LABORATORY INVESTIGATION OF NANO-POLYMER FLOODING IN CARBONATE RESERVOIRS

by

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ORIGINALITY STATEMENT

I, Kassymzhomart Ulasbek, hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at Nazarbayev University or any other educational institution, except where due acknowledgement is made in the thesis.

Any contribution made to the research by others, with whom I have worked at NU or elsewhere is explicitly acknowledged in the thesis.

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Signed on 08.04.2022

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ABSTRACT

The traditional chemical Enhanced Oil Recovery (EOR) method like polymer flooding is widely used in the petroleum industry. However, a new method of chemical EOR has been paid much attention in the field of research. It comprises a combination of silica nanoparticles with polymer. Researchers have conducted various experiments on silica nanoparticles/polymers flooding.

The focus of this study is to investigate the silica nanoparticle's behavior dissolved in hydrolyzed polyacrylamide (HPAM) by coreflooding experiments and calculate the oil recovery. It is known that polymer solution has a high viscosity, decreases the mobility ratio, thus, affects to the macroscopic sweep efficiency, which increases the oil recovery. At the same time, it was investigated that nanoparticles have the capability of wettability alteration, decreasing the interfacial tension (IFT) and protection from polymer degradation, therefore, increasing the microscopic sweep efficiency.

The optimum concentrations for hydrolyzed polyacrylamide (2000 ppm) and silica nanoparticles (0.1 wt %) were selected via rheology experiments and contact angle measurements. Zeta-potential tests showed an addition of salt decreases the stability of nano-silica/polymer solutions. The result of the contact angle measurements revealed that silica nanoparticles alter the wettability of surfaces. For 0.1 wt % nanoparticle solution, there is a maximum deviation of 45.6° in contact angle. Rheology experiments indicate that the addition of silica nanoparticles to polymer solution increases the viscosity, so the nano-silica/polymer has a higher viscosity than the polymer solution itself. A series of core flooding experiments are provided using brine, hydrocarbon, polymer, silica nanoparticles, and salt. The maximum oil recovery of 87.045 % was determined from the second scenario, injecting silica nanofluid followed by nano-assisted polymer solution as an EOR technique.

It is a unique study since different flooding sequences are applied combining silica nanoparticles and modified synthetic polymer. Therefore, the use of silica nanofluid followed by nano-assisted polymer solutions as an EOR technique demonstrated a great impact on oil recovery mechanisms. In porous media, silica nanoparticles enhance the performance of polymer solutions. Such research will open new avenues for hybrid EOR applications.

Keywords: EOR, coreflooding, nanoparticles, polymer, wettability alteration, stability, viscosity, oil recovery.

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ABBREVIATIONS

EOR	Enhance Oil Recovery
IFT	Interfacial Tension
IOR	Improved Oil Recovery
HPAM	Hydrolyzed Polyacrylamide
NP	Nanoparticle
PV	Pore Volume
RF	Recovery Factor
NWP	Naturally wet polysilicon
HLP	Hydrophobic and lipophilic polysilicon
OOIP	Oil original in place
RRF	Residual resistance factor
RF	Resistance factor
CA	Contact angle
ZS	Zeta sizer
HAP	Hydroxyapatite
IUPAC	International Union of Pure and Applied Chemistry
ASP	Alkali-Surfactant-Polymer
HASP	Hydrophobically associating polyacrylamide
API	American Petroleum Institute

SYMBOLS

μ	Viscosity
φ	Porosity
γ	Shear rate
π	Mathematical constant
ρ	Density

1. INTRODUCTION

1.1 Background

The lifecycle of a producing oil field is comprised of several stages. The initial production of oil in a field occurs as a result of the reservoir pressure in the primary stage, when oil flows naturally to the surface. It is usual to inject water into the secondary stage when the reservoir pressure drops in order to boost the pressure and displace the oil. The primary and secondary methods of recovery, such as waterflooding or re-injection of natural gas produced, produce on average about one-third of the original oil in place (OOIP). A tertiary recovery (also referred to as Enhanced Oil Recovery, EOR) could however allow for the extraction of as much as 40-60% of the oil in the reservoir (Abubaker, Alagorni, Yaacob, & Nour, 2015). The two main types of EOR methods are nonthermal and thermal. Chemical floods and gas floods are examples of nonthermal methods. Thermal methods, on the other hand, include steam injection, hot water injection, and situ combustion. Finally, the remaining oil can be recovered using a variety of methods, including CO_2 injection, natural gas miscible injection, and steam recovery in a tertiary or enhanced oil recovery process (Al-Mutairi, Saad, Kokal, Sunil, & Aramco, 2011).

EOR refers to the process of extracting oil by injecting fluids and energy that are not normally present in the reservoir. It aims to achieve two main objectives with the injection of fluids. As a first step, it boosts the natural energy in the reservoir, then it interacts with the reservoir rock/oil system to create conditions that allows a portion of residual oil to be produced, by altering fluid properties or rock and fluid interactions, which includes reducing water-oil interfacial tension, increasing capillary number, reducing capillary forces, increasing drive water viscosity, providing mobility control, creating oil swelling, reducing oil viscosity, modifying rock wettability (Taber, SPE, F.D.Martin, & Seright, 1997).

Carbonate reservoirs are known to contain an important portion of the world's hydrocarbon reserves. Low porosity and fractures are common features of carbonate reservoirs. Hydrocarbon recovery rates are normally lower because of these two characteristics and oil-to-mixed wet rock properties. The fluids injected during EOR will pass through the fracture network and bypass the oil in the underlying rock. The fracture network has a high permeability factor, and the equivalent porous volume is low, which frequently results in the injection fluids reaching the surface early (Manrique, et al., 2010).

The use of polymer flooding in EOR processes increases sweep and displacement efficiency by decreasing the mobility ratio and fingering tendency. It may be possible to consider polymer

flooding as an alternative to waterflooding of an oil reservoir if water production is premature or the oil recovery factor is low at water breakthrough (Bera., et al., 2020). In harsh oil reservoir conditions, such as high salinity and temperature, polymer flooding can be successfully implemented using a water-polymer solution that can cope with these limitations (Li, Zhai, Xu, Shen, & Mao, 2000). Nanofluid flooding is a new technique for chemical EOR that involves injecting nanomaterials or nanocomposite fluids into oil reservoirs to effectively displace oil or enhance injectivity. Nanofluid flooding has several advantages over conventional chemical flooding such as wettability alteration, reduction of interfacial tension, change of disjoining pressure for oil displacement, and controllable viscosity.

In recent years, developments in nanotechnology have demonstrated that adding nanoparticles to polymer flooding increases oil recovery, but few published studies have examined polymer performance with nanoparticles (Maghzi A. e., 2013). In the studies of Maurya & Mandal, (2016) the nano-polymer suspension was prepared by mixing silica nanoparticles with polyacrylamide polymer. Results showed that compared to polyacrylamide solution alone, silica nanoparticle-induced polyacrylamide showed better viscosity.

1.2   Problem definition

The oil production rate has declined significantly in most mature oil reservoirs. Increasing energy demand cannot be met by discovering new oil resources. Consequently, after primary and secondary recovery, the oil industries are paying attention to enhanced oil recovery (EOR) techniques in order to recover the remaining trapped oil. For the 21st century; where energy demand continues to increase every day, it is necessary to develop new advanced EOR methods to supply crude oil. New methods of eliciting trapped hydrocarbon oil can be developed in response to reservoir properties. EOR techniques like polymer flooding allow the process of recovering crude oil from the reservoir to be improved by injecting fluids to increase sweep efficiency. Fluid mobility and reservoir heterogeneity can lead to viscous fingering and a decrease in oil recovery. Water viscosity can be increased by using polymers. The viscous polymer solution formed by adding them to a necessary concentration is used as a displacement fluid. In turn, this minimizes mobility, increasing sweep efficiency. Using nanoparticles as catalysts for chemical EOR studies is a promising approach, and recent studies show this can significantly increase the oil recovery factor when used properly. Rodriguez, (2009) and Zhang, (2015) found that silica nanoparticles coated with polymer molecules have a great transport behavior across the pores of

different permeability with weak retention. Ponnapati, (2011) discovered that polymer modified silica nanoparticles could mobilize the residual oil and produce 7.9% of the OOIP in laboratory experiment. Polymer/silica nanoparticles solution, according to Behzadi & Mohammadi, (2016), can regulate oil and water interfacial tension (IFT) and adjust the wettability of glass micromodel from oil-wet system to a water-wet system, resulting in a greater EOR effect than unmodified silica nanoparticles. The use of silica nanoparticles with synthetic polymers can therefore substantially increase the oil recovery efficiency and increase flooding efficiency by changing capillary and viscous forces. Despite this, existing research has not been applied to harsh environments. The concept of nano-assisted polymer flooding in high salinity and high temperature is relatively new. Therefore, studying the behavior of those chemicals in porous media at harsh conditions is important to further improve EOR. The main questions are "What is the effect of silica nanoparticles on polymer viscosity?", "Is nano-assisted polymer solution more efficient than polymer alone?", "Which flooding scenario is the best in terms of oil recovery and why?". Various experiments will be conducted in this study to answer these research questions.

1.3   Objectives of the Thesis

1.3.1   Main Objectives

The main objective of the thesis is to examine the combination of silica nanoparticles and polymer as prospective EOR method for carbonate rock. In this study, the effectiveness of those chemicals in oil recovery mechanisms under harsh conditions (high temperature and high salinity) is tested. The following is the primary objective of the research:

- An evaluation of silica nanofluid's stability
- Identifying optimal concentrations of silica nanoparticles and modified synthetic polymers that can withstand salinity levels of 40,000 ppm and reservoir temperatures of 80°C.
- Selection of best injectivity sequence in terms of oil recovery factor using polymer, silica nanofluid and nano-assisted polymer solutions

1.3.2   Thesis structure

The thesis structure was developed in order to meet the research objectives outlined above. The thesis generally consists of four main sections, such as methodology, results,

conclusion, and recommendations. Every section has a subsection that aims to accomplish the primary goal of the research.

Materials and procedure sections are included in the methodology part. The Materials presented the main resources needed for conducting the research. It includes formation water, injection brine, crude oil, polymer, nanofluid, and a few samples of carbonate core. The Procedure portion of the work describes how the experiments are conducted, the devices that are used, how cores are prepared before coreflooding experiments, wettability alteration, zeta-potential and rheology tests.

The Results section comprises determined data and discussion about them. This part examines the zeta potential test, rheology experiment, contact angle measurement and coreflooding experiment results. Zeta potential tests conducted to analyze the stability of silica nanofluids. Rheology measurements were used to evaluate the optimum polymer concentration, while contact angle measurements determined the optimum concentration of silica nanoparticles.

Conclusion and recommendations elaborate on the most important aspects of the study on the combination of silica nanoparticles and polymers for tertiary recovery technique. The recommendations are to perform contact angle measurements using nano-assisted polymer solutions at different polymer concentrations to analyze the effect of polymer on wettability.

The plan and organizational elements for completing all experiments are shown in Table 1. It took nearly 1 year to complete all experiments.

Table 1 – The plan of the thesis

Procedure	April	May	June	July	August	September	October	November	December	January	February	March	April
Literature review	■	■	■	■	■	■	■	■	■				
Design and Methodology			■										
Core selection and preparation			■										
Absolute and effective permeability measurements				■									
Aging of the core					■	■	■	■	■	■	■		
Fluid preparations				■	■	■					■	■	
Zeta potential tests						■							
Contact angle measurements							■						
Rheology measurements							■	■	■				
Coreflooding experiments										■	■		
Writing Thesis										■	■	■	
Defense													■

2 LITERATURE REVIEW

2.1 Oil recovery stages

There are several production stages performed during the oil production in the field. At the primary stage, oil moves by nature to the surface because of the pressure in reservoir. When pressure starts to decline, injection of water provides to maintain the reservoir pressure in order to produce more oil. After all, tertiary or enhanced oil recovery methods as natural gas miscible injection, CO_2 injection, chemical solutions or steam injection can be applied to recover remaining hydrocarbons (Saad, Al-Mutairi, & Kokal, 2011).

Primary recovery – is the stage, where the reservoir's natural energy is used to move hydrocarbons to and from the extraction wells. The premature possible identification of the drive mechanism is a primary target in the reservoir's early life, as this information will vastly enhance reservoir maintenance and regeneration in the reservoir's middle and later life. The main primary stage mechanisms are:

- Gas cap drive;
- Water drive;
- Solution gas drive;
- Gravity drainage;
- Combination drive;

Secondary recovery – is the stage of oil and gas development, where water injection (water flooding) or gas injection (gas flooding) is pumped into the formation in order to maintain the reservoir pressure and produce the hydrocarbon. This method is usually effective in recovering an additional 30% of the initial oil in situ, although the figure can vary based on the oil and the rock surrounding it.

Water flooding is achieved by pouring water into the wells while producing from adjacent wells at the same time. Water flooding projects are usually used to maintain formation pressure, as a brine water storage location, and as a water drive to carry oil from injectors to producers.

Gas Flooding. In principle, this approach is analogous with water flooding and is applicated for retain gas cap pressure, even though oil displacement is not required. Rather than displace the hydrocarbon, the natural gas, that has been produced is usually re-injected into the reservoir to retain the formation pressure (Hite, Avasthi, & Bondor, 2006).

2.2 Enhanced Oil Recovery

Enhanced Oil Recovery – is the type of oil recovery technique by injection of substances, which are normally does not present in reservoirs. EOR plays a key role in the petroleum industry since oil discovery is declining last decades. Tertiary or EOR, the third stage of production of oil that determined after water flooding or gas flooding. Since the secondary recovery process became uneconomical, tertiary methods used additives, miscible gas or thermal energy to displace additional crude (Al-Kaabi, Kokal, & Abdulaziz, 2010).

EOR is mainly achieved by the gas or liquid chemicals injection, as well as the application of thermal energy. EOR systems use carbon dioxide (CO_2), hydrocarbon gases, nitrogen, and flue gases, in a row of other gases. If the oil recovery is substantially dependent on a process different from immiscible displacement described by high interfacial tension (IFT) permeability, it is called an EOR method. Polymers, surfactants, and hydrocarbon solvents are among the liquid chemicals widely used. Thermal processes usually use steam injection, hot water injection, or lean on in-situ thermal energy formation by oil combustion in the reservoir rock (Figure 1).
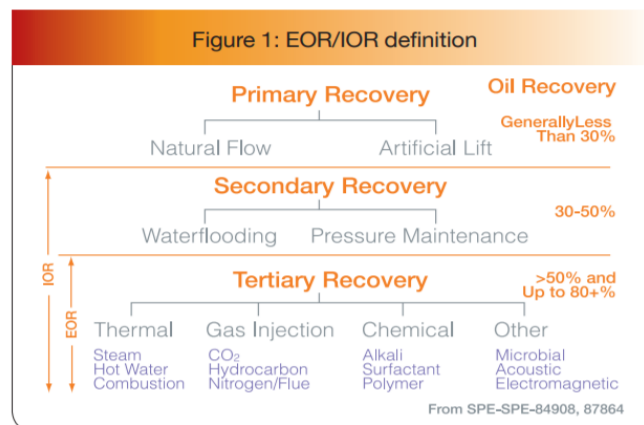
Figure 1 – Oil recovery stages *(Al-Kaabi, Kokal, & Abdulaziz, 2010)*

Classification of EOR by mechanism of oil displacement:

- Viscosity alteration and mobility control
- Miscible or solvent extraction processes
- Interfacial tension reduction processes

Oil displacement efficiency enhances as the oil viscosity decreases, also by reducing capillary forces, or IFT.

Volumetric sweep efficiency improves by a favorable mobility ratio (M<1) between injectants and remaining oil in the reservoir. It is essential to determine remaining oil and important mechanisms to increase oil recovery before implementing EOR.

2.2.1 Chemical EOR

Chemical methods entail the injection of particular chemicals that, because of their phase-behavior properties, essentially displace oil, lowering the IFT of the displacing liquid and the oil. Polymers, alkali, and surfactants are some of the most common traditional EOR chemicals. The injection of polymers with water raises the aqueous phase viscosity, resulting in increased movement as the polymers move from the injector to the producer. Furthermore, the polymer solution improves recovery of oil by lowering reservoir permeability to water. Surfactants minimize the interfacial tension of water and oil by interacting with those crude oil components, inducing emulsification and solubilizing interphase films. Capillary forces of trapped or residual oil are reduced as the IFT is reduced. Furthermore, surfactants adsorb on reservoir rocks, changing their wettability and thereby increasing oil recovery. Alkali flooding works in the same way as surfactant solutions do, but with various injectants. Foam flooding guarantees that pumped fluid is diverted from thief areas to low permeable reservoir areas. Meantime, alkaline-polymer, alkaline-surfactant, and alkaline-surfactant-polymer (ASP) flooding are based on incorporating various strengths and performance of surfactant, alkali or polymer slugs to enhance the size of pores and sweep efficiency of the initial oil in place (Abubaker, Alagorni, Yaacob, & Nour, 2015).

2.3 Polymer Application in Petroleum Industry

Polymer flooding may be used where water flooding method is no more effective due to fingering phenomenon resulting in early water breakthrough. In order to raise the viscosity of the injectant, polymer flooding includes injecting polymers with a high molecular weight that are water soluble together with water phase (Ojha, 2013). The injectant's gradual viscosity enhances the injected slug's mobility and conformance control while also eliminating viscous fingering. As a result, early water breakthrough, which is common in the water flooding method, is reduced, and an incremental oil recovery factor is obtained. For decades, polymer flooding has been applied in vast majority of oil fields with success, also on a pilot scale or on a commercial scale. These oil fields are: Daqing oilfield in China, the East Bodo Reservoir and Pelican Lake field in Canada, the Marmul field in Oman, and the Tambaredjo field in Suriname.

Furthermore, in the current energy market, polymer flooding has retained its rising significance. The informed incremental production of oil of up to 300,000 bbl/day from China's Daqing oil field is the most notable contribution.

2.3.1 Polymer types that are used for polymer flooding

Synthetic polymers and biopolymers are the two basic classifications for polymers applied in polymer flooding recovery operations. Polyacrylamides and their forms, like partly hydrolysed polyacrylamide (HPAM), hydrophobically associating polyacrylamide (HASP), and acrylamide copolymers, are examples of synthetic polymers (Wang, 2009).

