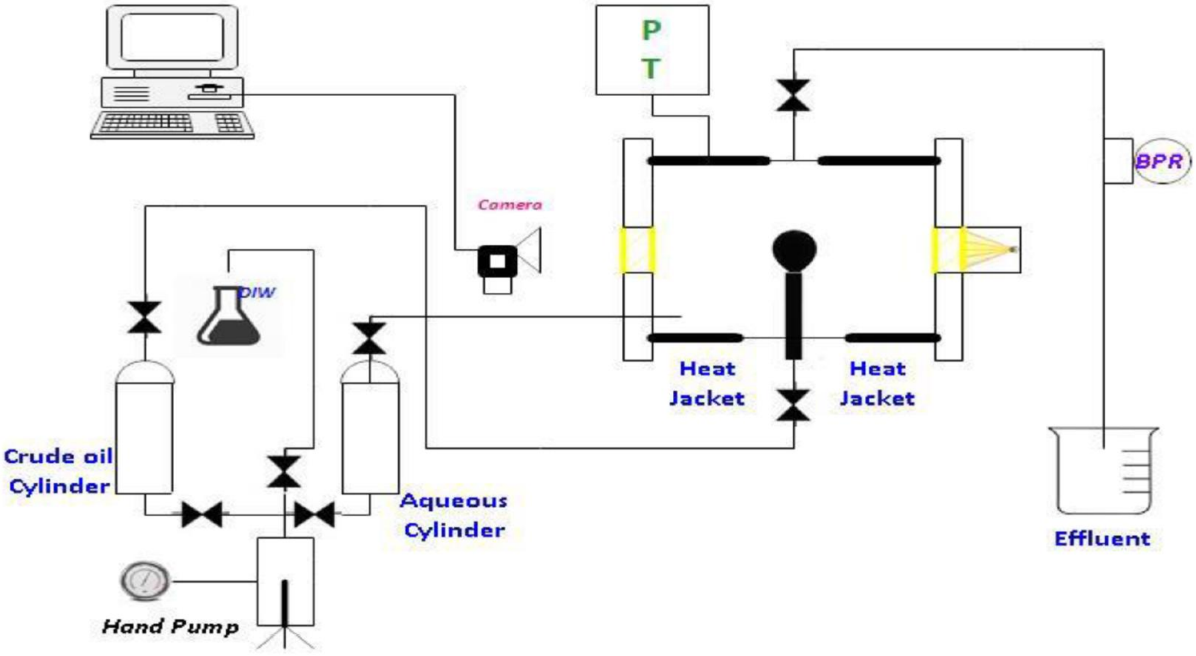


Figure 8 Schematic of IFT setup (This figure was drawn by Negar Nazari [1])

All the measurements were conducted at 40 degree Celsius temperature and it was maintained using heat jackets. In regard to pressure, it is known that it has no significant effect on IFT compared to temperature. The pressure normally has more effect on gases, while all the systems were liquid to liquid [24]. However, pressure was maintained between 600-800 psi.

3.2.6 Contact Angle Measurements

The contact angle experiment measures the quality of tension forces between liquids and solid surfaces. It is one of the methods of wettability indication towards solid surfaces. The aim in this study was to evaluate the wettability properties between crude oil and rock using the nanoparticle system. The core was cut into a number of thin chips with the same diameter of core and having a thickness of 3 millimeter. The same setup that was used in IFT experiment, was used for contact angle measurements as well, only the top valve was replaced to hold and fit the rock chip, see Figure 9.

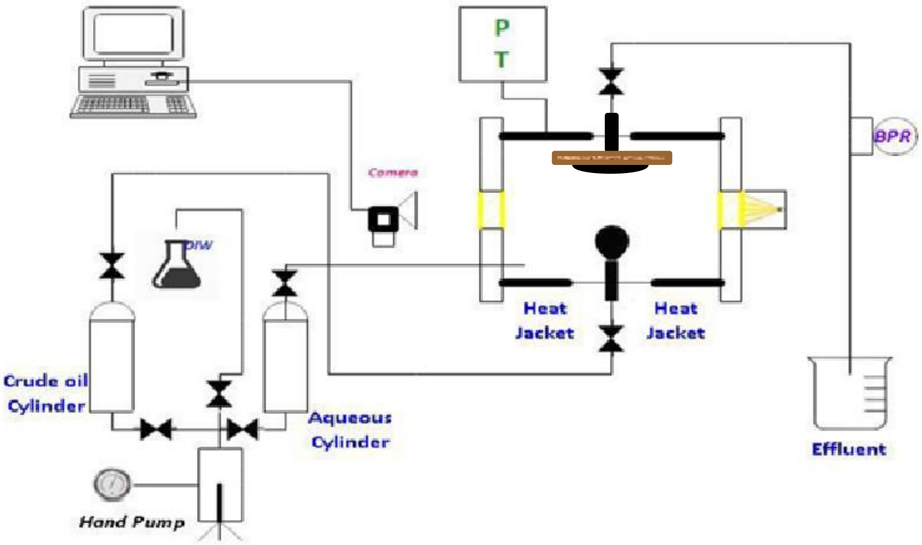


Figure 9 Schematic of contact angle setup (This figure was originally drawn by Negar Nazari [1] and modified by author)

Similar to IFT measurements, all the materials in Table 3 were tested in order to analyze the data by comparing the results of all the prepared fluids. The view cell was filled with each fluid and the experiment was performed while the rock chip was submerged in the same fluid. After stabilizing the pressure and temperature, a single oil drop is initiated then the first contact angle was measured using the software tools. The same process was then repeated by adding more oil drops until the angle starts to stabilize. All the measurements were conducted at 40 degree Celsius temperature and it was maintained using heat jackets.

3.2.7 Amott Test

Amott test was used as an alternative approach to measure the average wettability of the rock. Both spontaneous imbibition and forced imbibition of oil by water were used for each fluid system. After the aging process of cores, four cores were picked and placed into four Amott test cells, see Figure 10. The fluids used for this experiment were 2 wt% NaCl brine, 1% PEI, 1% DS and PECNP. The pH level that was used for this experiment is equal to pH=8, which is for PEI. All the setup was placed in oven at 40 degree Celsius for 3 weeks. Frequent readings for production were recorded and presented in plot that is explained in the result section. The cores were selected based on similarity in terms of rock properties in order to have a fare comparison result.

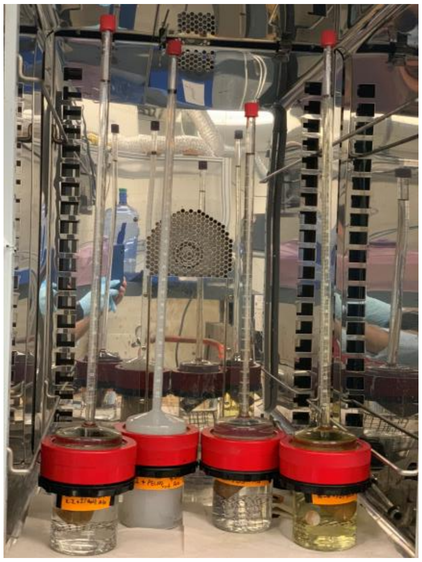


Figure 10 Amott test cells setup in oven at 40 degree Celsius

The forced displacement test was done using a core flood system that is defined in the next section in terms of setup and schematic. The four cores were flooded separately, each with the same fluid that was used for the spontaneous imbibition test. Oil recovery from the forced displacement was recorded using long glass tubes. Finally, the ratio of spontaneous displacement volume to the total displacement volumes in both tests is used as a wettability indicator [25].