Polymer Types that are often Used for Polymer Flooding

- Hydrolyzed Polyacrylamide (HPAM)
    - Polyacrylic acid
    - Polyacrylamide (PAM)
    - Hydrolyzed polyacrylamide (HPAM)
    - Co-polymers of the above
- Polysaccharide
    - Xanthan gum (a biopolymer)
- Hydrophobically Associating polymers (HASP, AP)

2.3.2 Polymer stability and rheology

2.3.2.1 Salinity effect on viscosity

Supplementation of polymer to distilled water makes the structure of the system elongated because it is negatively charged, however, in the brine molecules of the polymer will be coiled. The reason is positive cations such as Na^+, $Ca2^+$ seat on the polymer and make the polymer become coiled. Most polymers are sensitive to salinity and hardness, but not to pressure.
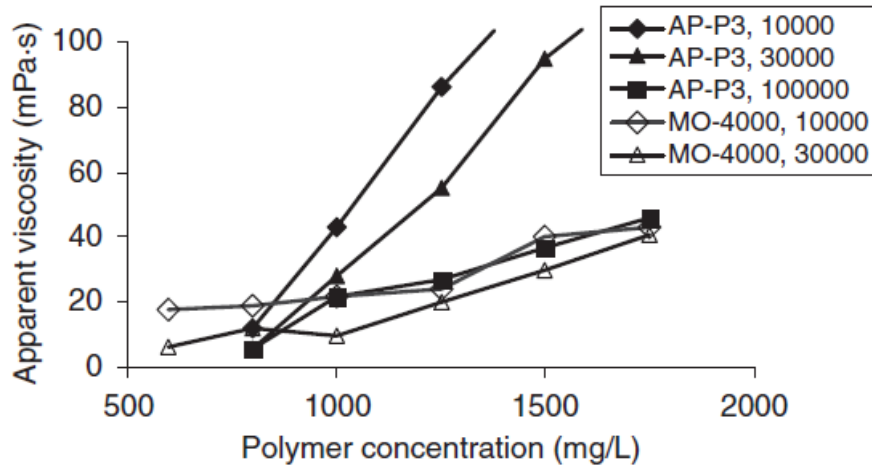
Figure 2 – Viscosity vs concentration of two typed of polymer. *(Luo, 2006)*

Figure 2 illustrates the comparison of the viscosity rise by concentration of two types of polymers at various salinity such as 10,000, 30,000, and 100,000. It is shown that the viscosity of polymer AP-P3 was more than the polymer of MO-4000 at the identical concentrations of polymer, particularly at high salinity. Intermolecular association enhances by increase of salinity, for that reason viscosity rises. However, at a salinity solution of 4 mol%, 5 mol% and more the intermolecular association also rises, and polymer viscosity reduces (Figure 3) (Jiang, 2003a).
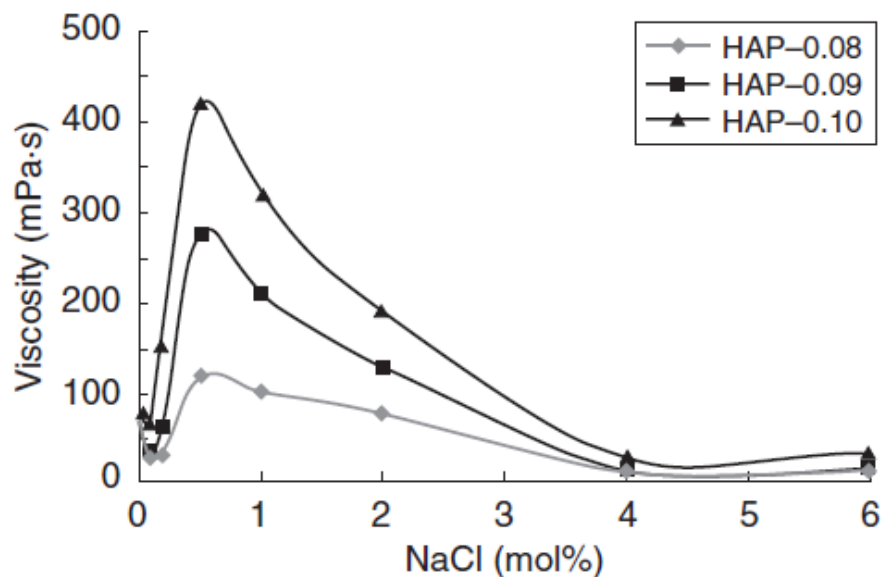
Figure 3 – Viscosity changes of HAP with NaCl. *(Jiang, 2003a)*

2.3.2.2 Effect of shear rate and polymer concentration

Normally, when shear rate rises, the perceived viscosity of polymer solutions utilized in EOR methods reduces. Shear thinning refers to fluids that have this rheological property. Since the polymer molecules can coordinate themselves with the shear field to minimize internal friction, the visible viscosity decreases. The power-law model (Bird., Stewart, & Lightfoot, 1960) presented in Eq. 1 can also be used to characterize the rheological properties of a shear-thinning fluid.

$$\mu = K\dot{\gamma}^{(n-1)} \tag{1}$$

where μ = apparent viscosity, K = power-law constant, n = power-law exponent, γ = shear rate, and consistent units should be used.

A standard rheogram for a shear-thinning fluid is illustrated in Figure 4 (Willhite, Stahl, & (Eds.), 1988), which is a plot of viscosity vs. shear rate. At the small shear rate fluid behaves like a Newtonian fluid, with constant apparent viscosity. This area is known as a lower Newtonian region. As the shear rate grows, the shear-thinning regime described by the power-law model takes over. Another transition from shear-thinning to Newtonian behaviour occurs at high shear speeds. This section is called the upper Newtonian flow region. High polymer concentration makes the polymer heavier, thus viscosity will be high. In the Figure 5 shown comparison of viscosity changes by concentration of two types of polymers.
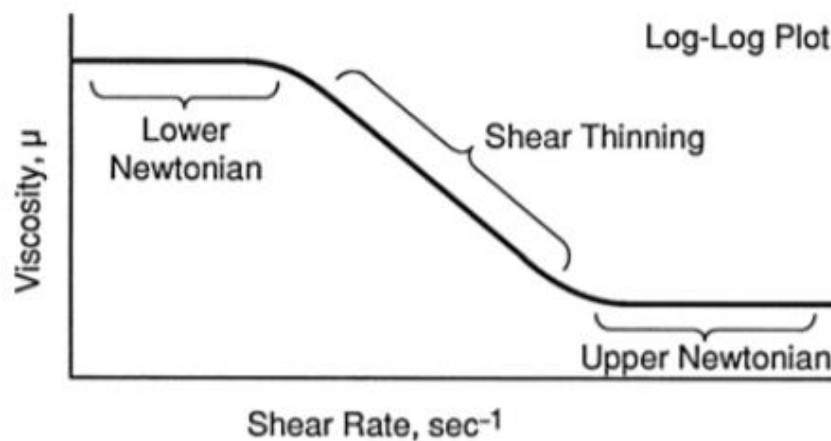
Figure 4 - Rheology of a shear-thinning fluid *(Willhite, Stahl, & (Eds.), 1988)*.
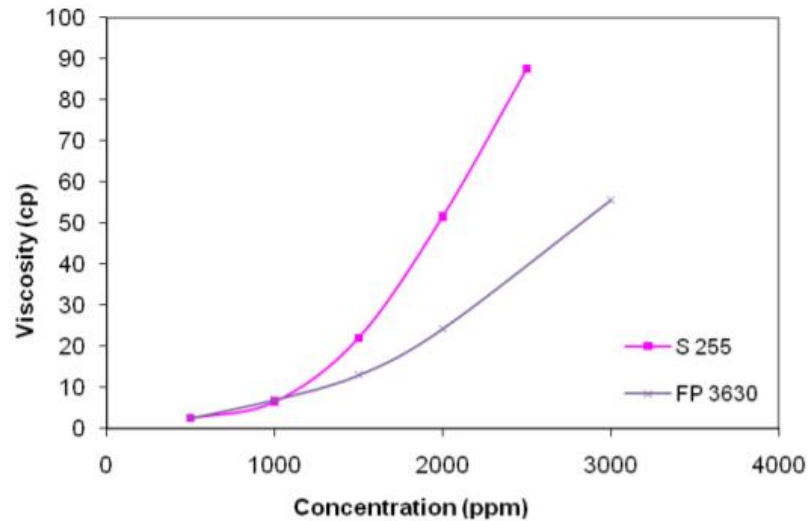
Figure 5 - Viscosity versus concentration. *(M. Buchgraber, T. Clemens, & and L.M. Castanier and A.R. Kovscek, 2009)*

2.3.2.3 Thermal instability and pH effect

In the Figure 6 it is evident how apparent viscosity changes by temperature for the polymer concentration of 2800 mg/L. The shear rate is 19.8 s^{-1}. Up to 35°C viscosity slightly increases firstly. In the range of 35°C and 45°C apparent viscosity is stable, however, above 50°C sharply reduction of viscosity observed and at the 70°C viscosity is 15.8 mPa-s (Zhou, Han, Xiang, Zhang, & Jiang, 2006). Hydrolysis is considered to be affected by pH. As a result, the viscosity of HPAM is pH-dependent. As alkali is applied, the pH rises at first. However, due to the salt effect, adding alkali can inevitably cause HPAM viscosity to decrease (Figure 7).
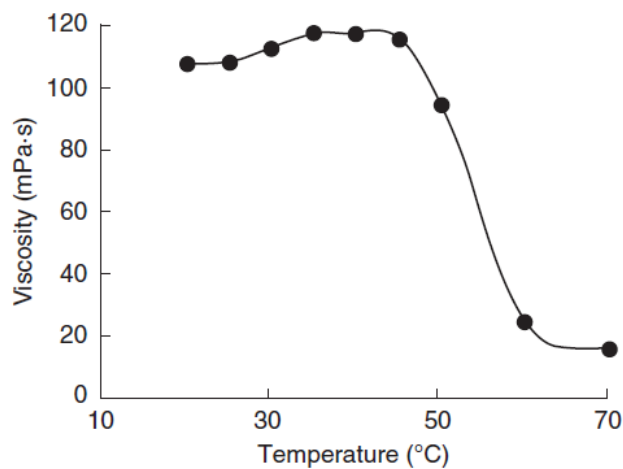
Figure 6 – Viscosity vs temperature. *(Zhou et al. 2006)*
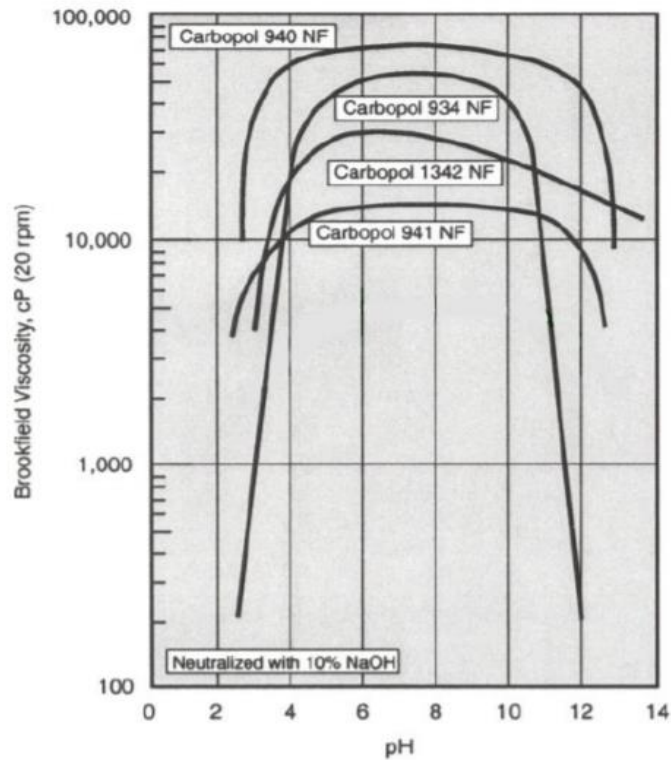
Figure 7 - Effect of pH on viscosity of a 1.0% solution of carbopol polymer in water **(Ojha, 2013)**

2.3.3 Retention of polymer and permeability reduction

Retention can be characterized by adsorption of polymer on the surface of the porous media and mechanical entrapment in pores, which are small with respect to the size of the molecules of polymer in solution. (Willhite & Dominguez, 1977) explored these various processes. Mechanical entrapment and hydrodynamic retention are similar phenomena that exclusively exist in porous system of flowing fluid.

Essential parameters:

- Rock type
- Permeability
- Salinity
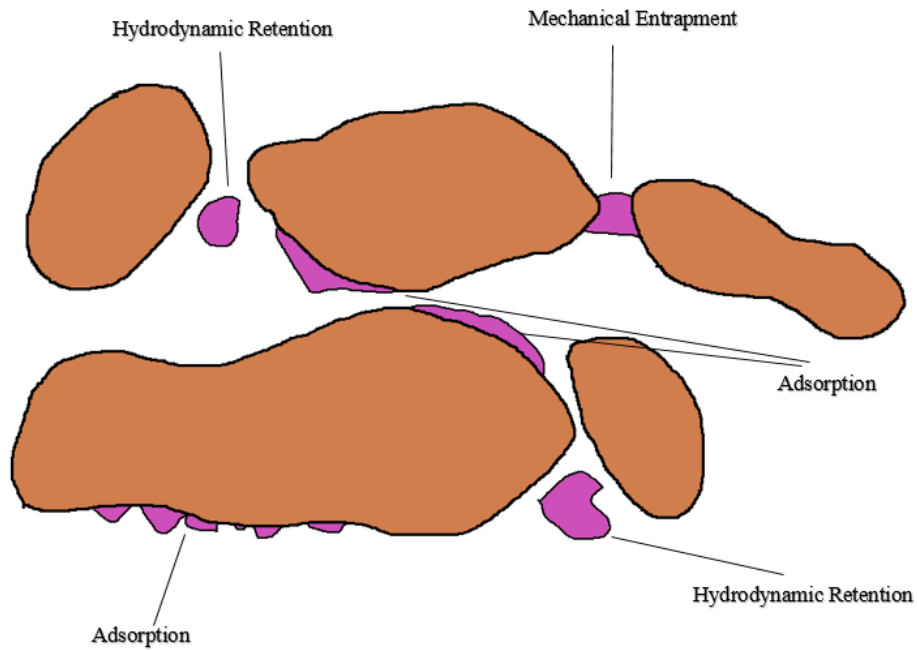
Figure 8 – Polymer retention

Due to heterogeneity in the formation, where polymer molecules cannot migrate through narrow pores, hydrodynamic trapping occurs.

When the injection fluid's molecules are larger than the small tube, fragments of the injection fluid are caught, halting the current and perhaps causing mechanical entrapment.

Polymer adsorption causes pore blocking, which reduces permeability. Thus, permeability is decreased during polymer injection, rather than waterflooding. This reduction of permeability is characterized by the permeability reduction factor (James J. Sheng, 2011).

$$RRF = \frac{Rock\ perm.\ when\ water\ flows}{Rock\ perm.when\ aqueous\ polymer\ solution\ flows} = \frac{k_w}{k_p} \tag{2}$$

2.4 Nanoparticle application in Petroleum Industry

Nanoparticles have the ability to revolutionize both upstream and downstream processes in the petroleum industry, including exploration, fracking, processing, and EOR, as well as refining processes (Kong, 2010). It offers a diversity of technology and material alternatives for use in petroleum engineering. The secret to modern technical developments of materials in nano scale in different shapes, like rigid components, dynamic fluids, and practical nano-fluid hybrids (Zhang, Modeling of Nanoparticle Transport in Porous Media., 2012). The series of investigations on nanotechnology in the Petroleum Industry has increased dramatically last years.

Nanotechnology is now regarded as a game changer in the exploration and extraction of oil/gas resources, and it is anticipated to play a major role in the advancement of fossil-based energy technologies within the next 30 years. One of the most significant areas of use for nanoparticles is Enhanced Oil Recovery (EOR), which produces greater volumes of oil during extraction and thereby ensures a quicker return on investment. (N.A. Ogolo, 2012) recently published results from EOR studies using various nanoparticles such as magnesium oxide, aluminum oxide, zirconium oxide, zinc oxide, iron oxide, tin oxide, nickel oxide, hydrophobic silicon oxide and silicon oxide treated with silane, which showed increased recovery and hydrocarbon output. The results of these compounds include a change in rock wettability, a reduction in oil viscosity, a reduction in IFT, a decrease in mobility ratio, and permeability changes. Figure 9 comprises the portions of the investigations have been carried out of nanoparticles across the Petroleum Industry
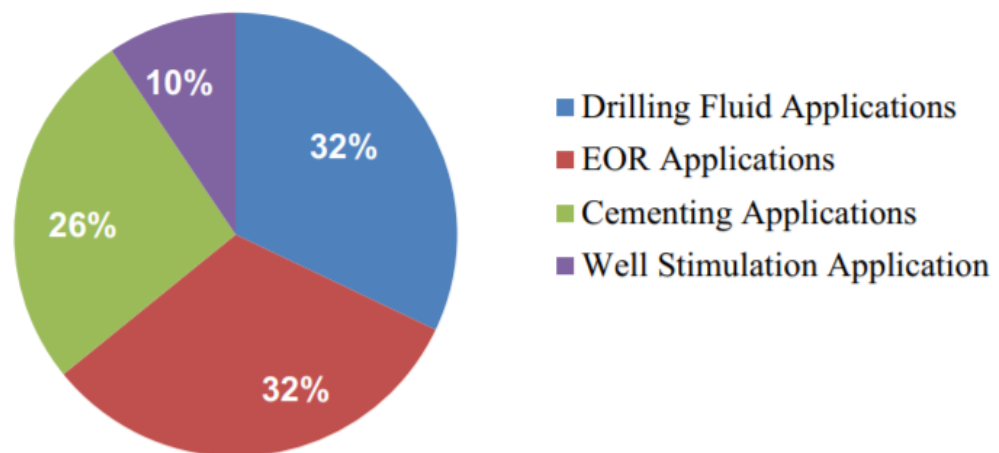
Figure 9 - Portions of the investigations carried out of nanoparticles in the Petroleum Industry *(Mortadha T. Alsaba, 2020)*

2.4.1 Nanomaterials: Nanoparticles and Nanofluids

Miniaturization of materials and nanotechnology became a worldwide scientific research subject after Gerd Binnig and Heinrich Rohrer developed the scanning tunneling microscope (STM) in 1981. (Hendraningrat, 2015; Das, 2007) described nanotechnology as the regulation of matter at the nanoscale (10^{-9} m) and the exploitation of phenomena and properties at that scale to alter materials, devices, and systems. Nanoparticles are described by IUPAC (McNaught, 1997) as a sub-fraction of a colloid with a size range of 10^{-9} to 10^{-7} meters.

The initial particles and the coating layer, all of which are transplanted or covalently connected surface molecules, make up nanoparticles. This causes nanoparticles to have an unusual physical and chemical properties, like mechanical, electrical, and size dependent properties, as well as affinity and behavior. By the materials, that have a specific particles and coating films, depending on the circumstances and specifications, greatly improves engineering performance. Nanoparticles will benefit from efficiency enhancements using this system such as (Buzea, Pacheco, & Robbie, 2007):

- adsorption properties
- light adsorption and emission
- high mechanical power
- high electrical conductivity
- superparamagnetism
- catalytic properties
- high thermal conductivity
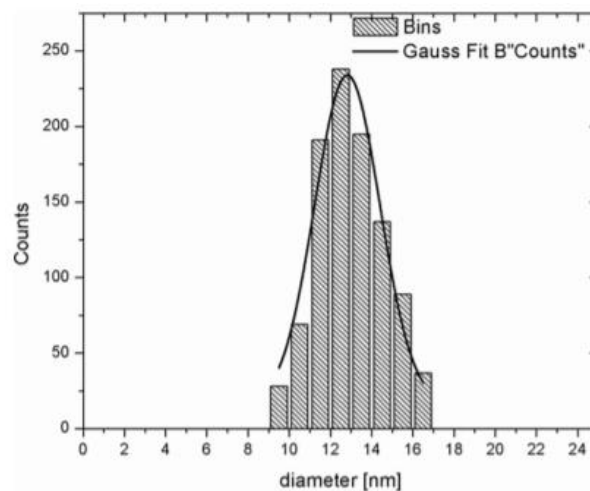
Figure 10 – Size distribution of nanoparticles *(Kamil R. Wierzbinski, 2018)*

2.4.2 Nanoparticles structure

A nanoparticle is made up of many layers, including core, surface, and outer shell. The nucleus of a nanoparticle is found at the center of its surface and is used to distinguish between different types of nanoparticles (Christian, 2008). The properties of nanoparticles related to the structure of the core, which is mainly made of inorganic material. The nanoparticle's surface is an exterior layer of the core that has been functionalized with metal ions, surfactants, or polymers. The shell is an exterior layer of structures made up of a variety of chemically distinct materials. It's made of oxide, nitride, or an organic substance. The extension layer of a core may be called a shell of certain inorganic nanoparticles (e.g. silica nanoparticles) Li S., (2016). Furthermore, the molecular shell is split into three groups: the tail group, the hydrocarbon chain, and the active head group (Hendraningrat L. , 2015).
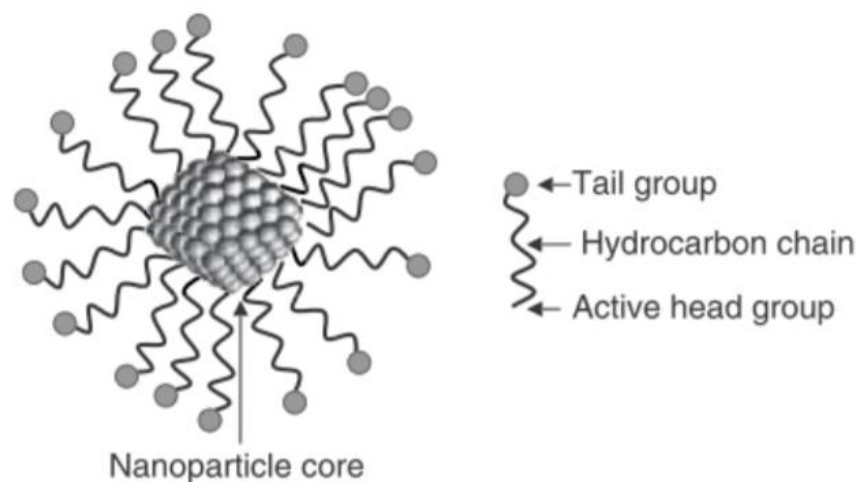
Figure 11 – Nanoparticle scheme *(Das, Choi, & Patel, 2006)*

2.4.3 Stability

Nano-fluids are fluids that have been designed to diffuse nanoscale materials in a complex fluid (Yu, 2012). A polar (water or alcohol) or non-polar (oil or toluene) fluid may be used (Li S. , 2016). It means that a nano-fluid is made up of solids and liquids, with nanoparticles scattered as solids in a liquid known as the base fluid (Hendraningrat L. , 2015). Since nanoparticles are dispersed in the base fluid, the nano-fluids will not have the same properties as the pure base fluid. Nano-fluids have been shown to have higher thermal conductivity, diffusivity, viscosity, and heat transfer than pure base fluids, allowing them to be used in a variety of applications (Yu, 2012).

Preparing stable nanofluid is difficult because nanoparticles appear to accumulate to form larger particles (Hendraningrat L. a., 2014). As nanoparticles are scattered in a liquid, their high surface energy is stabilized by creating larger particles (agglomerates). When the repulsion forces are relatively strong, as seen in Figure 12, a stable state is achieved. The particles will remain together until the attraction force begins to overpower the repulsion force. Particles will form dimers and trimers at first, then sedimentation will most likely occur as aggregation and agglomeration proceed. Peptization is the act of reversing an unstable suspension or dispersion under some conditions (Trefalt, 2014; Ghadimi, 2011).
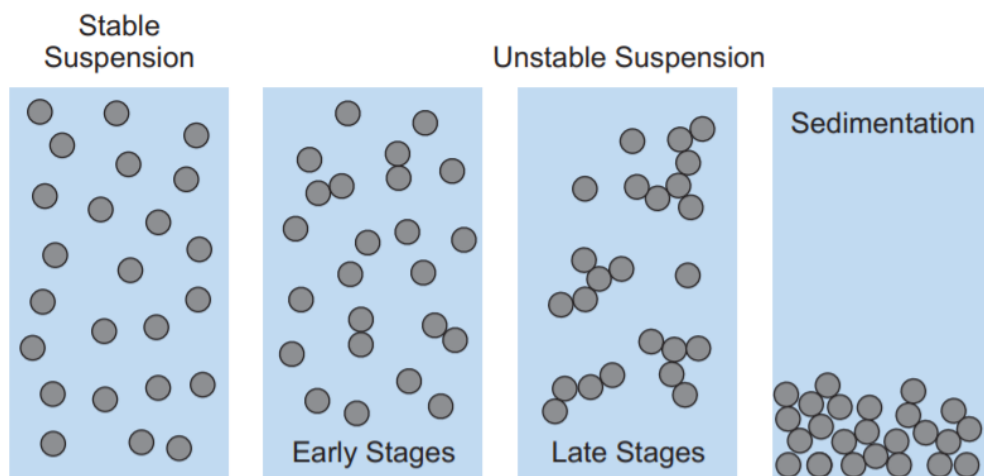
Figure 12 – Suspension of NPs *(Trefalt, 2014)*

2.4.4 Effect of nanoparticles concentration

One of the essential variables that influences the EOR mechanism is the concentration of injected nanoparticles. According to Chengara, (2004), increasing concentration raises disjoining pressure and Brownian motion, which increases repulsion powers. Figure 13-14 illustrates the influence of concentration on oil recovery and IFT. By the raise of concentration of injected NPs, the interfacial tension between reservoir fluids was stated to decrease significantly (Hendraningrat L. S., 2013). The wettability modification effect is also increased when the concentration is high. A higher concentration is correlated with greater oil recovery.
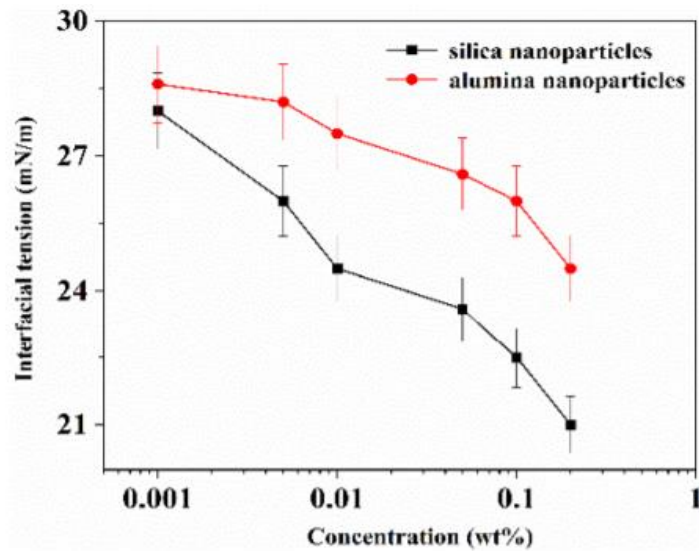
Figure 13 – Concentration effect on IFT *(Zhou & Hongda, 2019)*
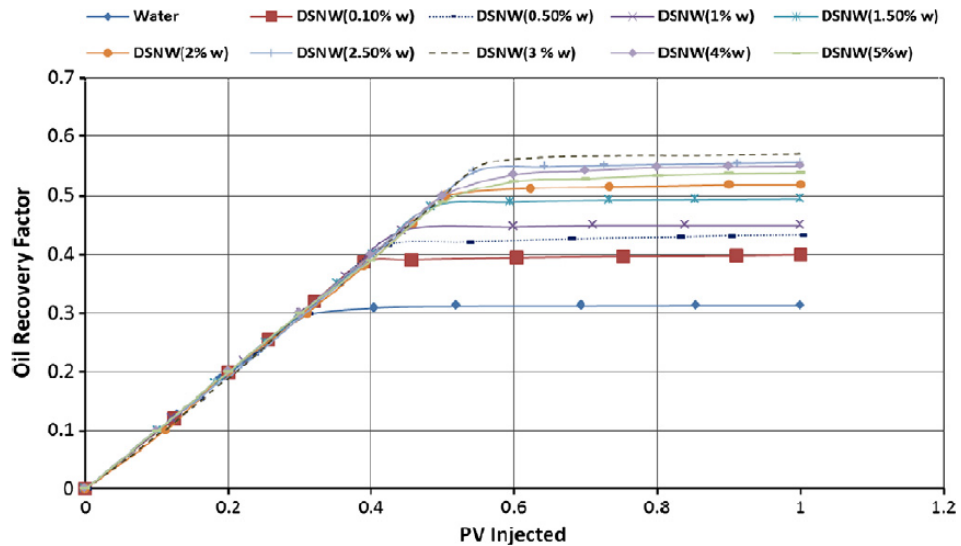
Figure 14 – Concentration effect on RF *(Maghzi et al.2012)*

2.4.5 Salinity effect on nanoparticles

Salinity of the fluid in the formation and the nano-fluids have a major impact on the dispersion's stability. Increasing salinity has been shown to lower the zeta potential of individual particles, allowing for smoother agglomeration (Mcelfresh, 2012). The potential at the shear plane near a solid-liquid interface with zero liquid velocity is referred to as the zeta potential. Because of the strong ionic strength in the fluid due to the existence of salt, electrical repulsion between particles is decreased, allowing the attraction forces to take over. Since most of the rock surface is charged, particle-particle attraction and collision can occur, but not

particle-surface collision (Somasundaran, 1967). As a result, in high salinity environments, nanoparticle modification is needed to keep the stability, that can be accomplished by modification of surface, ionic control through surfactant, or a combining both (El-diasty, 2015).

Laboratory research, on the other hand, found that oil recovery improves in high salinity environments. Hendraningrat, (2015) demonstrated, that injection of nano-fluid with high salinity could increase the wettability modification to be water-wet by using high stability silica nanoparticles. Because of the increased physicochemical interaction at high salinity, nanoparticle adsorption improves (Zhang, Investigation of nanoparticle adsorption during transport in porous media., 2014). At the same time, Kanj, (2009) discovered that high salinity on the dispersion did not inhibit nanoparticle transport but did improve adsorption on the rock surface. Raise of salinity tends to improve nanoparticle adsorption and oil recovery. However, in the environment with high salinity, the stability of nanoparticles may be compromised. In order to avoid the agglomeration of nanoparticles, the proper salinity level and surface coating are critical factors to take into account.

2.4.6   Recovery mechanisms
2.4.6.1 Wettability alteration

The tendency of a liquid to distribute over a rigid surface is known as wettability. In the oil recovery process rock wettability was shown to be a key factor in fluid differentiation and distribution in porous media. Nanomaterials are commonly applied to change wettability in EOR methods. Silica and poly silicone nanoparticles, in particular, have better characteristics (Sheshdeh, 2015; Carpenter, 2015). Silica nanoparticles is found to decrease the interfacial tension (IFT) of water and oil, resulting in the spontaneous imbibition of water into narrow pores. The mean recovery ratio improved by 10% when silica nanoparticle-based nano-fluid was used instead of a traditional surfactant (Roustaei, 2014). Decreasing the size of silica nanoparticles and coating them with xanthan gum have been shown to enhance the overall recovery from waterflooding (Ragab AMS, 2015). Recent research was carried out to determine the properties of different forms of polysilicon nanoparticles. Naturally wet polysilicon (NWP) nanoparticles were found to have a high wettability-altering ability, while hydrophobic and lipophilic polysilicon (HLP) nanoparticles were found to greatly reduce oil-water IFT. The EOR efficiency was improved by both agents (Roustaei A, 2012). In the

Figure 15 microscopic pictures shows the ability of silica nanoparticle to alter the wettability, mainly in high concentration of silica nanoparticles.
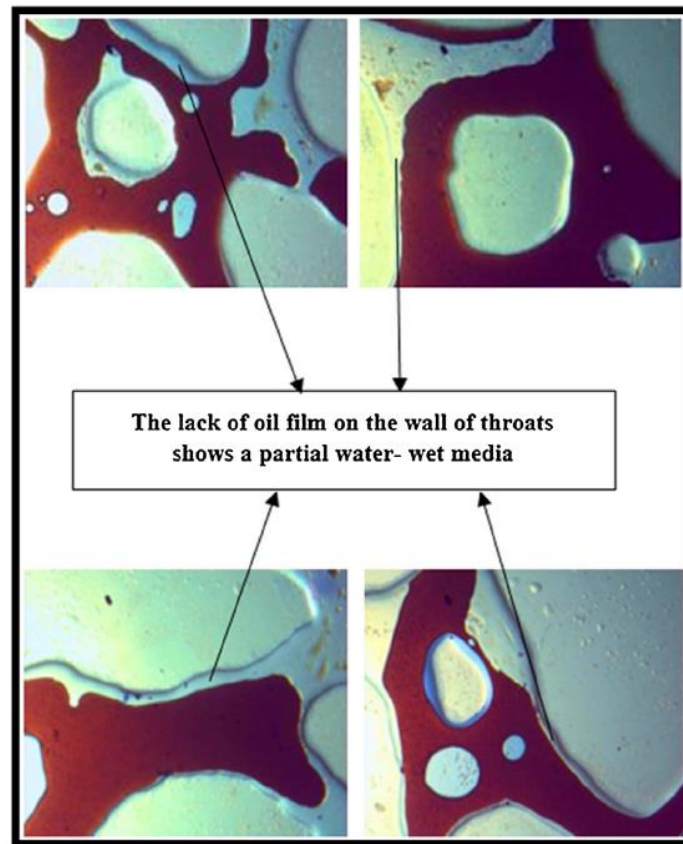
Figure 15 – Wettability alteration by injecting silica nanoparticles *(Maghzi et al. 2012)*

2.4.6.2 Disjoining pressure

Generally, disjoining pressure in a thin liquid film is defined as the difference in pressure between the liquid film and its bulk solution. As a result of particle confinement in the film region, more structural disjoining pressure is produced as compared with the bulk liquid, where particles have more freedom to move. The principle of disjoining pressure is well-established and has been extensively researched (Derjaguin & Churaev, 1974). Disjoining pressure is widely characterized by Chengara, (2004) as the exceeding pressure in the film compared to the bulk solution. As a result, nano-fluid was believed to have a substantial impact on the disjoining pressure between two immiscible fluids.

The action of nano-fluid on a rock surface in terms of spreading and adhesion is very complicated. Since a three-phase interaction area occurs, it varies from simple liquid characteristics. Nanoparticles immersed in liquids form wedge-shaped structures which exert

pressures against the oil-solid interface area in three phase areas (Figure 16). The wedge film's orderly structures improve the spreading and wetting ability of nano-fluid on a solid surface (Wasan, 2011). Brownian motion and electrostatic repulsion are the processes that cause this phenomenon. In a nutshell, the disjoining force causes the oil to separate from the solid surface, causing the nano-fluid to expand further.
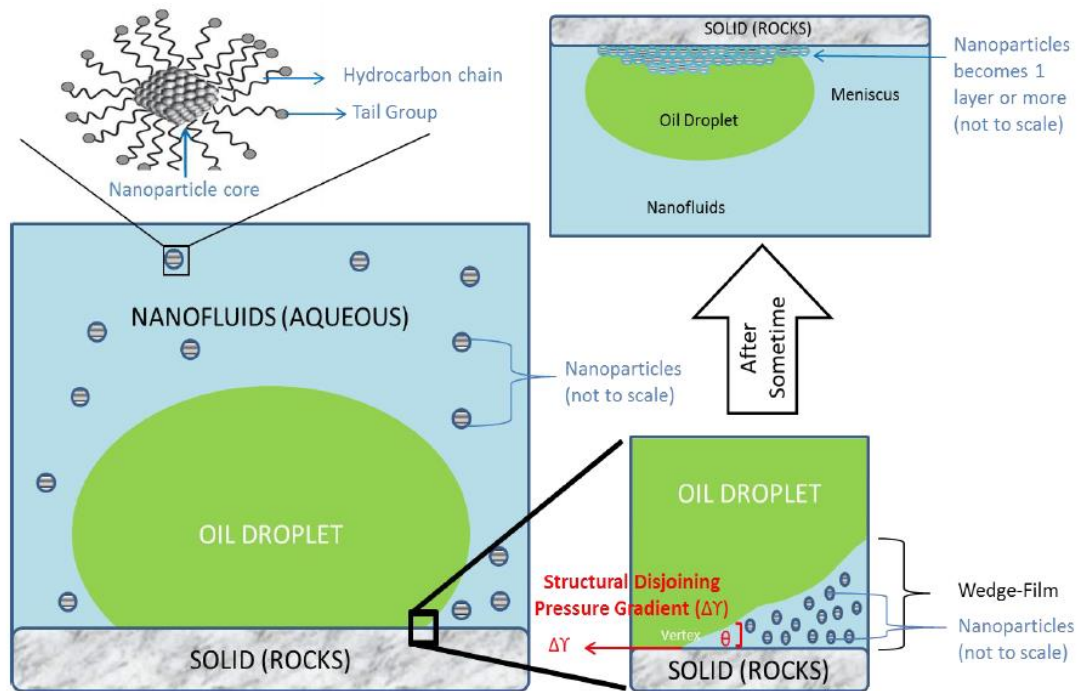
Figure 16 – Schematic of structural disjoining pressure gradient mechanism (*Hendraningrat L. , 2013*)

2.5 Combination of silica nanoparticles and polymer
2.5.1 Effect of silica nanoparticles on the polymer performance

An innovative polymer-coated nanoparticles have piqued the interest of the Petroleum Industry in relation to their increased solubility and resilience, greater emulsion stabilization, and enhanced mobility across porous media (ShamsiJazeyi, 2014; Gbadamosi, et al., 2018). Such characteristics for oil recovery have been recorded in a few articles. Since their reversible adsorption on the solid surface, Rodriguez, (2009) and Zhang, (2015) found that silica nanoparticles coated with polymer molecules have a great transport behavior across the pores of different permeability with weak retention. Ponnapati, (2011) discovered that polymer modified silica nanoparticles could displace the residual oil and produce 7.9% of the OOIP in laboratory experiment. Polymer/silica nanoparticles solution, according to Behzadi & Mohammadi, (2016) can regulate oil and water interfacial tension (IFT) and adjust the

wettability of glass micromodel from oil-wet system to a water-wet system, resulting in a greater EOR effect than unmodified silica nanoparticles. In the study of Rahul Saha, (2018) core flooding experiments of silica nanoparticle assisted polymer flooding were conducted and by minimizing droplet sizes and size distributions, the IFT was reduced, resulting in more consistent oil-water emulsions. Furthermore, wettability system changed from intermediate oil-wet to strongly water-wet system.

2.5.2 Recovery mechanisms
2.5.2.1 Wettability alteration

In EOR systems, alteration of wettability is a crucial mechanism. As a result, nanoparticles have recently played a critical role in rising of hydrocarbon determination by switching from an oil-wet to a highly water-wet system. Many researchers recently realized that nanoparticles had an immediate influence on wettability modification and could boost oil production rates. To comprehend the process of the reservoir's wettability change from oil wet to water wet, it is important to consider the principle of disjoining pressure during nano-fluid injection.

The vast majority of researchers have lately looked into the use and mechanism of nanoparticle in wettability modification for improved recovery of oil. Most of them claim that as nanoparticles cooperate with other additions including a surfactant or/and polymer, their ability to change the wettability of the system to a completely water wet and increase recovery value improves (Lim S Horiuchi H, 2015; Wang J, 2019).

In EOR, combining nanoparticles with a surfactant or polymer is a prospective process. Yousefvand HA & A, (2018) investigated the influence of polymer coated silica nano-fluid on oil recovery in a heavily oil wet environment and found that adjusting the surface wettability to water wet considerably increased oil recovery, which is consistent with Gbadamosi, (2018) experimental findings.

In the three-phase system the contact angle is the coefficient, which described force balance of water on a rigid surface adjoining with both oil and water (Aminian & ZareNezhad, 2019). Various methods, including contact angle estimation, Amott inspection, and core displacement, are used in laboratory tests to assess wettability (Agi, Junin, & Gbadamosi, 2018). In Figure 17 shown the results of contact angle reduction for xanthan gum with silica nanoparticles system.