3.2.8 Core Flooding

Core flooding system was used several times in this research beginning from permeability test to primary drainage. Furthermore, the forced imbibition experiment of Amott test was conducted using the same setup. Finally, the main core flooding experiment that includes secondary and tertiary recovery process were performed also using this setup which is shown in Figure 11.

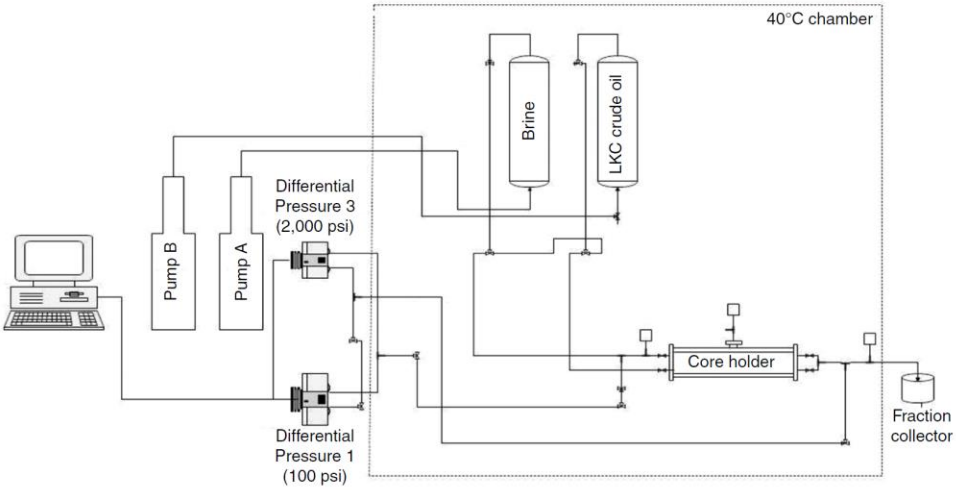


Figure 11 Schematic of core flooding setup (This Figure was drawn by Joel Tetteh [26])

The experiment was conducted for four IL cores using different flooding schemes in order to evaluate the optimum case. All the flooding tests included three fluid systems of brine (2 wt% NaCl), 1% PEI and PECNP. The pH value for the nanoparticle system was equal to 8 as this was the most stable system. For the main core flooding experiment, the production was collected in small tubes with a volume of 1.5 ml (Figure 12). All the cases are explained in detail in the results section.

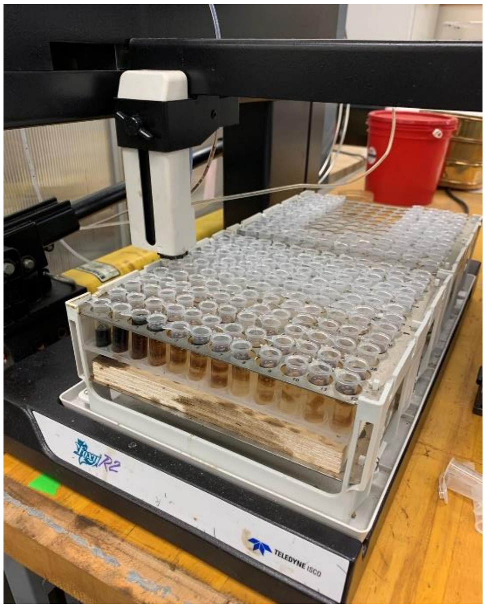


Figure 12 Production tubes for core flooding experiment

Chapter 4: Results and Discussion

This chapter presents all the experimental work performed during the period of this research. The first sections cover the initial screening and preparation of the nanoparticle system by choosing the most stable ones based on precipitation and quality. The samples that passed this initial screening are then moved to the next part which is particle sizing and zeta potential (surface charge), for further screening process. The next sections cover measurements of Interfacial tension, Contact angle, and Amott test. Finally, the core flooding experiment was performed to validate all the previous test result.

4.1 Preparation of Samples

As mentioned previously in materials section, the nanoparticle system is prepared and synthesized in the lab by mixing both of PEI and DS at a specific ratio, depending on the purpose of the research. This mixture is also diluted with 2 wt% NaCl which is the main brine that was used during all the study. Table 4 shows the samples that were initially prepared and their properties.

Table 4 Properties of the initially prepared samples

Chemical	Viscosity (cp)	Density (g/cc)	pH @21C
2% NaCl (brine)	0.69	1.006	6.05
1% PEI	0.74	1.007	10.86
1% DS	1.18	0.991	6.71

All the previous samples were prepared based on weight percentage. The only difference is that brine is prepared using R.O. water while the other samples are prepared using the brine itself. For example, 1% PEI was prepared using 1 gr of PEI chemical and 99 gr of brine (2% NaCl).

4.1.1 Synthesizing of PECNP at Different Ratios of PEI, DS and BRINE

This section presents the first part of this study and the most critical results. Synthesizing nanoparticle using a ratio of (PEI : DS : brine) results in creating a sample with a certain size of particle and a surface charge. Since PEI is positively charged and DS is negatively charged, adding more PEI with respect to DS creates a positively charged nanoparticle which is the desired type of charge for this research. Different batches of nanoparticles were prepared based on different solutions ratio and different pH level. The pH level was adjusted by adding approximately between 2 to 5 ml of HCl drops into PEI solution to reduce its pH to the desired value. The average pH for PEI solution is 11 which is higher than desired and therefore it requires to add pH modifier for further reduction. The batches that had high precipitation and poor quality were removed. The remaining batches were moved to the next step, which is PALS and DLS measurements, for further analysis.

4.1.2 Particle Size (DLS) and Zeta Potential (PALS)

The stability of nanoparticle system is very essential to achieve the objective of the study. This part of the research leads to important indication of the quality of nanoparticle system. Table 5 shows the results of both DLS and PALS at different mixture ratios and different pH for the batches that were prepared.

Table 5 Results obtained from DLS and PALS for PECNP batches

Batch #	**Ratio**	**pH**	**DLS**			**PALS**		
			Eff. Diam (nm)	**Std. Dev.**	**Count rate**	**Zeta Potential (mV)**	**Std. Dev.**	**Count Rate**
1	PECNP (3:1:0.1)	9	148	18.57	550	26.39	3.28	860
2	PECNP (3:1:0.1)	8	125	12.26	450	17.05	5.62	low
3	PECNP (4:1:0.1)	9	132	17.62	400	13.7	5.18	low
4	PECNP (4:1:0.1)	8	137	15.93	650	28.51	10.11	300
5	PECNP (2:1:0.1)	9	342	34	600	22.08	8.01	800
6	PECNP (2:1:0.1)	8	212	20	520	31.77	0.8	290

As shown in Table 5, a total of 6 batches were prepared which are divided into three groups in terms of PEI : DS ratio. Batch 1 & 2 used a ratio of 3:1, while batch 3 & 4 used a ratio of 4:1, and finally batch 5 & 6 used a ratio of 2:1. Each of these groups were prepared at two different pH levels as shown in the table. Looking at the count rate result for zeta potential measurement, it is noticed that batches from 1 to 4 are unstable when pH changes. During operation it is necessary that the system remains stable under different range of pH as it may get changed once its contaminated with reservoir fluids. Therefore, batch 5 & 6 were picked as the final solution system to proceed to the next experiments for further analysis.