Nanoparticles change the solid's wettability by removing carboxylic particles on the surface, forming a wedge film that displaces droplets of oil from the solid surface due to pressure

disjoining (Figure 18). A lot of researchers have noted that nano-fluid can change the wettability of rock surfaces in this matter (Monfared, Ghazanfari, M, & A., 2016).
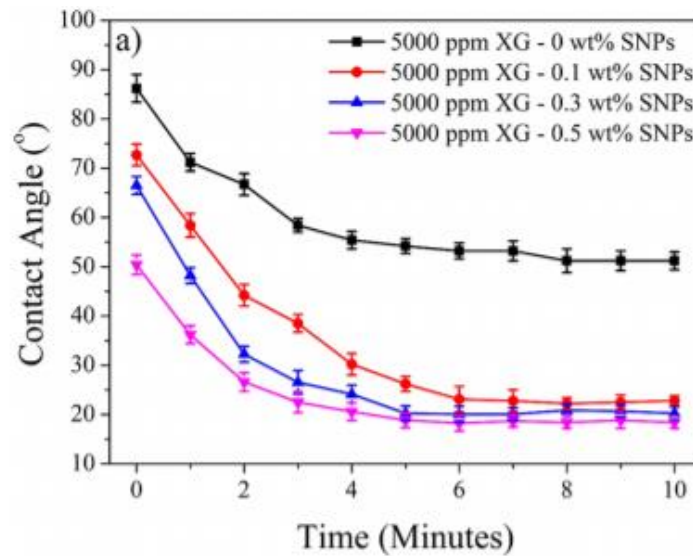
Figure 17 – Contact angle reduction for differen xanthan gum/silica nanoparticle concentrations with time (Rahul Saha, S., & Uppaluri, 2018)
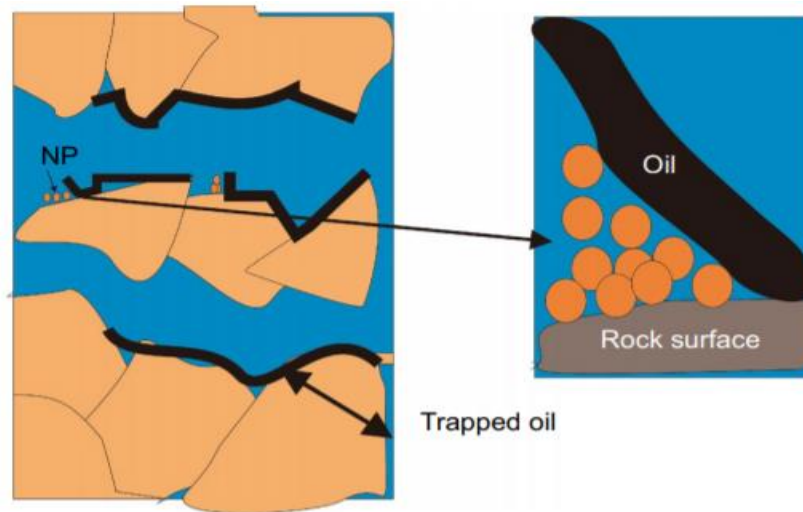
Figure 18 – Mechanism of wettability alteration *(Hilmy Eltoum, 2020)*

2.5.2.2 Interfacial tension (IFT) reduction

One of the most critical forces in a reservoir that limits oil recovery is capillary force (Towler, 2017). Interfacial tension (IFT) of reservoir fluids and wettability of rock determines the importance of capillary force (Chatzis, I., & N.R. Morrow, 1984). The capillary pressure would be minimized by lowering the IFT and changing the wettability of the rock. That would result in a rise in oil recovery (Melrose, 1974). One of the essential pathways for mobilizing

residual oil in the chemical EOR phase is reducing interfacial tension with surfactant (Towler, 2017). Nanoparticles may help minimize interfacial tension during EOR methods, whether with or without surfactants. Nanoparticle addition to the surfactant will enhance the surfactant solution's rheology and improve the IFT-lowering effect of the surfactant. The adsorption of nanoparticles onto the fluid's surface essentially reduces the IFT between the two fluids (Suleimanov, 2011).

Rahul Saha, (2018) observed that, when silica nanoparticles were added to the polymer, the viscosity of the polymer solution increased, and this behavior was maintained even at high temperatures. IFT reduction phenomena showed a similar pattern of beneficial behavior. By minimizing droplet sizes and size distributions, the IFT was reduced, resulting in more consistent oil-water emulsions (Figure 19). According to the Alberto Bila, (2019) injection of polymer coated silica nanoparticles reduced the tension between crude oil and seawater.
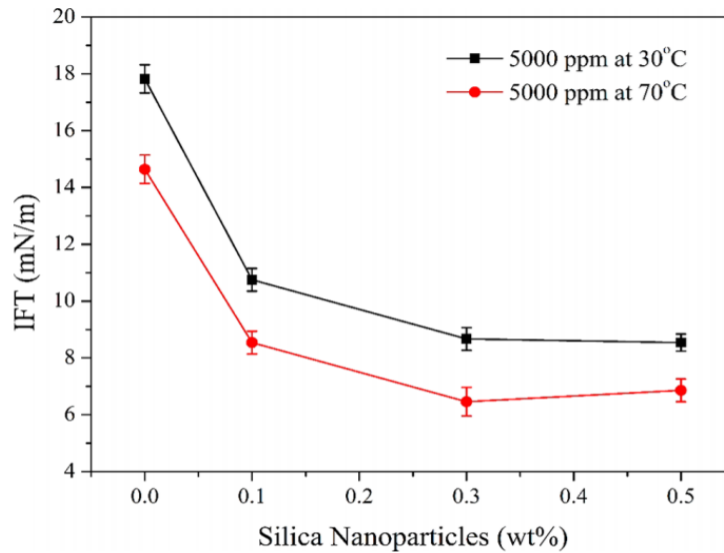
Figure 19 – Effect of silica nanoparticle on IFT *(Rahul Saha, S., & Uppaluri, 2018)*

2.5.2.3 Mobility control and oil recovery

High mobility of the displacing fluid induces viscous fingering during the EOR process, resulting in low sweep efficiency and conformance (Sun, 2017). In order to implement better sweep efficiency and higher recovery of oil, it is important to control the mobility of the fluid that is injected. As a function of relative permeability and viscosity of the displacing/displaced fluid, mobility ratio can be expressed as:

$$M = \frac{k_{rw}\mu_o}{k_{ro}\mu_w}$$

(3)

where M is the mobility ratio, k_{rw} and k_{ro} are relative permeability of water and oil, μ_o and μ_w are viscosities of water and oil.

Polymer flooding has been shown to increase sweep efficiency when used as a viscosity control agent (Wang, 2009). However, polymer solution is often deteriorated in formations with rough conditions like high pressure, temperature, or salinity. Its viscosity and sweep efficiency will be reduced because of the degradation (Ramsden, 1986). Thus, nanoparticles have been suggested to improve the viscosity of polymers in injected fluids, as this enhances the polymer solution's stability and prevents degradation.

The ability of nanoparticle to shape a network structure through hydrogen bonding causes the thickening phenomenon (Zeyghami & Ghazanfari, 2014), which has an immediate impact on the fluid shear stress (Cheraghian & Hendraningrat, 2015). Since the high polarity of water, Zeyghami, (2014) found that viscosity enhancement by silica nanoparticles in water phase is comparatively small. In the polymer solution, however, nanoparticles seem to be able to significantly improve pseudo-plasticity behavior even at low shear rates (Maghzi A. e., 2013). Furthermore, they inhibit premature polymer degradation in high salinity conditions by stopping the polymer from reacting with ions, and nanoparticles can take the role of the polymer in attracting cations.

Maghzi, (2013) investigated the effect of silica nanoparticle dispersion on polymer flooding in various fluid salinities. Degradation can be greatly decreased by applying silica nanoparticle to the polymer solution. Increase of concentration, can mobilize trapped oil more effectively. Oil recovery values by waterflooding, polymer flooding and silica nanoparticle-polymer flooding illustrated in Figure 20 showed that silica nanoparticle-polymer-flooding has the highest oil recovery compared to other two methods (Yousefvand, 2015). Highest recovery was achieved due to the improvement on the fluid viscosity for about 35 cP while the conventional polymer only yields 8 cP.
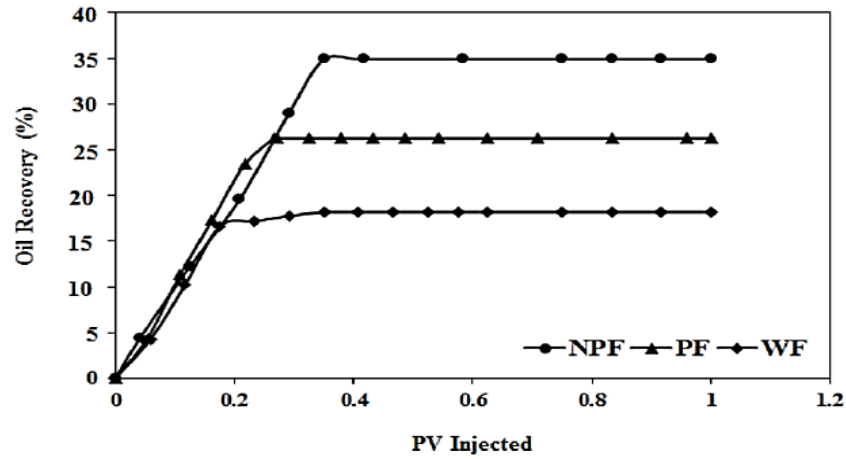
Figure 20 – Comparison of oil recovery injecting NPF, PF, WF *(Yousefvand, 2015)*

The studies of Rahul Saha, (2018) performs core flooding experiments on the Berea core using xanthan gum polymer and silica nanoparticles with various concentration. Initially, with only xanthan gum (5000 ppm) injection recovery factor of oil was 14.5 %. Addition of 0.1 wt % of silica nanoparticles improves recovery factor up to 16.3 %, while with 0.3 wt % it increased for about 20.8 %. However, at 0.5 wt % recovery decreased down to 18.51 % because of the reduction of permeability and porosity. Results shown in the Figure 21 and Table 1. The results of the coreflooding experiments of Alberto Bila, (2019) illustrates that, polymer coated silica nanoparticles improved oil recovery factor from 2.6 % to 5.2 % in tertiary recovery mode.

Table 2 – Oil recovery data from core flooding experiments *(Rahul Saha, S., & Uppaluri, 2018)*

sr. no.	porosity (%)	Brine permeability (mD)	xanthan gum concentration (ppm)	nanoparticles concentration (wt %)	slug size (PV)	initial oil saturation (%)	temperature (°C)	water flooding recovery (% OIP)	polymer flooding recovery (% OIP)	cumulative total recovery (% OIP)
1	26.0	927	5000	0	0.5	78.3	30	31.84	14.47	46.32
2	25.8	834	5000	0.1	0.5	79.6	30	32.12	16.29	48.41
3	26.5	1002	5000	0.3	0.5	80.1	30	33.31	20.82	54.13
4	25.1	746	5000	0.5	0.5	80.5	30	31.17	18.51	49.68
5	25.3	772	5000	0.3	0.5	80.2	80	32.50	18.44	50.94
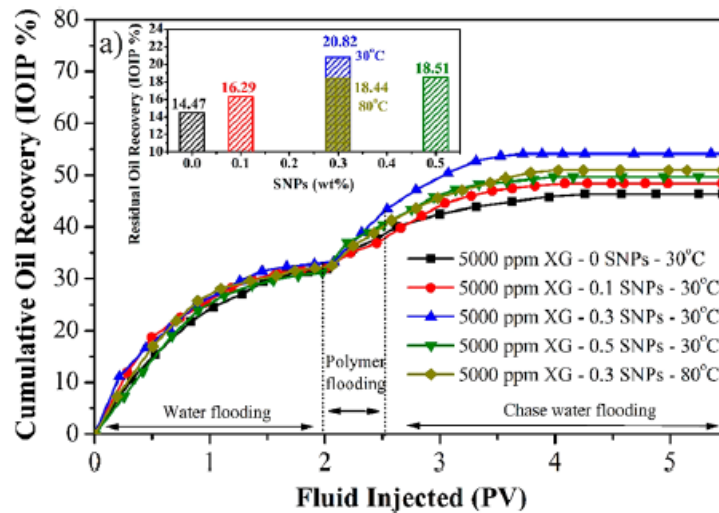
Figure 21 – Oil Recovery by xanthan gum/silica nanoparticle injection *(Rahul Saha, S., & Uppaluri, 2018)*

In the article of Achinta Bera, (2020) core flooding experiments conducted using sandstone sample with the type of polymer slug called guar gum solution (4000 ppm), 0.2 wt % nano-silica solution and silica nanoparticles/polymer solution (4000 ppm of guar gum and 0.2 wt % silica nanoparticles). Core displacement study illustrated that maximum value of additional oil of 44.28 % recovered by combination of polymer (guar gum) solution with silica nanoparticles.
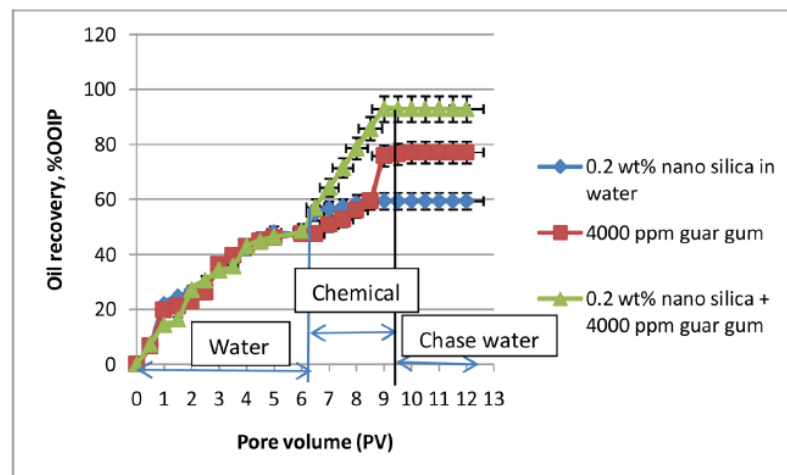
Figure 22 – Oil recovery with different chemical slugs *(Bera., et al., 2020)*

Furthermore, Achinta Bera, (2020) states that increase of silica nanoparticles concentration improves guar gum polymer viscosity at high temperature conditions, therefore, polymer can adequately perform. Raise in viscosity of guar gum solution related with silica nanoparticles is attributed to the formation of an interlink association between the guar gum

solution and the silica nanoparticles, which results in the formation of a consistent polymer slug (Figure 23).
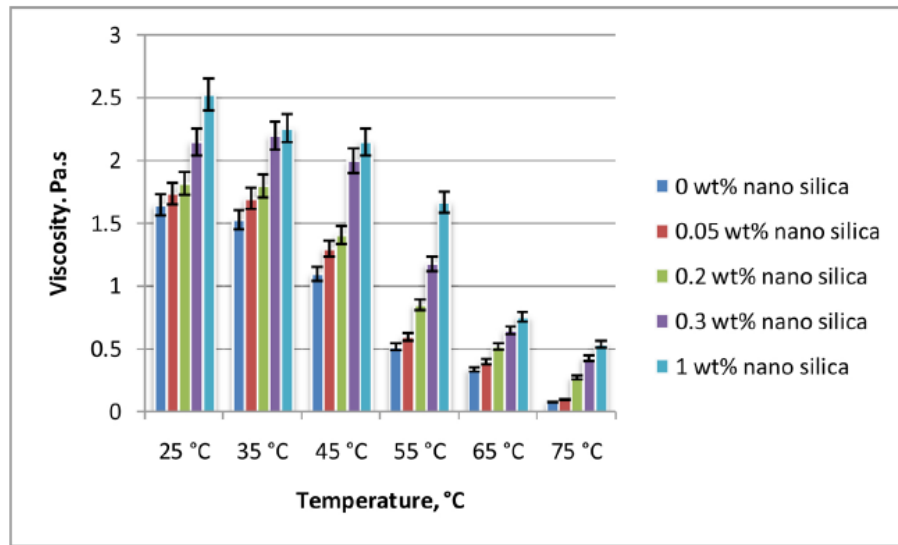
Figure 23 – Effect of silica NP concentration on polymer viscosity *(Bera., et al., 2020)*

In the investigations of Alberto Bila, (2019) coreflooding experiments performed using polymer-coated silica nanoparticle at different concentrations. The average recovery of oil after water flooding was 56 %. Then injection of nanofluid determines incremental oil recovery from 2.6 % up to 5.2 % and sweep efficiency varies from 6.3 % to 11.8 %. Improvement of oil recovery achieves by the displacement of residual oil by nanofluid flooding to some extent. In the secondary recovery system nanofluid injection increases the recovery factor up to 16 %. The oil recovery plots by PV injected is illustrated in Figure 24 and 25.
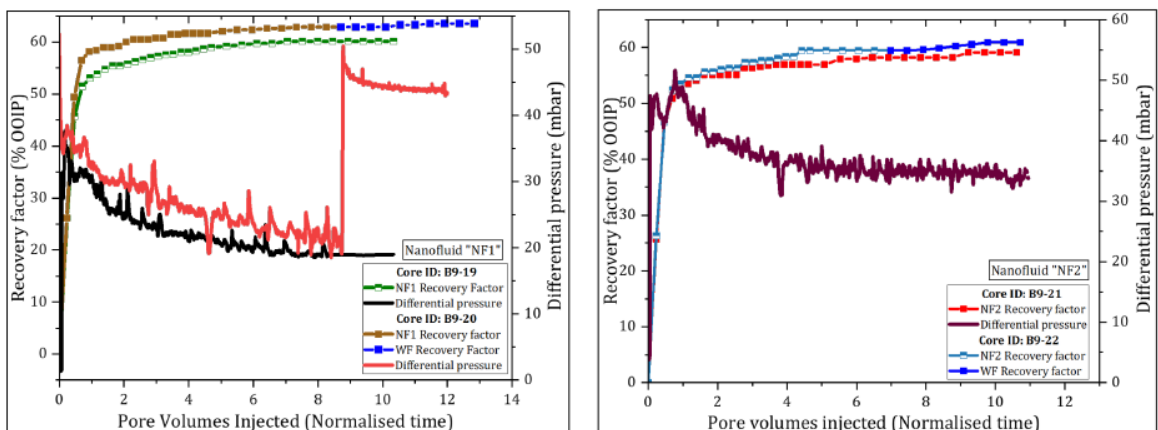
Figure 24 – Secondary oil recovery by nanofluid flooding *(Bila, Stensen, & Torsæter, 2019)*
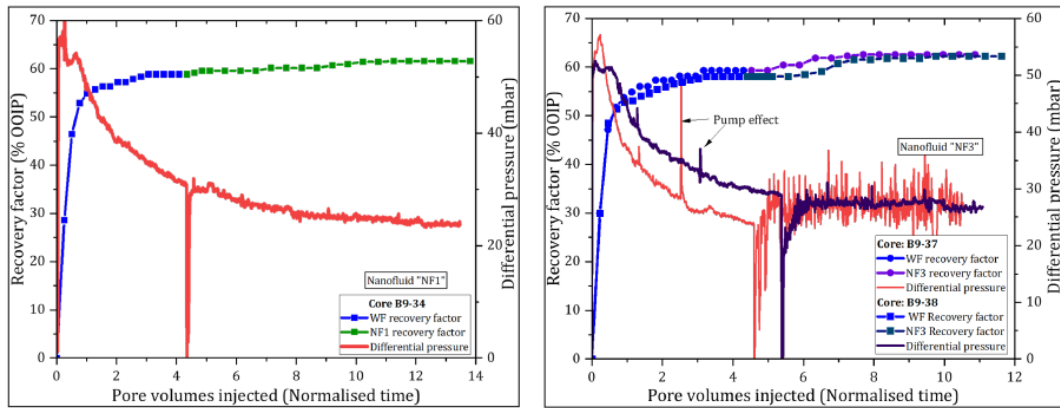
Figure 25 – Tertiary oil recovery by nanofluid injection *(Bila, Stensen, & Torsæter, 2019)*

Other studies of Cao, (2018) core flooding tests on the three-layer artificial vertical heterogeneous high-permeability core were conducted. Two flooding experiments of only polymer solution (PM) and nano-silica/PM were tested with 0.3 PV slug. The results illustrated that polymer flooding produces additional 6 % of oil recovery, while nano-silica/PM increases this value up to 10.84 %. The oil recovery, pressure and water cut are shown in the Figures 26-27.
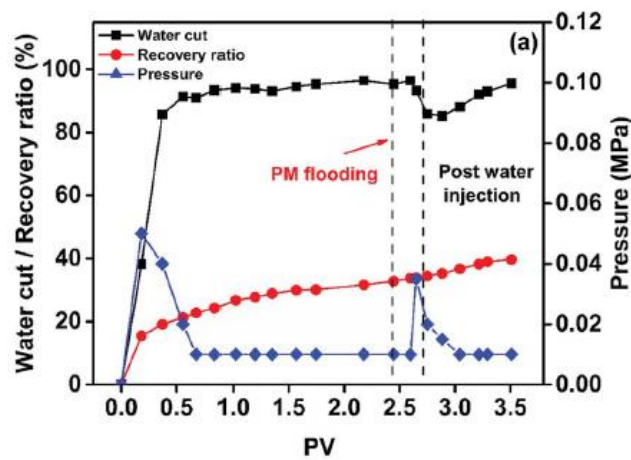
Figure 26 – PM solution (Cao, et al., 2018)
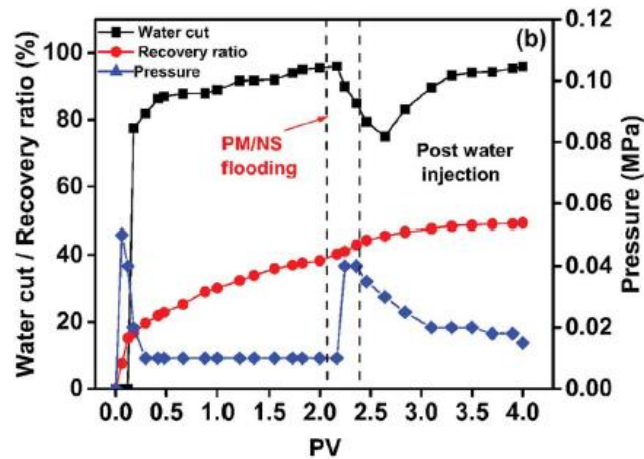
Figure 27 – NS/PM solution *(Cao, et al., 2018)*

The literature review provided some information about the effect of nano-silica to the polymer solution. Various investigations showed that silica nanoparticles have an ability to alter the wettability, reduce the interfacial tension (IFT), enhances the viscosity of the polymer solution performing better mobility control and prevent the retention of polymer. Moreover, some investigations illustrated that thermal stability of polymer will be effective. Some papers illustrated favorable recovery mechanisms using nano-assisted polymer solution. In the literature, however, no experiments have been conducted to evaluate nano-polymer solutions under adverse conditions (high temperature, high temperature), and combinations of chemical slugs (nanofluid, polymer, and nano-polymer) have not been tested.

3. METHODOLOGY

In designing the Methodology, the main objectives of the thesis were taken into account. During the research, silica nanoparticles and modified synthetic polymers are combined with complicated laboratory experiments to analyze the improvement of recovery mechanisms. Generally, the research process consists of four main stages. First, zeta potential experiments were performed to analyze the stability of the nanofluid at different concentrations. Preparing stable nanofluid solutions has been a challenging task. Secondly, it should be screened for optimum concentrations of silica nanoparticles as well as modified synthetic polymers that can withstand high temperatures and salinity. Since silica nanoparticles exhibit wettability alteration, contact angle measurements were used to determine the optimum concentration of nanoparticles. The purpose of the rheology experiment was to select the optimal concentration

of the modified synthetic polymer. In the third step, we conducted tests to compare the viscosity values of nano-assisted polymer solutions with polymer solutions at different concentrations. Lastly, we applied designed flooding sequences using polymer, nanofluid, and nano-assisted polymer solution in core flooding experiments. Based on the results of contact angle measurements, rheology tests for polymer and nano-assisted polymer solutions, and zeta potential tests, the most appropriate solution of nano-assisted polymer is identified. The following experiments have been completed:

Bulk Fluid Phase Experiments:

- Select concentration range for nanofluid and polymer
- Analyze the nanofluid stability using zeta-potential tests
- Contact angle measurements
- Identify the optimum concentrations of nanofluid and polymer solutions
- Rheology tests for polymer/nano-assisted polymer

Dynamic experiments:

- Core flooding experiments
- Select injectivity scenarios
- Evaluate the behavior of nano/polymer solution at dynamic conditions
- Calculate the oil recovery vs PV injected
- Select the best coreflooding scenario
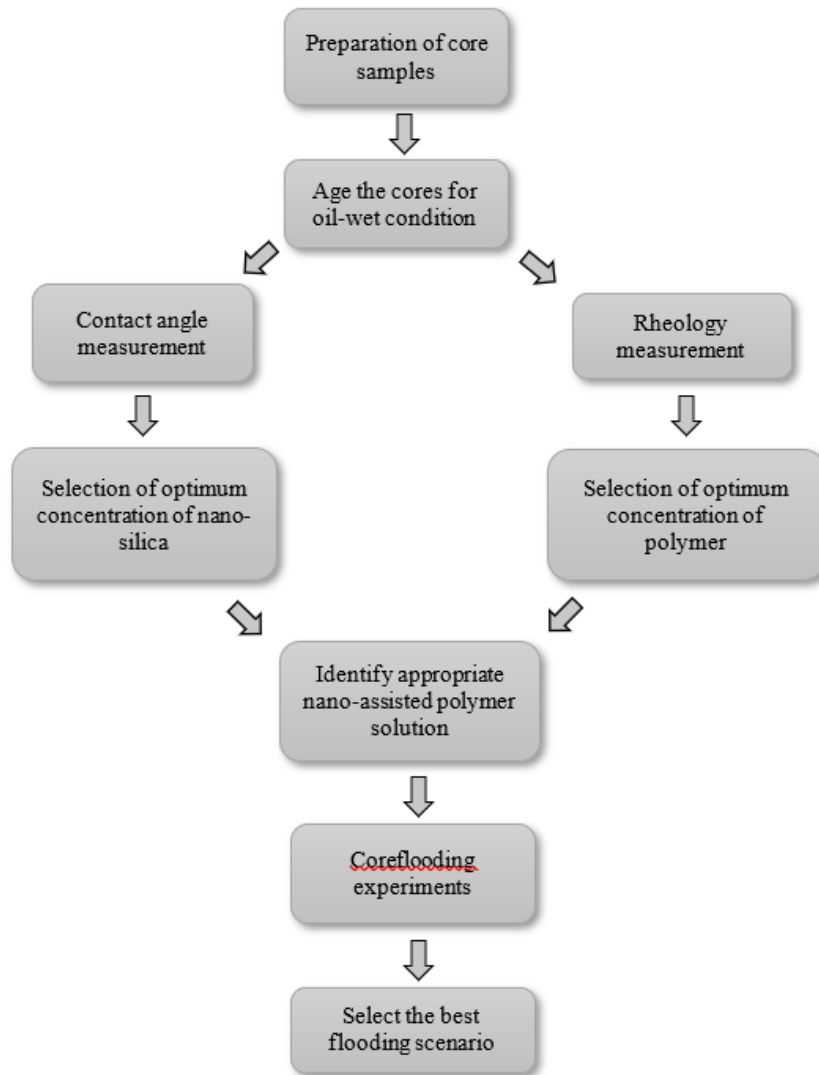
Figure 28 – The flow chart of the experiments

3.1 Materials

The Materials presented the main resources needed for conducting the research. It includes formation water, injection brine, crude oil, polymer, nanofluid, and 4 samples of carbonate core.

3.1.1 Carbonate cores

Indiana carbonate rock samples were used in this research. 4 core samples for coreflooding experiments and 12 pellets for contact angle measurements were cut from this carbonate rock. The diameter of the pellets is 0.75 inches.

Table 3 – Dimensions of the core samples

Core №	Length, cm	Diameter, cm	Dry weight, g	Vp, ml	Vb, ml	φ, %
1	7,95	3,812	200,28	17,096	90,686	18,852
2	7,27	3,812	182,04	16,132	82,93	19,452
3	7,13	3,812	180,09	15,096	81,333	18,561
4	7,15	3,812	178,44	15,368	81,561	18,843

Figure 29 – Indiana carbonate core samples

3.1.2 Crude oil

A sample of crude oil obtained from a field of the Caspian Sea in Kazakhstan was used in this experiment with 35 API gravity. Filtration was used to remove solid particles, water, and gas impurities from the oil. A table of the oil's properties is shown in Table 4.

Table 4 – Crude oil properties

Temperature, ºC	Dynamic viscosity, cp	Density, g/cm^3
25	5.66	0.8459
80	2.89	0.8162

3.1.3 Formation water and injection brine

In this research, brine salinity selected as 40 000 ppm and was used as an injection fluid, while formation water with a salinity of 183 000 ppm was used as a formation water. Brine salinity 40 000 ppm is the highest salinity of the solution, where silica nanofluid is stable

according to the (Zhangaliyev, Hashmet, & Pourafshary, 2022). Formation water was used to set the initial reservoir conditions for the cores. Ionic composition of formation water and injection brine are illustrated in Table 5.

Table 5 – Ionic composition of brines

Ions	Formation water, ppm	Brine, ppm
$Na^+ + K^+$	81 600	13 600
Ca^{2+}	1470	1590
Mg^{2+}	9540	245
Cl^-	90 370	15062
SO_4^{2-}	0	0
HCO_3^-	0	0
TDS	182 980	40 000

3.1.4 Polymer

In this study, a commercial polymer (SUPERPUSHER SAV 10) was used. It is partially hydrolyzed polyacrylamide (HPAM) supplied by SNF Floerger in a white powder. Chemically, this polymer is able to sustain harsh conditions, which is one of the reasons they were selected (Zhangaliyev, Hashmet, & Pourafshary, 2022), (Hashmet, Qaiser, Mathew, AlAmeri, & AlSumaiti, 2017). In this research, harsh conditions are high temperature of 80 °C and salinity 183 000 ppm. Figure 30 illustrates HPAM-based polymer group's molecular structure.
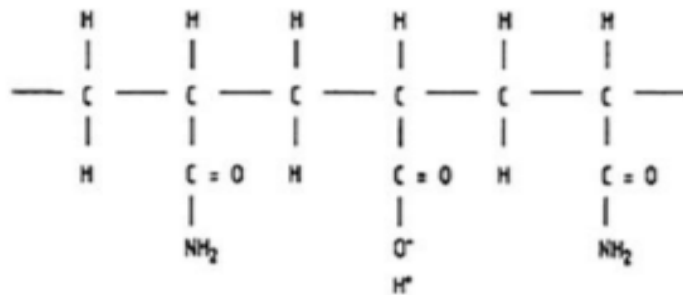
Figure 30 - Molecular structure of partially hydrolyzed polyacrylamide (*Salih, Sahi, & Hameed, 1997*)

3.1.5 Silica nanoparticles

Silicon oxide (SiO_2) nanoparticles were used in this study and supplied by SkySpring Nanomaterials (Houston, TX, USA). It has been demonstrated by many researchers that silica nanoparticles are the most effective nanoparticles in the EOR process (Maghzi, Mohammadi, Ghazanfari, Kharrat, & Masihi, 2012), (Bila, Stensen, & Torsæter, 2019), (Zeyghami & Ghazanfari, 2014). The main features of the nanoparticles are illustrated in the Table 6.

Table 6 – Nanoparticle characteristics

Nanoparticle type	Size	Specific surface area (SSA)	Morphology	Density	Purity
Silicon oxide (SiO2)	10-20 nm	640 m2/g	Spherical	2.4 g/cm3	99.50%

3.2 Procedure

The working process is described in this section, as well as the steps involved in getting the results. Preparation of the core samples, chemicals such as nanofluid, polymer, nano-assisted polymer, contact angle measurements, rheology experiments, zeta potential tests, and coreflushing experiments were thoroughly explained.

3.2.1 Preparation of the core samples

After core samples had been cut and their dry weights, lengths, and diameters measured, they were submerged in formation water in a saturator device in order to make initial reservoir conditions. Based on the saturation method, the following formula is used to determine the porosity of the cores:

$$V_{bulk} = \frac{\pi d^2}{4} L \tag{4}$$

$$V_{pore} = \frac{w_{wet} - w_{dry}}{\rho_{fw}} \tag{5}$$

$$\varphi = \frac{V_{pore}}{V_{bulk}} \tag{6}$$

In the saturator first two cores were saturated with formation water at 1200 psia for 24 hours. The same procedure repeated for another two cores.

Figure 31 – Saturation device
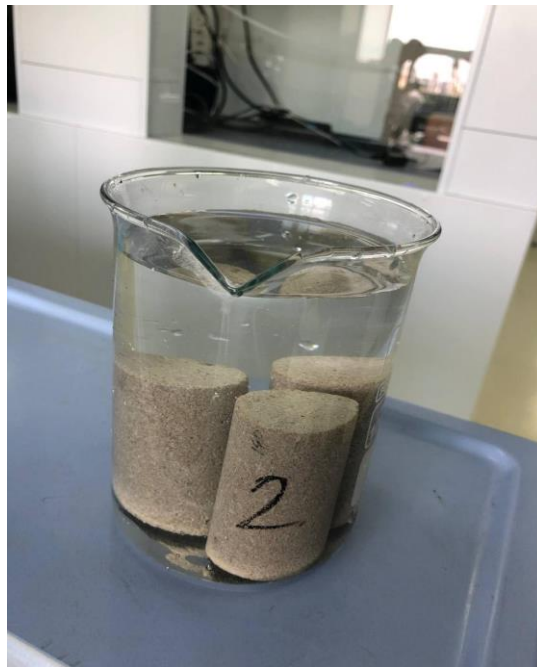
Figure 32 – Saturated core samples

It was necessary to flood the core samples with brine and measure their absolute permeability to make sure they were saturated. Afterward, oil was injected until there was no more water in the cores, so that irreducible saturation could be determined, and effective permeability calculated. The core samples were then aged in an oven at 80 °C for 6 months to ensure that they were fully oil-wet. Absolute and effective permeability of the cores calculated by Darcy's equation.

$$k_{abs} = \frac{q\mu_{fw}L}{dPA} \qquad (7)$$

$$k_{eff} = \frac{q\mu_{o}L}{dPA} \qquad (8)$$

3.2.2 Fluid preparation

The distilled water was used for preparing formation water, injection brine, polymers, nanofluids, and nano-assisted polymer solutions. Formation water and injection brine were prepared by adding necessary amounts of salts, such as $NaCl, CaCl_2 * 2H_2O, MgCl_2 * 6H_2O$ listed in material section Table 5.

Salts from the brine were added to the polymer solution after it had been prepared. Using a magnetic stirrer, dry polymer was added uniformly to distilled water at 600 rpm in order to prevent the formation of "fish eyes". A magnetic stirrer was subsequently set to 150 rpm when all polymers had been added. It was done to prevent solution mechanical degradation. Following this, the polymer solution was slowly stirred for 3 hours. Salts of brine were added to polymer fluid in a low rate for 1 hour and kept in solution overnight. Polymer solutions were prepared in salinity of 40 000 ppm (Zhangaliyev, Hashmet, & Pourafshary, 2022).

Using the methodology from the literature review (Salaudeen, Hashmet, & Pourafshary, 2021), nanofluids were prepared. The nanoparticles were mixed with distilled water and then homogenized using an ultrasonic homogenizer at 70°C for 45 minutes in order to achieve nanoparticle dispersion in distilled water. The ultrasonic homogenizer used in the experiment is shown in Figure. Immediately after cooling, the brine salt was slowly added for one hour.

This research involved the preparation of nano-assisted polymer solutions using the methodology of a literature review. The nanoparticles were mixed with distilled water and then homogenized using an ultrasonic homogenizer at 70°C for 45 minutes in order to achieve nanoparticle dispersion in distilled water. The ultrasonic homogenizer used in the experiment is shown in Figure. Immediately after cooling, using a magnetic stirrer, dry polymer was added uniformly to the prepared solution at 600 rpm in order to prevent the formation of "fish eyes". A magnetic stirrer was subsequently set to 150 rpm when all polymers had been added. It was done to prevent solution mechanical degradation. Following this, the nano-assisted polymer solution was slowly stirred for 3 hours. Salts of brine were added to prepared solution in a low rate for 1 hour and kept in solution overnight. Nano-assisted polymer solutions also were prepared in salinity of 40 000 ppm.
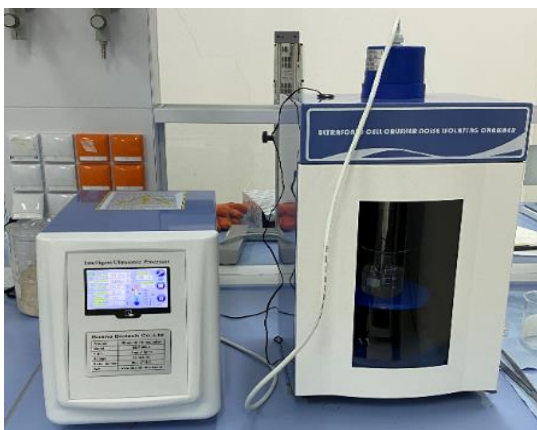
Figure 33 – Ultrasonic Homogenizer

3.2.3 Zeta potential tests

Zeta potential tests were performed to determine the stability of nanofluids at different concentrations and to examine the effect of salinity. The zeta potential (either positive or negative) > 5-10 mV lead to stable solutions, while low zeta potential values < 5 mV can lead to agglomeration. In accordance with API standards, nanofluids were prepared. Silica nanoparticle concentrations were 0.05, 0.1, and 0.15 wt%. Nanofluids were tested before and after salt addition to determine their zeta potential. Later, after the fluids had been prepared, the electric potentials of the fluids were measured with Zetasizer Nano ZS, as shown in Figure 34. A high-quality measurement was obtained by measuring each test three times. Tests on the zeta potential of silica nanoparticle concentration were carried out in order to select the optimal concentration. Maximum stability values among all measured samples were used in screening the optimum concentration.

Figure 34 – Zetasizer Nano ZS

3.2.4 Contact angle measurements

Numerous experiments with hydrophilic silica nanoparticles have been conducted in oil recovery, most focusing on wettability alteration. The contact angle measurements were conducted to select the optimum concentration of silica nanoparticles. For this experiment, 12 pellets were cut from the carbonate core and put them in the oven for 24 hours. Initially, the pellets should be completely oil-wet. By connecting a vacuum pump to the desiccator, pellets filled with light oil were placed inside the desiccator, then the air was removed by the vacuum pump. The vacuum pressure was 74 mPa. The oil gradually penetrated through the pellet pores after an hour. Following that, pellets saturated with oil were aged for 2 months at 80 °C in a light oil. Wetability of core was estimated using the captive bubble method using the OCA 15EC as shown in Figure 38, where a dropping phase was a light oil, while the ambient phase was formation water. Using captive bubbles allows reproduction of the original reservoir environment as oil drops from the bottom to the top. Oil-soaked carbonate pellets were measured for their contact angles. The next step was to soak the pellets in silica-based nanofluids for 48 hours. Next, contact angles were measured to determine whether nanofluids altered wettability. Three measurements were taken for one test to ensure an accurate result.