4.2 IFT Measurements

To evaluate and study the interaction between fluids, dynamic IFT measurements were performed using pendant drop technique. Total of six experiments were conducted between MLP crude oil and the various brine systems. Each system was injected into the view cell to fill it completely and pressurize it until no air exists in the system. Temperature is raised and maintained at 40 degree Celsius using electrical heater and thermal jacket. After pressure and temperature stabilization, the first drop of oil is initiated and starts recording. The IFT measurements were recorded at a time interval of one second for a maximum of one hour period. Some of the systems could not maintain up to one hour due to the low IFT values in which the oil drop releases before completing one hour. The base line system for all experiments was the main brine which is 2% NaCl solution. The other five solutions are 1% DS, 1% PEI and PECNP with two test for PEI and PECNP at two different pH values.

4.2.1 Experiment 1: IFT between Brine and Crude Oil

In order to establish a baseline, the first IFT measurement was performed for 2% NaCl brine. The initial IFT value started at 14 dynes/cm as shown in Figure 13.

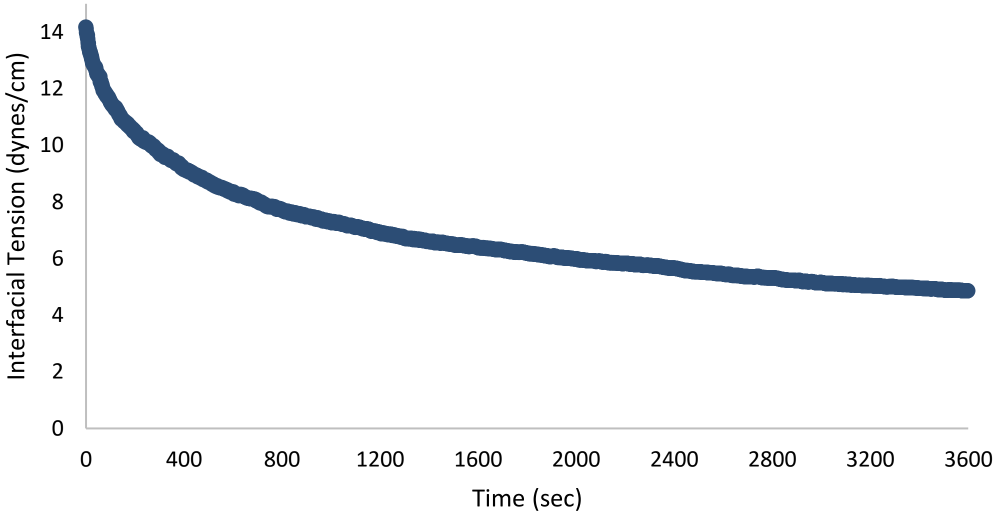


Figure 13 Dynamic IFT measurement between 2% NaCl brine and MLP crude oil

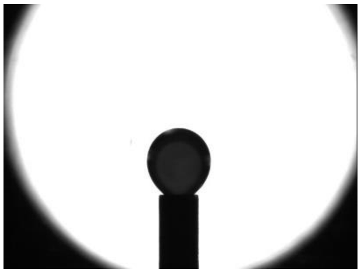


Figure 14 Hanging drop of MLP crude oil in 2% NaCl brine

Donaldson et al. (1969) reported values for IFT between 43 crude oils and 2% NaCl brine and it was ranging from 9.9 to 31.5 dynes/cm [27] [28]. Therefore, this value considered to be at the lower ranges of IFT. Moreover, the system reached equilibrium almost at the end of the experiment approaching a value of 5.8 dynes/cm. Figure 14 shows the hanging drop of MLP crude oil in 2% NaCl brine solution at the beginning of the experiment.

4.2.2 Experiment 2: IFT between 1% DS and Crude Oil

The initial IFT value is 10 dynes/cm. A significant decrease in IFT is observed using 1% DS solution compared to the base line brine. It is noticed that, the time required to reach equilibrium is much faster than the previous case. However, that value is measured to be 5 dynes/cm which is more or less close to the base case, see Figure 15. The hanging drop at the beginning of the test is shown in Figure 16.

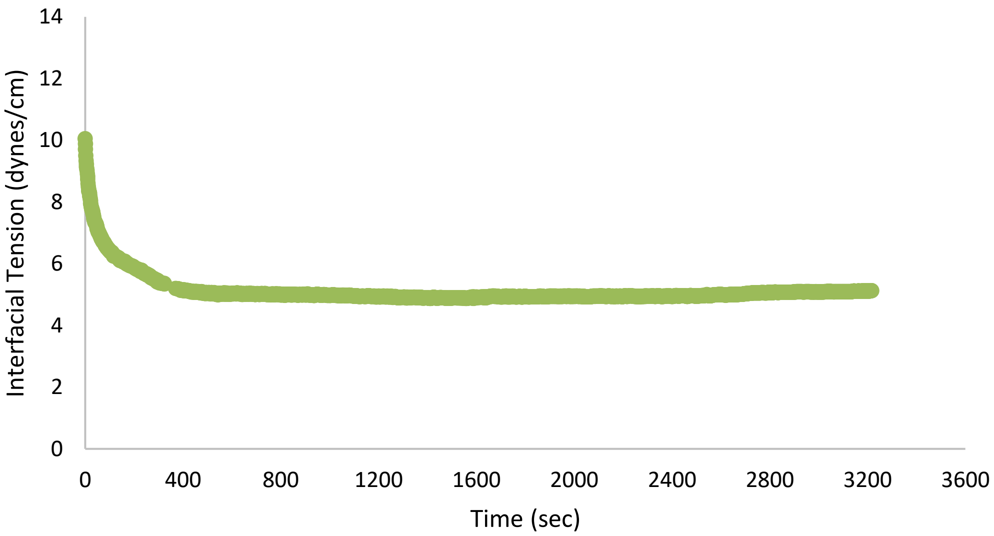


Figure 15 Dynamic IFT measurement between 1% DS and MLP crude oil

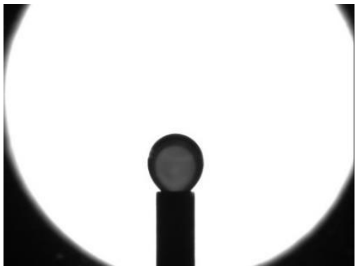


Figure 16 Hanging drop of MLP crude oil in 1% DS brine

4.2.3 Experiment 3: IFT between 1% PEI at pH=8 and Crude Oil

The initial value for this case is 7 dynes/cm using 1% PEI at pH of 8. By comparing this result with the base case, it is certainly proven that PEI has significant impact on IFT reduction. The IFT was close to half of the IFT measured for the baseline case. Moreover, not only the equilibrium was reached quickly, the values are very low in which it caused the drop to release with less than 20 min, see Figure 17. On the other hand, stabilizing the oil drop and optimizing the area size of the drop was difficult to manage due to low IFT values. Figure 18 shows the size of oil drop which was smaller compared to the previous cases.

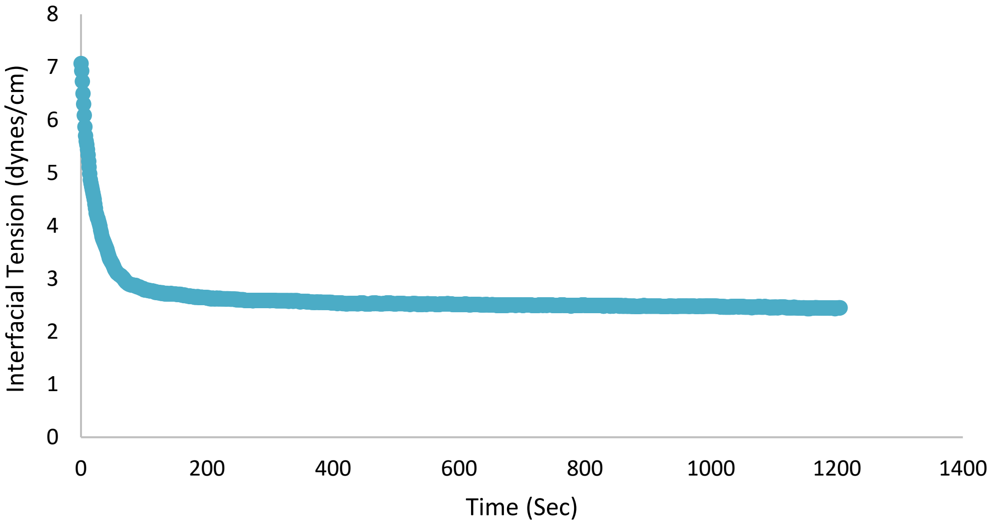


Figure 17 Dynamic IFT measurement between 1% PEI pH=8 and MLP crude oil

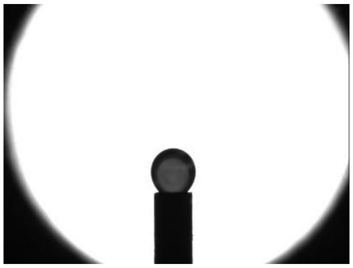


Figure 18 Hanging drop of MLP crude oil in 1% PEI pH=8

4.2.4 Experiment 4: IFT between 1% PEI at pH=9 and Crude Oil

The initial value for this case was 2.8 dynes/cm using 1% PEI with pH of 9. A significant drop occurred in IFT values by only modifying the pH of the solution. An equilibrium trend was achieved with less than 2 min because the initial values were very small, see Figure 19. As for the oil drop, similar to PEI with pH=8, it was small and tends to release faster, see Figure 20.

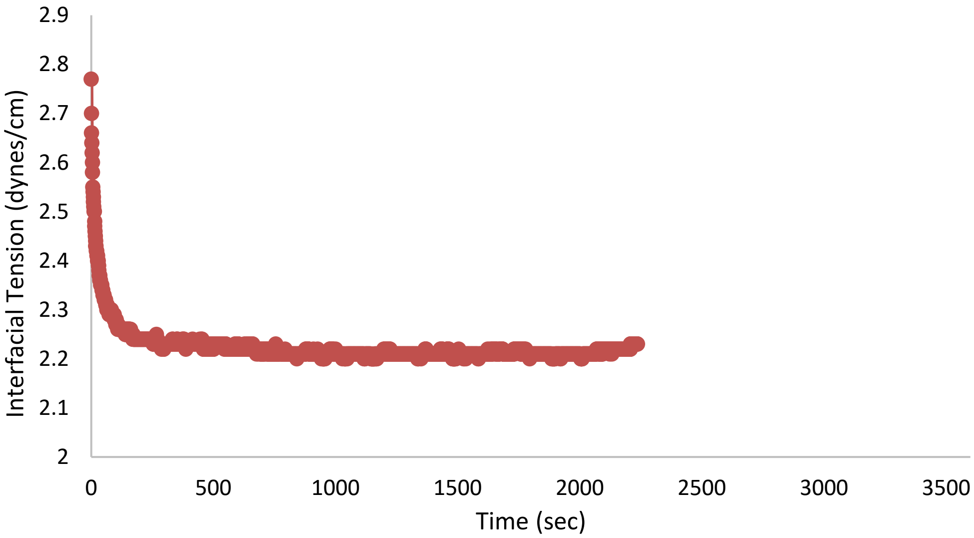


Figure 19 Dynamic IFT measurement between 1% PEI pH=9 and MLP crude oil

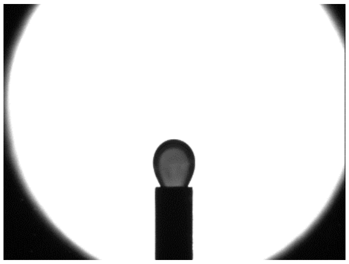


Figure 20 Hanging drop of MLP crude oil in 1% PEI pH=9

4.2.5 Experiment 5: IFT between PECNP at pH=8 and Crude Oil

The initial value of IFT was 3.8 dynes/cm for nanoparticle system with pH=8. The PEI with same pH value resulted in higher IFT, which means that the nanoparticles mixture succeeded in lowering the tension forces with crude oil at this pH level. Overall, the trend is the same compared to PEI except that it has lower values as explained, see Figure 21. Figure 22 shows the oil drop size at the beginning of the test, which is similar to the case of PEI solution.