In this experiment, the wetting angle was measured between the dropping phase of light oil and the carbonate surface. As a result, oil covering the carbonate rock surface was identified as wetting. According to the Figure 35, depending on the characteristics of the oil-rock-brine, contact angle less than 75º is water-wet, between 75° and 115º is intermediate-wet and more than 115° considered as oil-wet state.
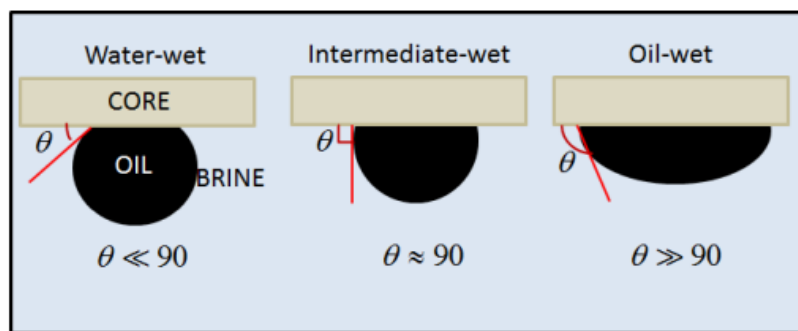
Figure 35 – Rock wettability diagram (*Teklu, Kazemi, & Alameri, 2015*)

Figure 36 – Vacuum pump and desiccator
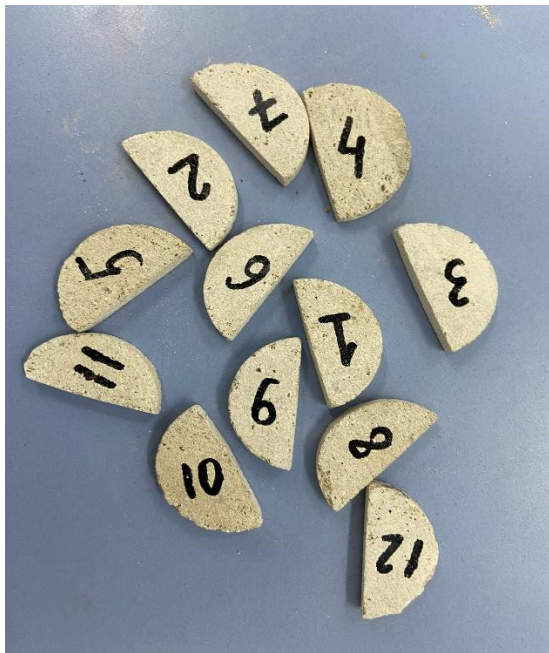
a)

b)

Figure 37 – a) Dry pellets b) Pellets soaked in light oil
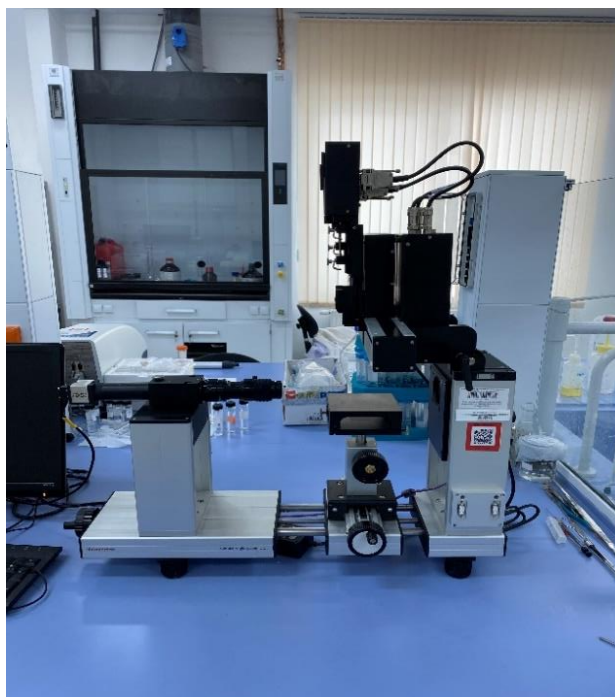
Figure 38 – OCA 15 EC device

3.2.5 Rheology experiments

In this study, the rheological behavior of polymer and nano-assisted polymer fluids was evaluated in relation to the presence of nanoparticles, temperature, salinity, and chemical concentrations. The MCR 301 rheology device was used to perform the test, as shown in Figure 39. A cylindrical measurement system was utilized due to its high temperature capability. The experiments were performed from room temperature up to 80℃ at 40 000 ppm salinity with varying concentration of SAV 10 polymer (1000, 1500, 2000, 2500 ppm) and optimum concentration of silica nanoparticles selected from contact angle measurements. In this respect, rheological tests were performed primarily for the purpose of identifying the best possible concentration of modified synthetic polymer. At a shear rate of 10 s^{-1} at 80 °C, an optimum concentration of 3-4 cP was found to be optimal. In addition, under high salinity, high temperature conditions, the selected polymer concentration was expected to show the maximum viscosity. These standards dictated the best concentration of modified synthetic polymer to be used in conjunction with a silica nanoparticle. Rheology behavior of nano-assisted polymer solutions was also investigated and compared to polymer solutions at different concentrations.

Figure 39 - Anton Paar MCR 301

3.2.6 Coreflooding experiments

The coreflooding experiments were conducted for the purpose of analyzing the effects of nanofluid, polymer, and nano-assisted polymer in dynamic conditions, as well as determining the oil recovery factor. Four coreflooding scenarios were carried out in this experiment, and the best scenario was determined based on its recovery value. There is also a graphs showing the recovery factor vs PV for each test.

Coreflooding experiments:

1. Brine ➡ Polymer ➡ Postflush

2. Brine ➡ Nanofluid ➡ Nano-polymer ➡ Postflush

3. Brine ➡ Nanofluid ➡ Polymer ➡ Postflush

4. Brine ➡ Nano-polymer ➡ Postflush

Figure 40 shows the components of the coreflooding equipment setup. They are: (1) an injection pump; (2) two accumulators; (3) the pump that applies the confining pressure; (4) a back pressure regulator; (5) heating jackets to apply desired temperature to fluid inside the

accumulator, and to the sample in the core holder; (6) core holder; (7) effluent collector; (8) pressure gauge and (9) control valves.
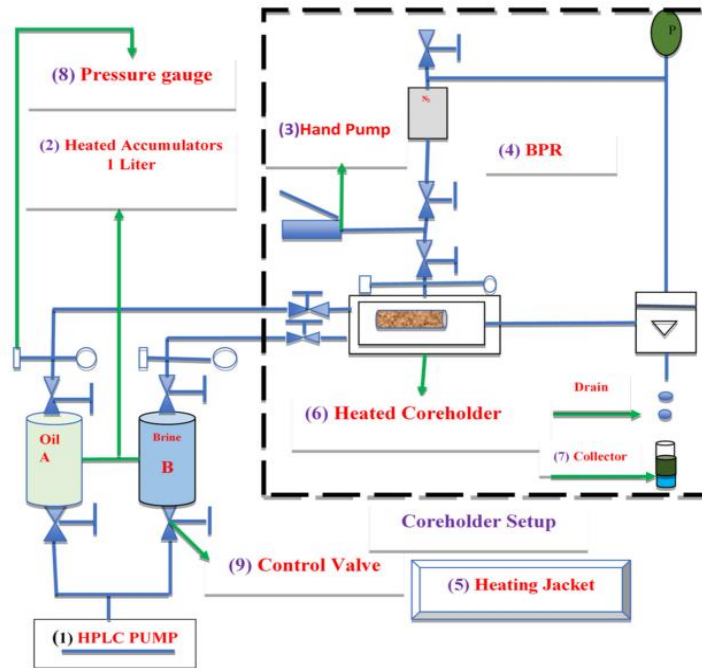
Figure 40 – Diagram of the core flood equipment.

4. RESULTS AND DISCUSSION

Various tests were conducted to determine the best nano-assisted polymer solution for enhanced oil recovery. It was first necessary to identify the optimum concentration for silica nanoparticles. Silica nanoparticles can alter the wettability of the system, so changes in contact angles were used as a screening criterion for the optimal concentration of nanoparticles. Additionally, zeta potential tests were used to verify the stability of the nanofluids. Based on contact angle and stability measurements, the most effective nanofluid was selected for the next round of experiments. In sections, contact angle measurements and zeta potential tests will be discussed.

The rheological experiments were used to screen the optimum concentration of modified synthetic polymers. A nano-assisted polymer solution was also tested to evaluate the effect of silica nanoparticles on the viscoelastic properties of a modified synthetic polymer at 40 000 ppm salinity and 80 ºC temperature. In these tests, the optimum concentration of SAV 10 modified synthetic polymer was determined.

Coreflooding experiments were conducted after choosing the most appropriate combination of nanofluid, polymer, and nano-assisted polymer. Four coreflooding scenarios have been developed to assess the effect of those chemicals on the recovery mechanisms. The scenario which has a high oil recovery value during coreflooding considered as the best case.

4.1 Preparation of core samples

As mentioned above, it was necessary to flood the core samples with brine and measure their absolute permeability to make sure they were saturated. Afterward, oil was injected until there was no more water in the cores, so that irreducible saturation could be determined, and effective permeability calculated. The permeability measurement results are shown in Table 7.

Table 7 – Permeability and porosity results

Core #	L, cm	A, cm2	Vp, cc	k (abs), mD	k (eff), mD	φ, %
1	7.95	11.413	17.1	30.27	14.92	18,852
2	7.27	11.413	16.13	39.23	23.92	19,452
3	7.13	11.413	15.1	43.43	24.06	18,561
4	7.15	11.413	15.37	25.03	15.25	18,843

Table 8 – Saturation results

Core #	Vp, ml	Soi, %	Swi, %
1	17.1	72.3	27.7
2	16.13	79.9	20.1
3	15.1	79.5	20.5
4	15.37	80.25	19.75

4.2 Zeta potential tests

Zeta potential test is useful to identify the stability of the nanofluids. The zeta potential (either positive or negative) > 5-10 mV lead to stable solutions, while low zeta potential values < 5 mV can lead to agglomeration.

Electrostatic interaction between cells and particles in a fluid environment is described by zeta potential. Generally, the liquid layer surrounding a particle consists of two layers: the Stern layer, which holds the ions firmly, and the diffuse (outer) layer, which is less firmly bound. An ion or particle is stable within the diffuse layer due to a notional boundary. A particle

moves when ions within its boundary move it (for example, by gravity). If the boundary is beyond the particle, the ions stay with the dispersion. Zeta potential is the potential at the boundary between these two planes (surface of hydrodynamic shear).

Since the polymer has a lower suppressed electric double layer than pure silica nanofluid, it does not agglomerate the silica nanoparticles. The reason for this could be the distribution of ions in brine between the polymer solution and nanoparticles. Polymers will form "coiled" structures at high salinity, where the polymer is a negatively charged long chain molecule. High salinity brine will replace negatively charged anion of polymer with positive cations (Na^{2+}, Ca^{2+}, Mg^{2+} and etc.). As a result, the electric double layer will be less affected by more ions in the brine. This implies that silica nanoparticles combined with modified synthetic polymer fluid makes for a more stable nanoparticle.
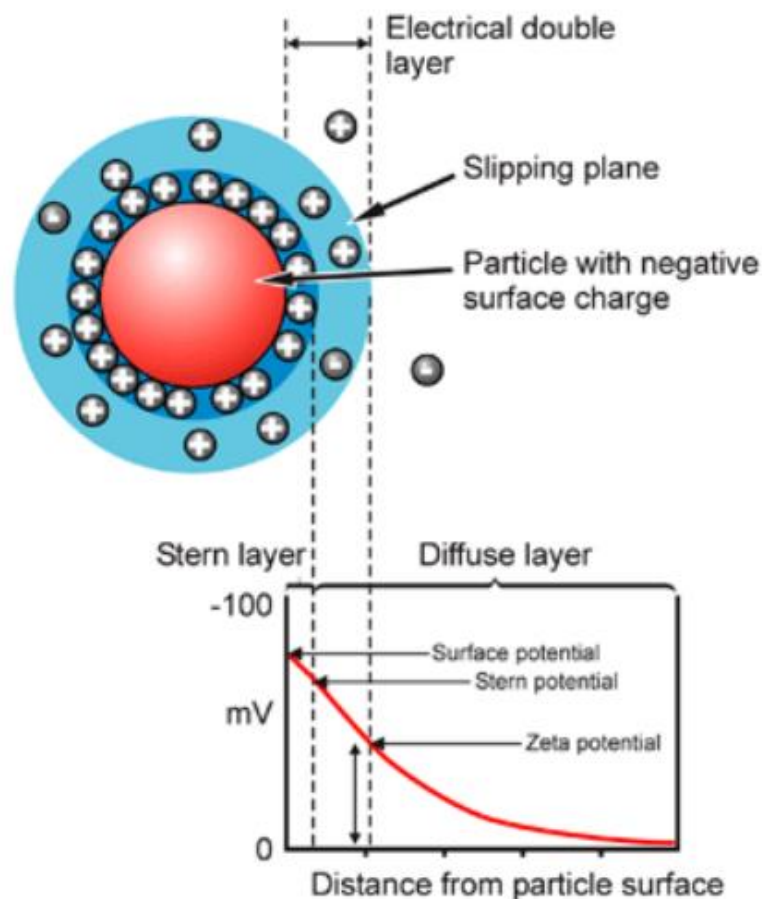
Figure 41 - Zeta potential illustration (*Mohd, Jaafar, & Rasol, 2017*)

Zeta-potential values measured three times for each silica nanofluid concentration in order to ensure an accurate result. Nanofluids tested before an addition of salt and then after. Figures 42-43 show the results of zeta-potential as a function of silica nanoparticle

concentration before and after an addition of salt. An orange line in Figure 42 shows average zeta-potential values at each silica nanofluid concentration (0.05, 0.1 and 0.15 wt %). Silica nanofluids are highly stable before addition of salt. The blue line in Figure 43 represents the zeta-potential results of each nanofluid concentration before addition of salt. This study showed a decrease in fluids stability.
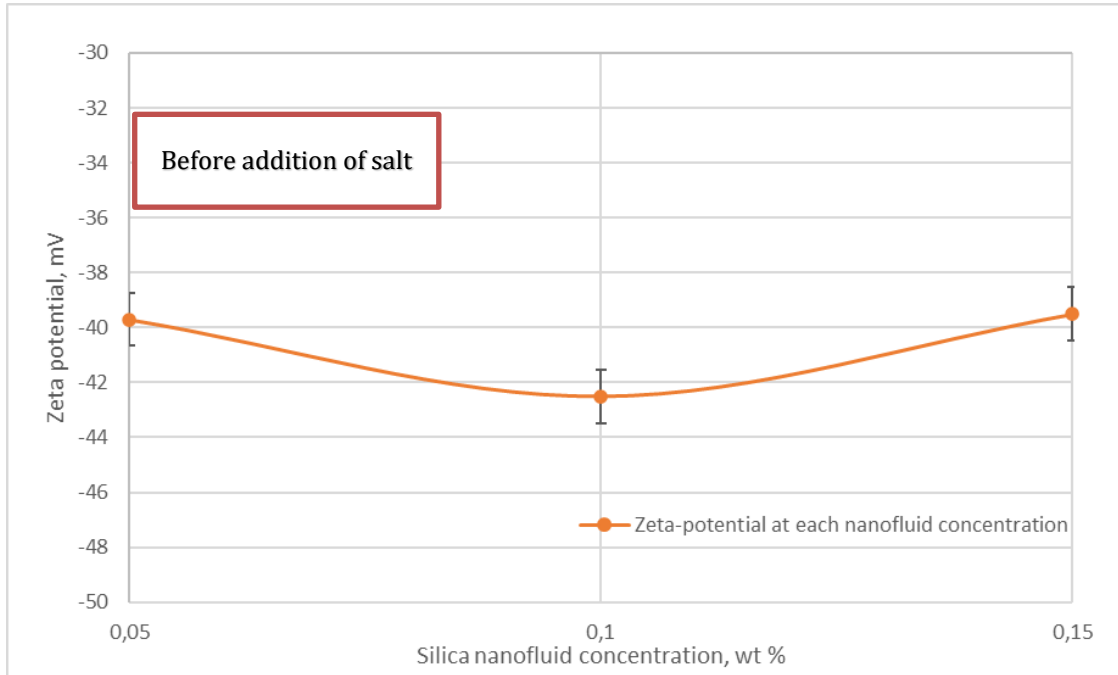
Figure 42 – Zeta-potential as a function of silica nanoparticle concentration
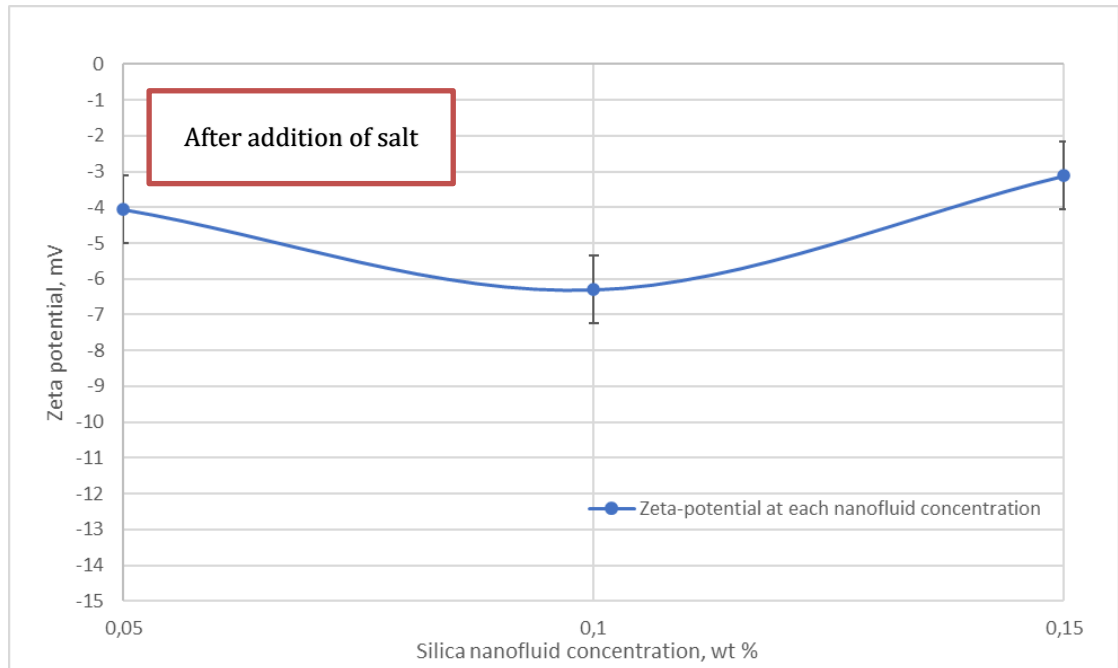
Figure 43 – Zeta-potential as a function of silica nanoparticle concentration

The stability of the nanofluids tested at concentrations 0.05, 0.1 and 0.15 wt %. The salinity of all solutions is 40 000 ppm, and, typically, this value is considered as relatively high. Addition of salts has an enormous effect on the stability of silica nanofluids. Table 10 and 11 illustrates zeta potential values of silica nanofluids before and after addition of salts at different concentrations. It was determined that at the salinity of 40 000 ppm silica nanofluid is stable.