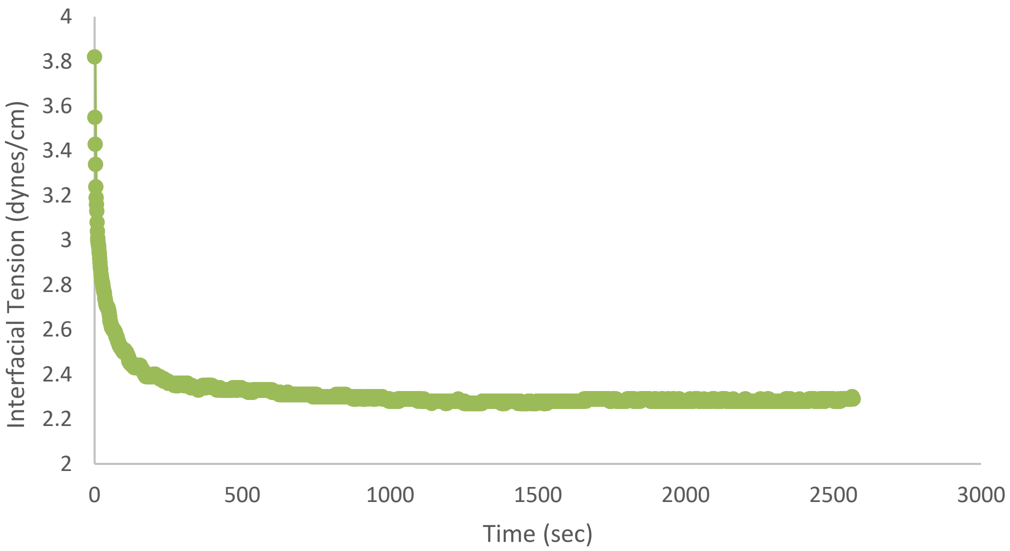


Figure 21 Dynamic IFT measurement between PECNP pH=8 and MLP crude oil

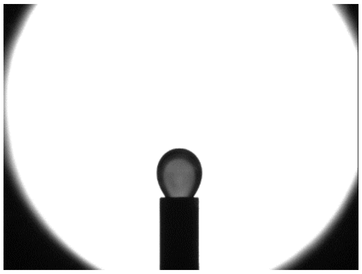


Figure 22 Hanging drop of MLP crude oil in PECNP pH=8

4.2.6 Experiment 6: IFT between PECNP at pH=9 and Crude Oil

The initial value of IFT was 3.3 dynes/cm for nanoparticle system with pH=9. Comparing the result for both PEI and PECNP at different pH values, it can be clearly seen that pH has inverse relation with IFT. Higher pH solutions have lower IFT values, which are more desirable up to this point. Similarly, the trend is the same regardless of pH value except that IFT values are lower compared to PECNP at pH=8, see Figure 23. An interesting observation for PECNP solution is that IFT does not change significantly by changing pH, on the other hand, PEI solutions showed a higher change in IFT for different pH values. Figure 24 shows the drop at the beginning of the test which is similar to PECNP at pH 8 and the other PEI solutions.

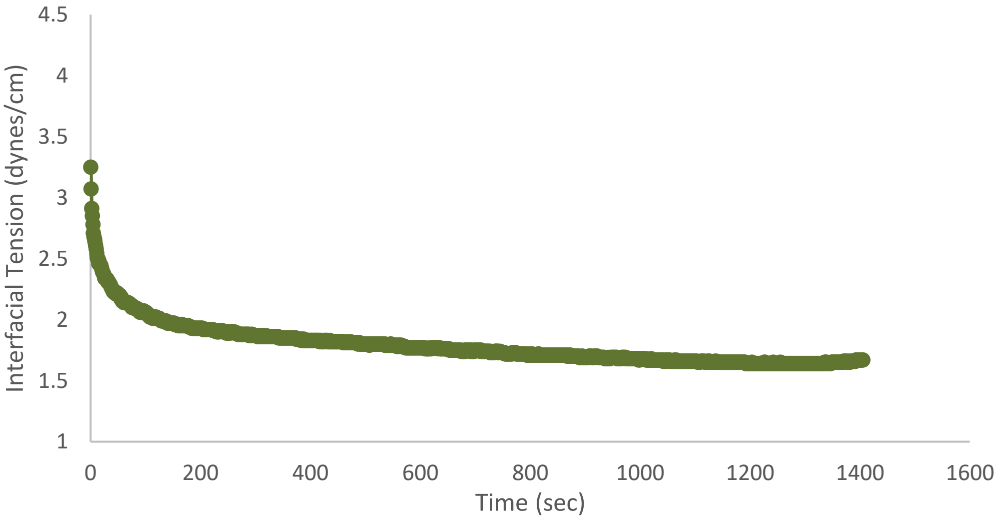


Figure 23 Dynamic IFT measurement between PECNP pH=9 and MLP crude oil

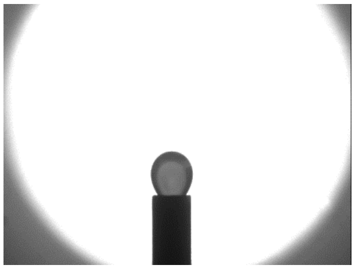


Figure 24 Hanging drop of MLP crude oil in PECNP pH=9

4.3 Contact Angle Measurements

Similar to IFT experiments, the list of fluids reported in Table 3 were used for contact angle measurements to estimate the wettability of the rock in oil/brine system. Firstly, 2% NaCl brine was tested and it showed reasonable results, which is explained in the next section. However, all the other fluids showed spreading effect where the drop tends to spread on the rock as if it is a strongly oil-wet condition. A further investigation and explanation are declared in section 4.3.2.

4.3.1 Contact Angle Test for the Brine-Oil-Rock System

Starting with the base case, the results for contact angle were realistic and reasonable. The average water contact angle was 120^o indicating an oil-wet system, see Figure 25. The results were reproducible with standard deviation of 0.3.

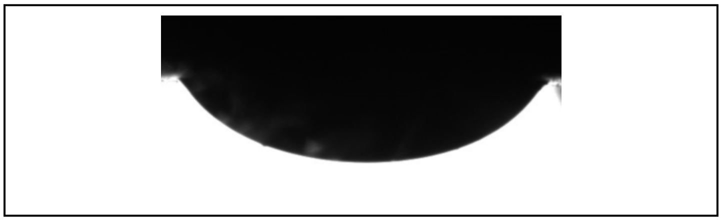


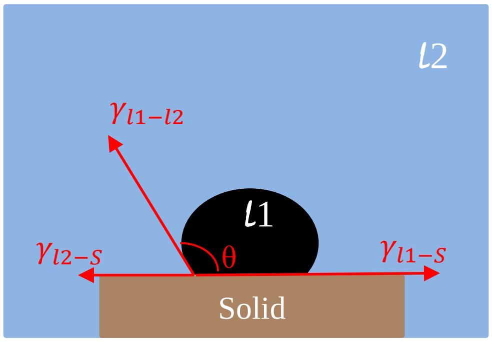
Figure 25 Contact angle of 2% NaCl brine / MLP crude oil / IL rock

4.3.2 Effect of Low IFT on Contact Angle Measurements

Contact angle measurement was also performed for all the other fluids (1% DS, 1% PEI and PECNP). Surprisingly, the oil droplet tended to spread on the rock in all the cases. This is usually an indication of strongly oil-wet system or a very low IFT. As introduced in Young’s contact angle definition, the contact angle of two fluid system (oil/brine) on solid surface (rock) is a function of the oil/rock, brine/rock, and oil/brine IFTs [29]. A possible explanation for this might be that measuring contact angle in case of low oil/brine IFT could not be conclusive for wettability determination.

Adejare et al. (2012) measured contact angle for oil/rock under low IFT system using surfactants and it caused the oil drop to spread on the rock immediately [29]. In order to explain the reason, they applied a different procedure by centrifuging the rock in the surfactant allowing it to alter the interfacial properties of the rock, then the contact angle was measured under their brine system without using surfactants. They confirmed that the conventional method of measuring contact angle under low IFT systems may not be representative due to the spreading effect as suggested by their analysis. In addition, Rao (1996) prepared a plot of contact angle against the interfacial tension between oil/brine/rock system. The analysis showed that there is critical spreading tension value below which oil droplets will spread on the rock surface [30].

On the other hand, as shown in Figure 26, based on Young's equation that calculates contact angle under liquid, the lower the IFT between two fluid system the higher the contact angle is, which means the lighter fluid in terms of density may spread on the rock surface which is oil in our case.



$$\cos\theta = \frac{\gamma_{l1-s} - \gamma_{l2-s}}{\gamma_{l1-l2}}$$

Figure 26 Calculation of Young's contact angle in three-phase system

Where:

$\gamma_{l1\text{-}s}$ is the surface tension of liquid (*l1*)

$\gamma_{l2\text{-}s}$ is the surface tension of liquid (*l2*)

$\gamma_{l1\text{-}l2}$ is the interfacial tension between the two liquids

θ is the contact angle of liquid (*l1*)

4.3.3 Contact Angle Test for Soaked Samples

A different procedure was performed to evaluate the wettability effect for one of the fluids from the previous section, in order to have further investigation on the spreading effect. The rock sample was soaked for two weeks before conducting the contact angle experiment. Figure 27 shows the result of contact angle using a rock chip that was soaked in 1% PEI (pH=8) to allow it for more reaction. A slight change was observed showing more tendency toward water-wet, which confirms that wettability alteration is achieved.

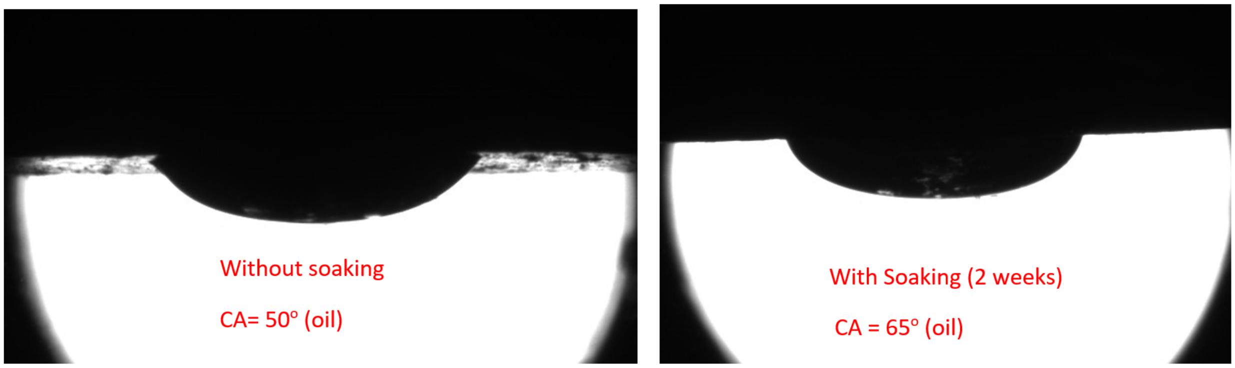


Figure 27 Contact angle measurement between 1% PEI (pH=8) and MLP crude oil on IL rock using soaking procedure

As mentioned in the previous section that due to low IFT between fluids, the oil tends to spread on the rock surface. That does not necessarily mean that it did not change its wettability, but in order to confirm that, an alternate method or approach should be implemented other than contact angle measurement. Therefore, the contact angle measurement is not representative as a wettability indicator in this case. It did improve the result due to stabilization, which also indicates that the wettability is imposing; however, a different approach is required to confirm the wettability of the rock.

4.4 Amott Test

In this experiment, a spontaneous imbibition along with forced displacement were combined in order to measure the average wettability of the core using the Amott's method. Both of these displacements were using different brines to displace the initial oil saturated in the core, in order to calculate the water imbibition index, I_w. The four cores that were picked for this test are core no. 2, 6, 12 and 14. The result is divided into two parts, Spontaneous Imbibition and Forced displacement as shown in the next sections.

4.4.1 Spontaneous Imbibition

As explained earlier in the methods section, the core have been placed in the glass cells inside the oven at 40 degree Celsius for approximately 3 weeks. Figure 28 shows the oil recovery reading vs time during the spontaneous imbibition. It can be clearly seen that, PECNP solution has the highest oil recovery reaching almost 12%. PEI solution has the second highest recovery, which means that it has the main impact on wettability alteration compared to DS. Looking at DS solution, it is slightly higher than the base case which is 2% NaCl. Therefore, all the solutions have shown improvement in wettability alteration compared to the base case, which is a positive indication. Moreover, the nanoparticles achieved their main goal by altering rock wettability. Adding chemical additives or modifying the concentration of nanoparticle would certainly add up to the efficiency of oil recovery. However, the aim for this research is to test the nanoparticle without involving any additives.

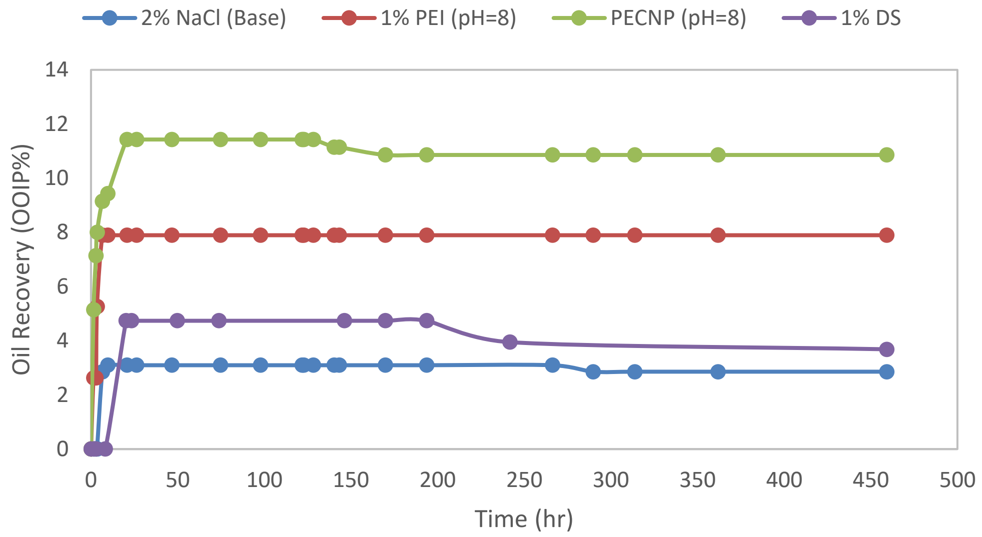


Figure 28 Oil recovery vs time from the spontaneous imbibition test (Amott)

4.4.2 Forced Displacement

After completing the spontaneous test, the cores were removed from the cells for a preparation of a forced displacement test using core flooding setup. Each core was displaced with the same fluid that was used in the previous test. A total of approximately 38 pore volume was pumped into each core. The temperature of the system was 40 degree Celsius. Table 6 shows the amount of oil produced for each test.

Table 6 Oil production from forced displacement test (Amott)

Core no.	Brine	Oil produced, ml
2	2% NaCl	2.75
6	1% PEI (pH=8)	2.35
12	PECNP (pH=8)	2.3
14	1% DS	2.3

It is observed that PECNP has the lowest production in this test, this is obvious because a higher volume was produced during the spontaneous imbibition experiment.