Table 9 – Zeta potential values before adding salts

Silica nanofluid concentration, wt %	Zeta potential, mV
0.05	-39.7
0.1	-42.5
0.15	-39.5

Table 10 - Zeta potential values after adding salts

Silica nanofluid concentration, wt %	Zeta potential, mV
0.05	-4.06
0.1	-6.3
0.15	-3.12

It was found that silica nanofluids were stable before adding salts, but the stability of the nanofluids decreased after adding salt to the solutions as depicted in Table 10 and 11. The least stable nanofluid determined at 0.15 wt % concentration. Among these three concentrations, zeta-potential of 0.1 wt % of silica nanofluid showed -6.3 mV and was still stable at 40 000 ppm salinity. Based on the results, the optimum concentration for stability of silica nanoparticles has been determined to be 0.1 wt %.

4.3 Contact angle measurements

In this study, three concentrations of silica nanofluid were used. Concentrations of silica nanoparticles in the water were 0.05, 0.1, and 0.15 wt % at 40 000 ppm salinity. Various solutions were compared to determine the optimal concentration based on the changes in wettability alteration. Oil/brine/carbonate rock contact angle is used as a screening criterion for determining the optimum concentration. Three measurements were taken for one test to ensure an accurate result. Figure 44 shows average contact angle values for each silica nanofluid concentration.
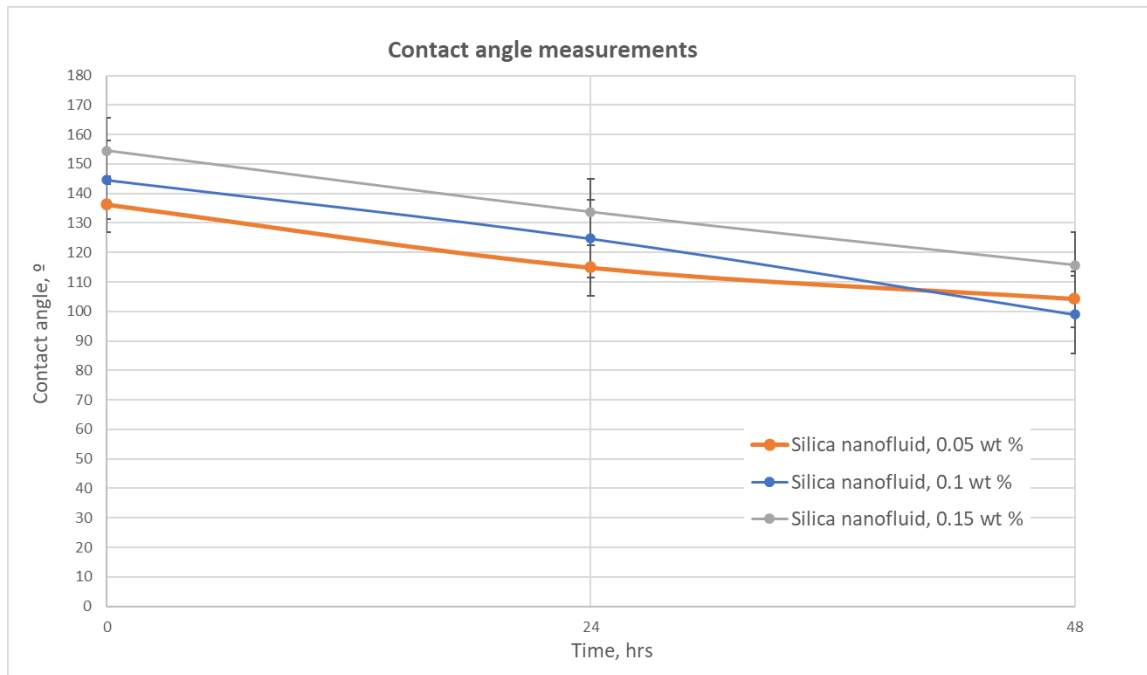
Figure 44 – Contact angle results for each nanofluid concentration (0.05, 0.1, 0.15 wt %)

Results proved that silica nanoparticles alter the wettability of the carbonate rock. A 0.1 wt % of silica nanofluid illustrated maximum alteration of the wettability towards water-wet. In the same way, silica nanofluids with 0.05 and 0.15 wt % also demonstrated approximately the same change of contact angle. Therefore, for other experiments 0.1 wt % of silica nanofluid concentration was selected.

The Figure 45 shows the average difference in contact angle at each concentration of silica nanoparticles after 24 and 48 hours. It was noted previously that the maximum average deviation in contact angle was caused by 0.1 wt % of silica nanofluid. The nanofluids with 0.05 and 0.15 wt % concentration showed lower results in altering wettability. Silica nanofluid with a concentration of 0.15 wt% also showed good wettability alteration, however it is better to use a lower concentration of nanoparticles to change the wettability. At the same time, the effect of 0.05 wt% silica nanofluid on wettability was not significant since there wasn't enough nanoparticle to alter the contact angle substantially. In Table 11 illustrated results of contact angle measurements. Maximum deviation by 0.1 wt % of silica nanofluid was 45.6 º.
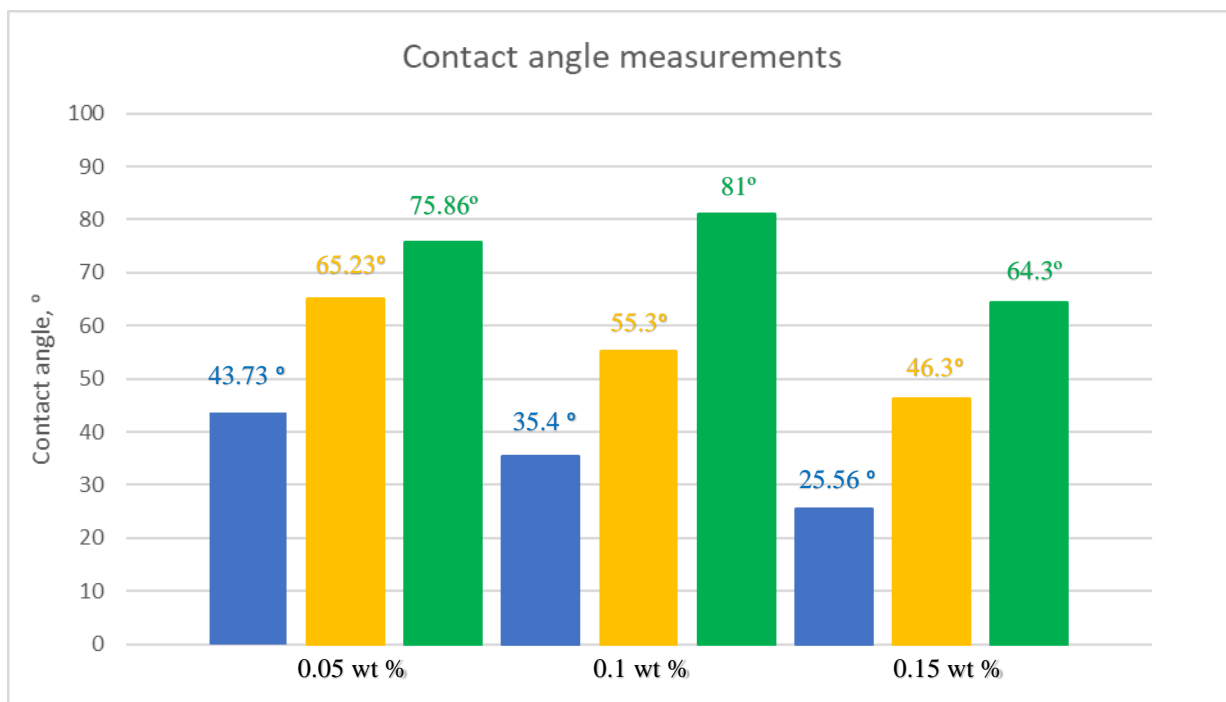
Figure 45 - Contact angle changes after 24 and 48 hours

Table 11 – Contact angle measurement results

Silica nanofluid concentration, wt%	CA (oil-wet)	CA (after nanofluid)	The difference CA
0.05	43.73	75.86	32.13
0.1	35.4	81	45.6
0.15	25.56	64.3	38.74

The Figure 46 illustrates the visual change in contact angles by silica nanofluids at different concentrations. The pellets were initially aged in light oil for two months at 80 °C. The Figure 46 shows the contact angle values at oil-wet conditions and their alterations after 24 and 48 hours. For each concentration, tests were repeated three times, and averages were calculated for the changes in contact angles. Formation water was the ambient phase, while a light oil was the dropping phase. As a result, it indicates that silica oxide nanofluid can diffuse into carbonate rocks and achieve an intermediate water-wetted state. The contact angle change was not significant for 0.05 wt % and 0.15 wt %. Silica nanofluid with a concentration of 0.15 wt% also showed good wettability alteration, however it is better to use a lower concentration of nanoparticles to change the wettability. At the same time, the effect of 0.05 wt % silica nanofluid on wettability was not significant since there wasn't enough nanoparticle to alter the contact angle substantially. Thus, silica nanofluid converted to its maximum wettability at 0.1

wt %. In the following experiments, 0.1 wt % concentration selected as the best nanofluid for significantly increasing oil recovery from carbonate reservoirs.
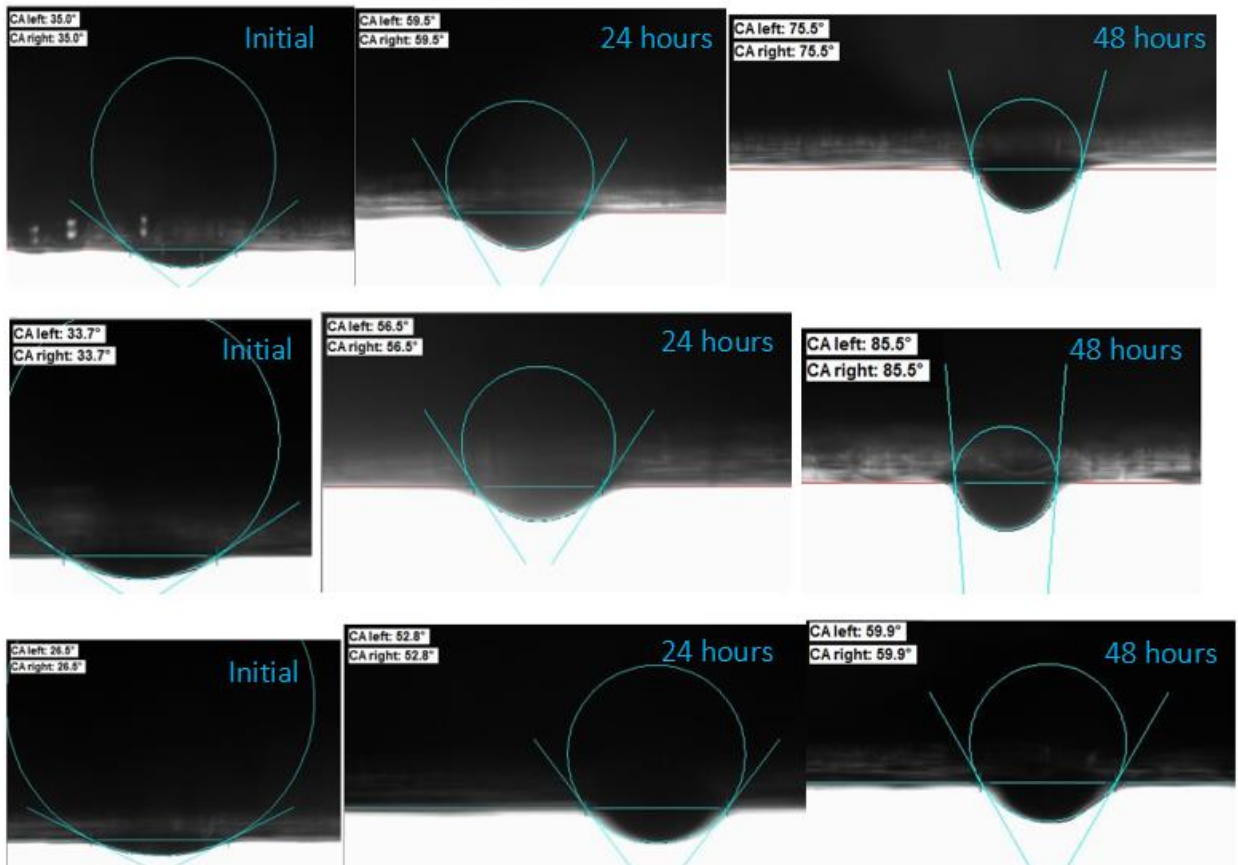
Figure 46 - Contact angle measurements from OCA 15EC 1) 0.05 wt % 2) 0.1 wt % 3) 0.15 wt %

4.4 Rheology experiments

It is vital to study rheological behavior of polymer for successful application with silica nanoparticles as an EOR technique. SAV 10 modified synthetic polymer was tested under ambient (25 °C) and high temperatures (80 °C). Stability of the polymer is the main parameter that influences viscosity. Figure 47 illustrates rheology results of polymer with increasing concentration. All polymers showed shear-thinning behavior by increasing shear rate despite 1000 ppm concentration. As indicated in Figure 47, polymer viscosity becomes higher by increasing concentration. The target viscosity for polymer was found 3-4 cP at shear rate of 10 1/s, 80 ºC. The following comparisons were made between nano-assisted polymer solutions and pure polymer solutions at 1000, 1500, 2000, and 2500 ppm using optimum concentration of silica nanoparticles (0.1 wt %).
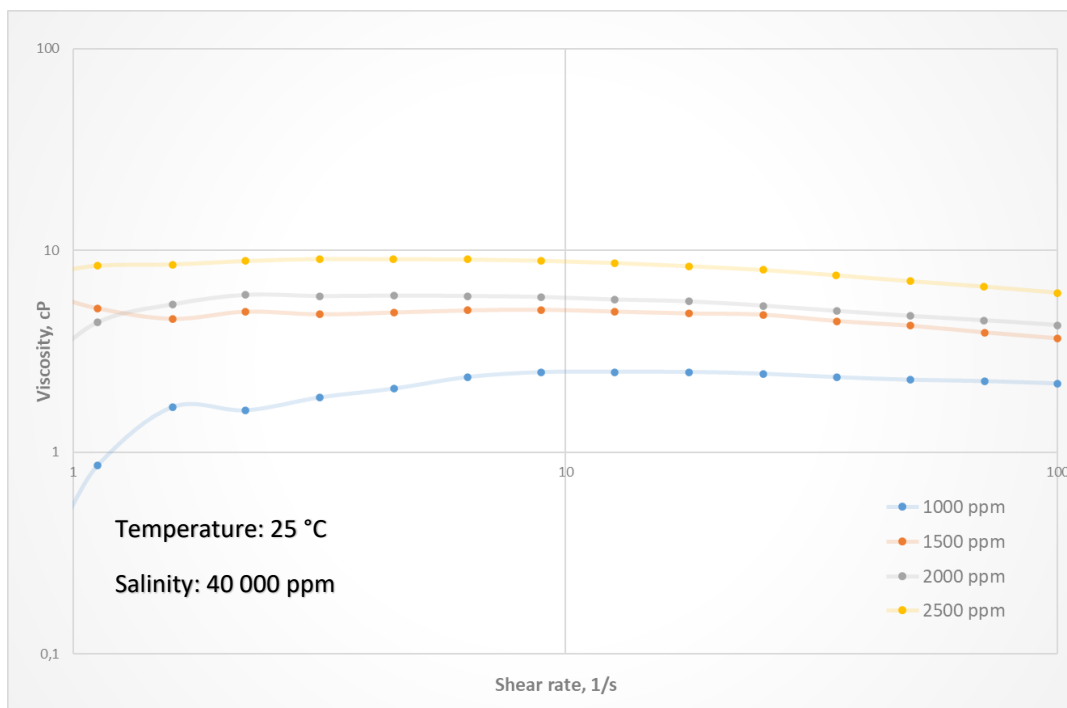
Figure 47 - Rheology values with increasing concentration

Figures 48-51 depict comparisons of pure polymer solutions with nano-assisted polymer solutions at different concentrations (1000, 1500, 2000 and 2500 ppm). The results prove that addition of silica nanoparticles (0.1 wt %) to modified synthetic polymer makes the solution more viscous. However, for both polymer and nano-polymer solutions at 2500 ppm polymer concentration, the rheology measurements showed approximately the same values of viscosity. Those comparisons conducted under ambient temperature, 25 ℃. Tables 12 and 13 illustrate rheology results of pure polymer and nano-polymer at different concentrations.

Table 12 – Rheology of pure polymer solutions

Solution	Temperature	Shear rate, 1/s	Polymer concentration, ppm	Viscosity, cP
Polymer	25	10	1000	2.5
			1500	5
			2000	5.75
			2500	8.7