4.4.3 Summary of Amott Test

As a summary, the cores that showed a higher water Amott index ratio are more towards water wet. The scale for this ratio is between zero to 1, where 1 means strongly water wet and zero means strongly oil wet [25]. Table 7 shows the calculated values for all the solutions. The PECNP has the highest ratio, which indicates that it is the outstanding system for altering wettability compared to the others.

Table 7 Calculated displacement ratio for Amott test

Core no.	Brine	I_w
2	2% NaCl	0.0418
6	1% PEI (pH=8)	0.1132
12	PECNP (pH=8)	0.1418
14	1% DS	0.0574

4.5 Core Flooding Experiment

Core flooding experiments were conducted in order to evaluate oil recovery by injecting all solutions that are tested during this study in terms of IFT and wettability. It is considered as a confirmation or validation of the results that are shown in the previous tests. As discussed previously, four aged cores were picked for this experiment (Core No. 1, 3, 5 and 11). The cores were chosen based on similarity in terms of permeability and oil saturations. Each core has different injection scheme based on the alteration sequence of the injected fluid. A total of approximately 120 pore volume was injected for each core. For an injection of three different solutions, each had approximately a 40 PV of injection before switching to the next solution. Table 8 shows the different schemes of fluid injection for all core flooding tests. The ambient temperature during the test was at 40 degree Celsius and at atmospheric pressure.

Table 8 Core flooding fluid injection sequences

Experiment No.	Core No.	First Injection	Second Injection	Third Injection
Experiment 1	11	1% PEI	PECNP	Brine
Experiment 2	3	Brine	PECNP	1% PEI
Experiment 3	5	Brine	1% PEI	PECNP
Experiment 4	1	PECNP	1% PEI	Brine

4.5.1 Experiment 1: 1% PEI → PECNP → Brine

The maximum recovery achieved for this case was 60%. First 1% PEI was injected in the core for a total of 40 PV followed by PECNP for the same volume, and finally similer volume of brine is injected at the end. Almost the same scenario was conducted for all experiments with only altering between the injected fluids as shown in Table 8. From Figure 29, It can be clearly seen that PECNP did not add extra oil production after PEI injection, the same thing for brine. It is possible that nanoparticle needs more time to affect the wettability of the rock in order to start recoveing more oil. Moreover, brine did not add any recovery when it was injected after PECNP This can be clearified more from the next experiments in next sections.

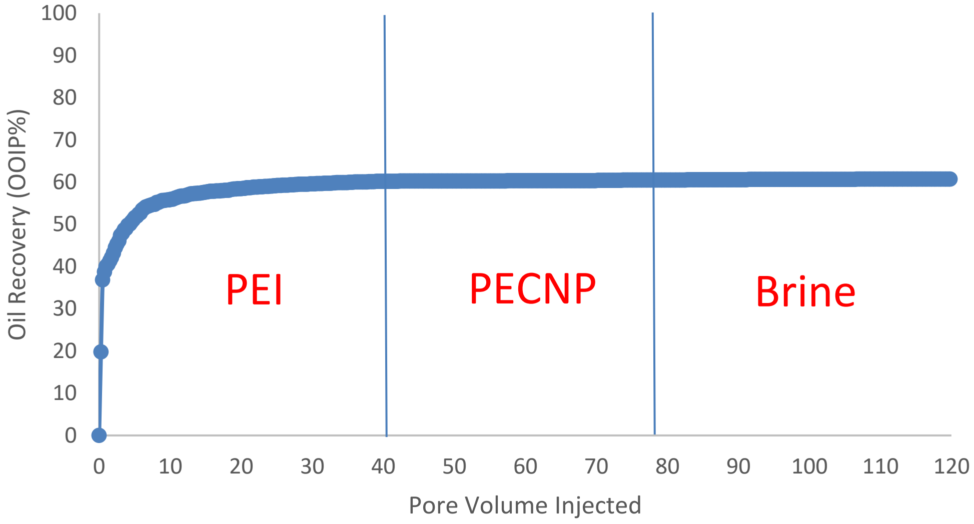


Figure 29 Cumulative oil recovery (OOIP %) vs pore volume injected (core no. 11)

4.5.2 Experiment 2: Brine → PECNP → 1% PEI

The maximum recovery achieved for this case was 67%. As shown in Figure 30, the injection started first with brine followed by PECNP then PEI. From the data, the effect of shifting to PECNP and PEI is not clear although the trend continued increasing but very gently. Because brine is the base fluid of all the solutions, they continued the same trend and it is possible that the nanoparticle system did not have enough time to react. Up to this point, it is declared that PECNP is not effective when injected as tertiary oil recovery. A further conclusion is verified in the last experiment when using PECNP as secondary oil recovery. Note that our saturation measurement method is not effective for such small volumes of produced oil and further work is needed to clarify this effect.

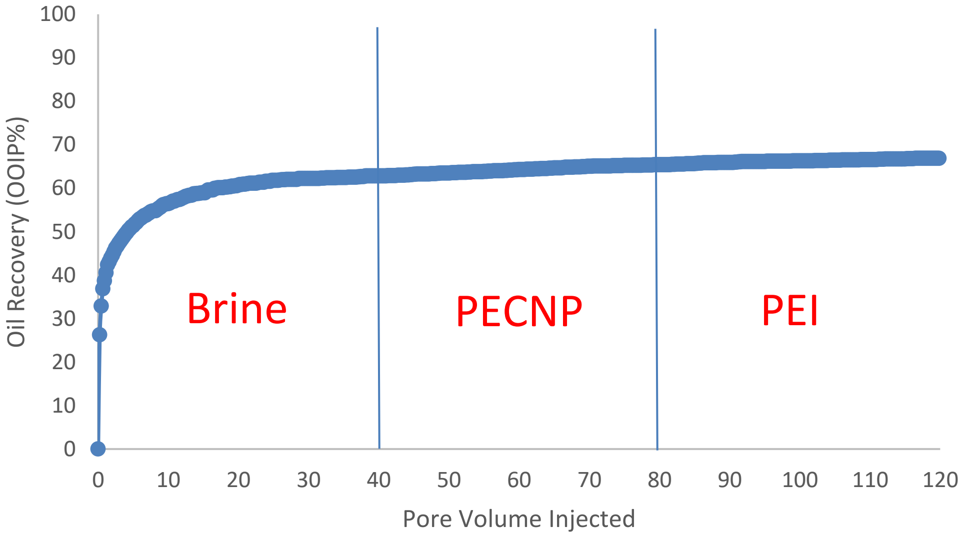


Figure 30 Cumulative oil recovery (OOIP %) vs pore volume injected (core no.3)

4.5.3 Experiment 3: Brine → 1% PEI → PECNP

The maximum recovery for this case was 76%. Figure 31 shows the sequence of injection staring with brine and ending by PECNP. The most surprising part in this test is with the high initial recovery that reached up to 74% with brine only. Many facts are involved in this aspect; one of them is due to the small OOIP of this core compared to the others. Moreover, no significant oil recovery added after shifting to PEI or PECNP. Up to this point, PECNP looks that it performs better when it is injected at the early stages. This is clarified more on the next scenario case.

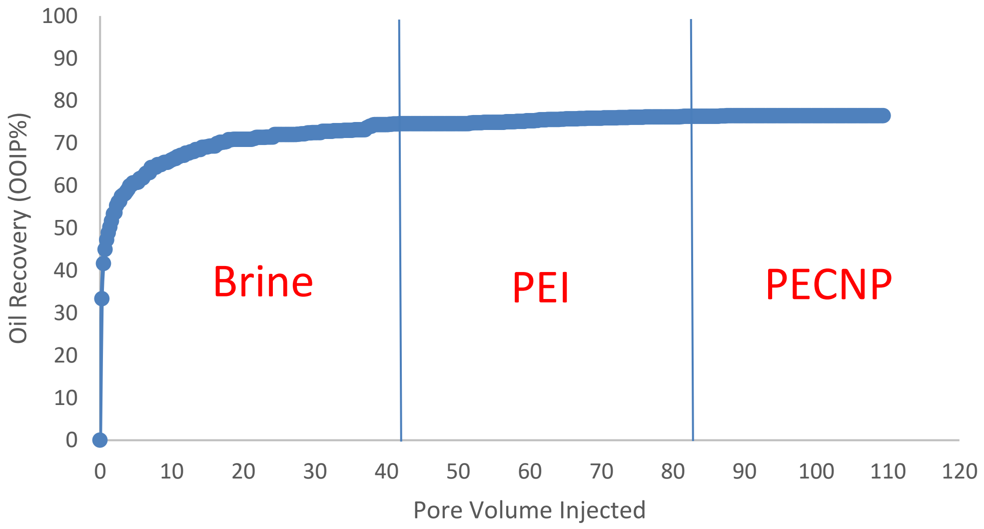


Figure 31 Cumulative oil recovery (OOIP %) vs pore volume injected (core no.5)

4.5.4 Experiment 4: PECNP → 1% PEI → Brine

The maximum recovery for this case was 80%, which is the highest production out of all the cases. As Figure 32 shows, the oil recovery keeps on increasing after injecting PECNP at the initial stage and adding approximately 4% to the recovery. After switching to brine at the final stage, no significant increase in production was observed. That could be typical because already the core has produced most of the producible oil. During and after injecting PECNP, most of the production was in emulsion condition. The low IFT between PECNP and crude oil in addition to a more water-wet system resulted by injection of PECNP tends to increase production. Moreover, production readings from small tubes is quite challenging and involve errors, it become more complex when the outcome is emulsion. That could be one of the limitations of core flooding experiment when using low IFT fluids. Figure 33 shows the emulsion in the production tubes.

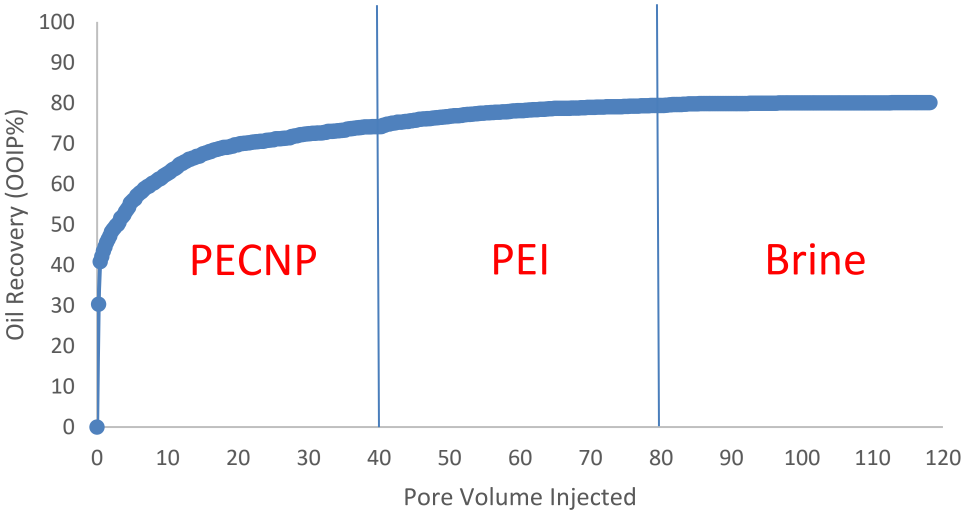


Figure 32 Cumulative oil recovery (OOIP %) vs pore volume injected (core no. 1)

Figure 33 Emulsion production of core flooding experiment #4

Chapter 5: Summary and Conclusion

In this study, the capability of Polyelectrolyte Complex Nanoparticles (PECNP) for wettability alteration of carbonate rocks was explored. First, preparation and screening through the most stable PECNP system took in place prior to the main lab experiments. Moreover, investigation was conducted to discover the possibility of reducing interfacial tension between oil and brine using PECNP. In addition, wettability measurement was performed using contact angle and Amott test to investigate the ability of PECNP in wettability alteration of IL carbonate rock. Finally, the research was concluded by applying core flooding tests using different schemes of injection. The purpose of all these experiments is to confirm and to know how PECNP can enhance oil recovery of carbonate rocks.

The results indicate that PECNP has the ability to reduce interfacial tension between oil and brine, and alter the wettability of the IL carbonate core sample. Interfacial tension has been reduced significantly using PECNP with a quick drop to equilibrium as compared to 2% NaCl brine. Due to low IFT values for nanoparticles system, the wettability using contact angle was difficult to measure. The wettability alteration evaluation was investigated using Amott test as an alternative method. A spontaneous imbibition of oil by water along with a forced displacement test were performed for different systems including PECNP. The highest oil recovery from Amott test was for PECNP, and the lowest was for 2% NaCl brine. As for PEI and DS, both performed better than brine. The DS showed slight improvement compared to brine while PEI was higher and closer to the PECNP system.

The core flooding experiments included different schemes of injection to obtain the preeminent one. However, it was difficult to identify which one is more efficient due to many facts. One of them is the emulsion between oil and PECNP which caused by low IFTs. The oil recovery estimation could be more than what is reported because of the error involved in readings due to emulsion and small volumes produced. Nevertheless, PECNP has shown a satisfying performance in oil recovery in terms of core flooding. The results report that PECNP is more efficient when it is used as a secondary recovery agent rather than for tertiary recovery.

A better understanding of the phenomena and physics behind wettability and IFT alteration using PECNP is required. The stability of nanoparticle system is controlled by many factors, one of them is pH acidity level. Including wide range of pH for PECNP and having more focus on the effect of pH on wettability alteration performance would add excessive values to the research. The concentration of nanoparticles also plays an important role on the quality of the system because of the direct effects on the particle size and its surface charge. Therefore, a study for the performance of PECNP on different concentrations is essential to improve the efficiency of the system, additionally, it also has economic impact for field operation scale. As for the core flooding experiment, the result was not clearly conclusive and needs to be investigated further. Looking for different injection schemes or modifying the injection rate might give better indications.

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