Table 13 – Rheology of nano-polymer solutions

Solution	Temperature	Shear rate, s^{-1}	SiO_2 concentration, wt %	Polymer concentration, ppm	Viscosity, cP
Nano-assisted polymer	25	10	0.1	1000	3.32
				1500	6.3
				2000	6.15
				2500	8.63
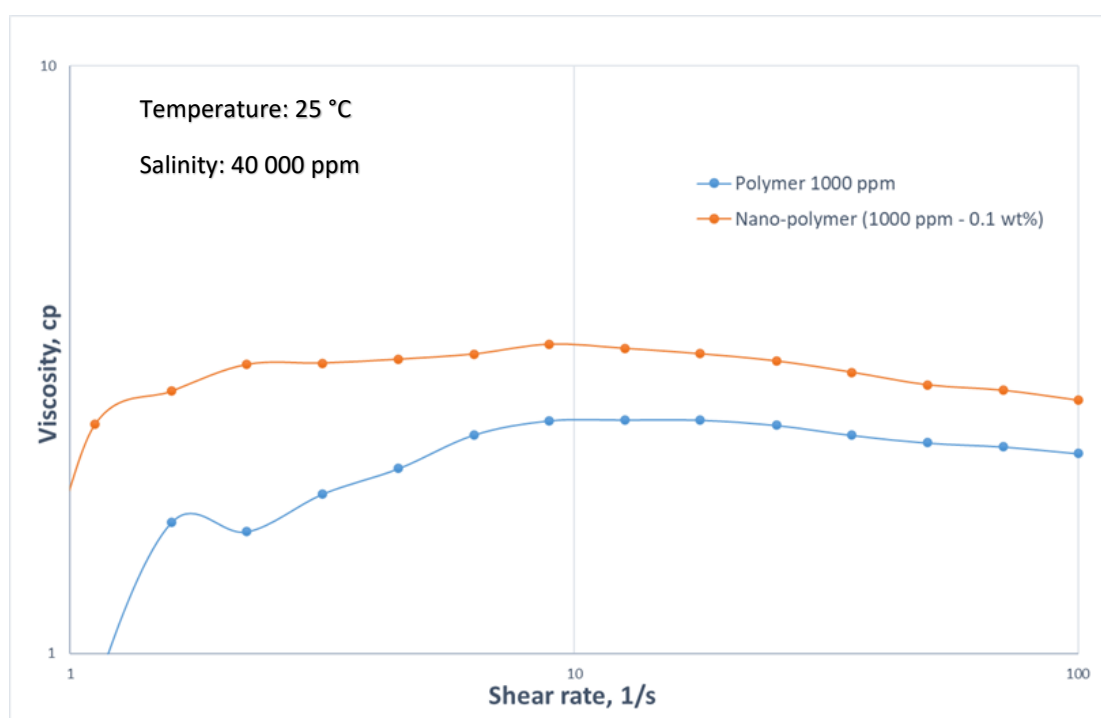
Figure 48 - Comparison of pure polymer and nano-polymer rheology (1000 ppm)
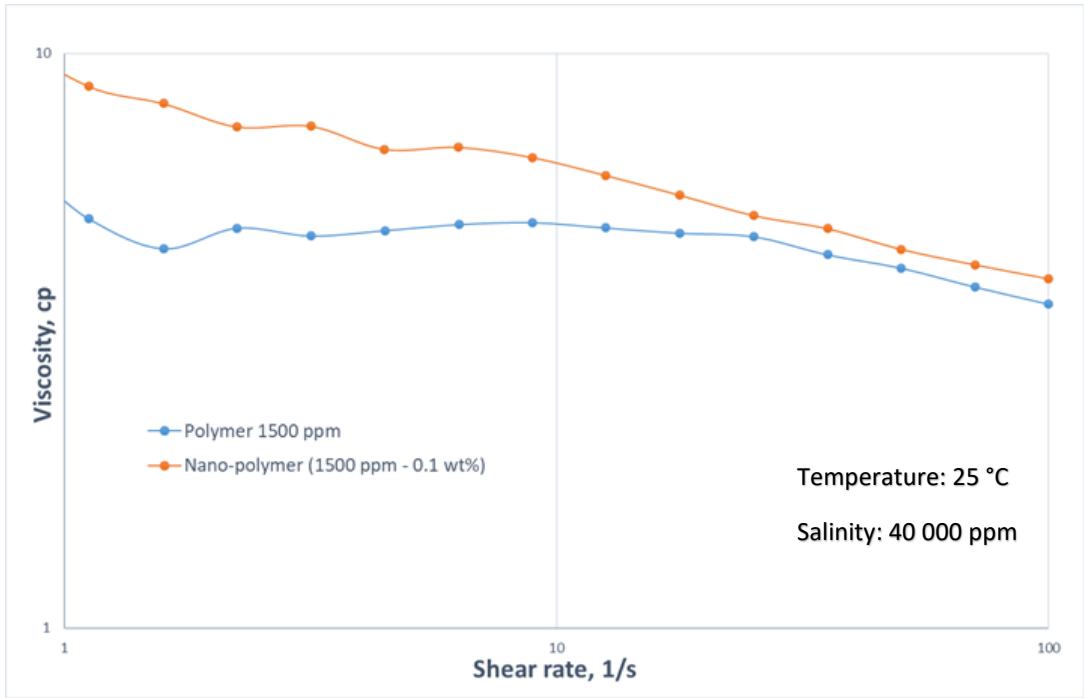
Figure 49 - Comparison of pure polymer and nano-polymer rheology (1500 ppm)
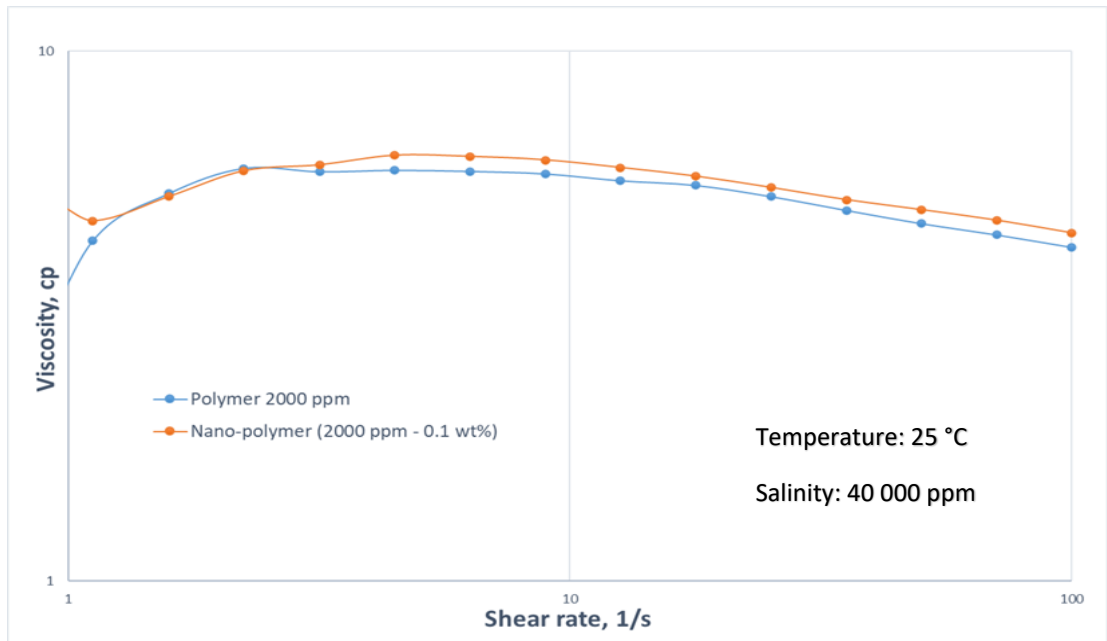
Figure 50 - Comparison of pure polymer and nano-polymer rheology (2000 ppm)
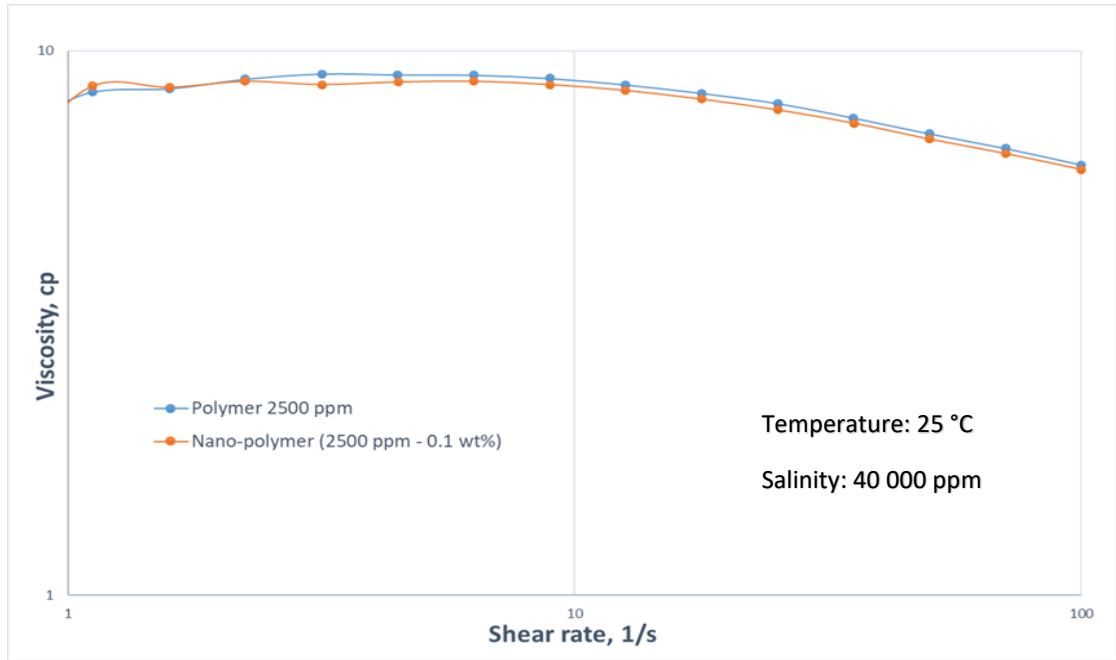
Figure 51 - Comparison of pure polymer and nano-polymer rheology (2500 ppm)

Nano-assisted polymer solutions with different concentrations of polymer were measured at ambient temperature (25 ºC). Figure 52 shows rheology measurements of nano-polymer solutions and all solutions mainly show shear-thinning behavior at all concentrations.
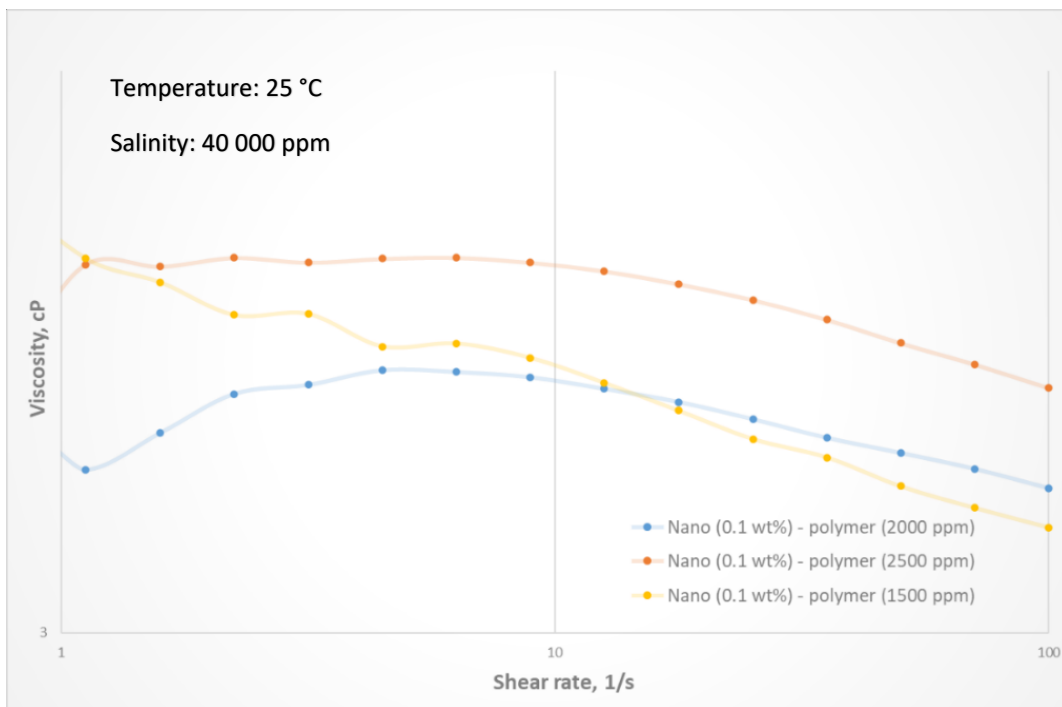
Figure 52 - Rheology of nano-polymer solutions at ambient temperature

Figure 53 depicts rheology measurements of SAV 10 polymers (1500 ppm, 2000 ppm, 2500 ppm) at temperature of 80 ºC. The target viscosity for polymer selected as 3-4 cP at shear rate of 10 1/s, 80 ºC. In the case of 1500 ppm polymer, viscosity was 1.9 cP, whereas with 2500 ppm, viscosity was 4.6 cP at a shear rate of 10 1/s. It is better to achieve the target viscosity at lower polymer concentrations. As soon as polymer viscosity of 2000 ppm reached 3.1 cP at 10 1/s shear rate at 80 ºC, it was selected as an optimum concentration. Table 14 shows the rheology results of pure polymer solutions at high temperature, 80 ºC.

Table 14 – Rheology of pure polymer solutions at high temperatures

Solution	Temperature	Shear rate, 1/s	Polymer concentration, ppm	Viscosity, cP
Polymer	80	10	1500	1.9
			2000	3.1
			2500	4.6
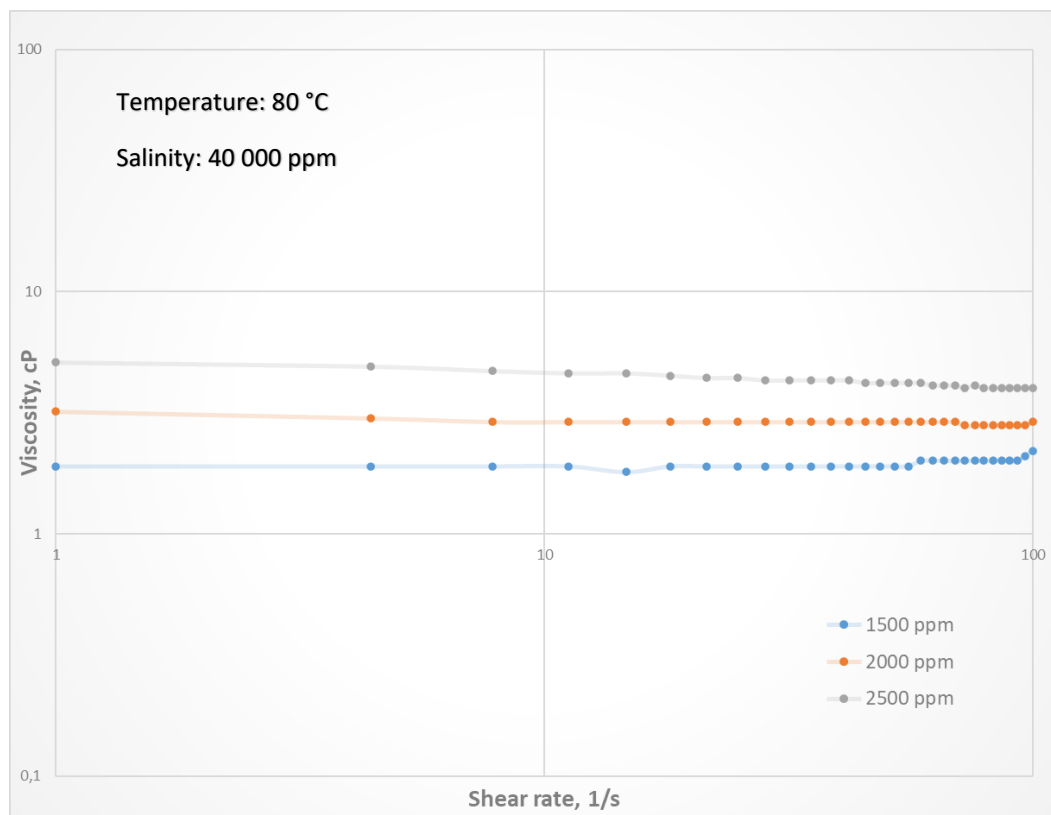
Figure 53 - Polymers (1500, 2000, 2500 ppm) at high temperature

Combination of silica nanoparticles (0.1 wt %) and modified synthetic polymer (2000 ppm) showed higher viscosity than pure polymer (2000 ppm) as illustrated in Figure 54. The viscosity of nano-polymer solution was 3.8 cP at shear rate of 10 1/s. According to Figure 54, silica nanoparticles increase the viscosity of polymer solution at high temperatures (80 ºC). The viscosity values of pure polymer and nano-polymer solutions were 3.1 and 3.8 cP, respectively. It means, that silica nanoparticles increase the polymer viscosity to 18.5 %. As a result, the combination of nanoparticles and polymer will give a better mobility ratio than a pure polymer solution. Nano-assisted polymer solution of 0.1 wt % silica nanoparticles and 2000 ppm polymer was the best choice for coreflooding applications.
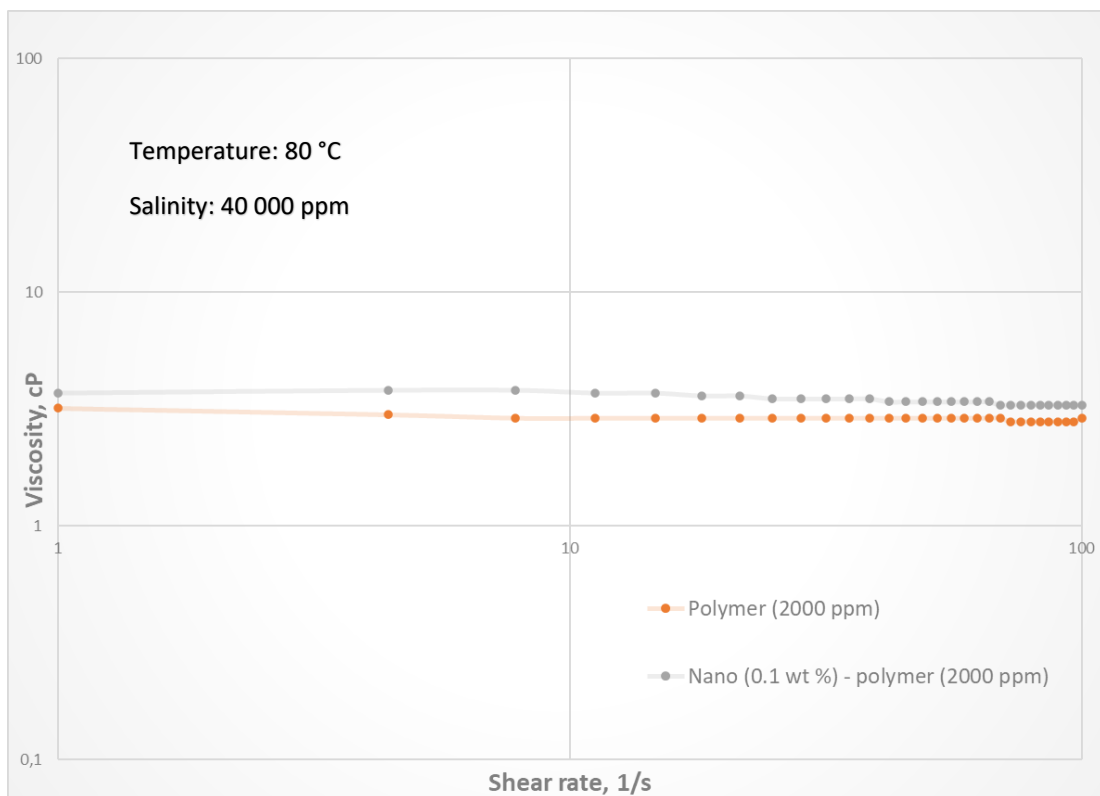
Figure 54 - Rheology of nano-polymer and pure polymer at high temperature

4.5 Coreflooding experiments

Various scenarios of coreflooding were tested to choose the best one based on the values of oil recovery. All scenarios comprised combination of silica nanofluid, polymer and nano-assisted polymer. A coreflooding was carried out by first injecting brine with salinity of 40 000 ppm until no further recovery of oil was recorded in all cases. The temperature was set to 80 ºC to imitate the reservoir condition. Four coreflooding scenarios selected for this study:

1. Brine ➡ Polymer ➡ Postflush

2. Brine ➡ Nanofluid ➡ Nano-polymer ➡ Postflush

3. Brine ➡ Nanofluid ➡ Polymer ➡ Postflush

4. Brine ➡ Nano-polymer ➡ Postflush

4.5.1 First coreflooding scenario

Initially, the brine was injected when the core was at initial water saturation, until no more recovery of oil was recorded. Starting at 0.5 cc/min, the flow rate gradually increased to 5 cc/min to prevent capillary end effects. Flow rate was only increased when oil was not being produced at the outlet. After certain PV of brine injection (24 PV) the oil recovery was almost stopped. The recovery factor by waterflooding comprised 63.96 %. Then, polymer was injected to investigate the efficiency of polymer flooding. The polymer concentration was 2000 ppm. The core properties and saturation results are presented in Table 12, while the results of flood test illustrated in Table 13. The additional oil recovery by polymer flooding was found to be 11.62 %. Finally, brine was injected as a postflush to preserve the core properties and there were no significant oil recoveries. Figure 55 shows the recovery factor and differential pressure vs PV injected.

Figure 55 depicts, that when injecting fluid with a higher viscosity, the differential pressure increases - mobilizing some of the average remaining oil in larger pores - when the injection rate is the same as in a waterflooding. The maximum value of differential pressure was 715 psi at 5 cc/min flow rate. It takes a certain degree of pressure gradient to mobilize trapped oil after flooding. When a polymer solution has a high viscosity, a higher pressure gradient is required to mobilize it. As effective viscosity of polymer solution increases, injecting pressure increases, allowing more polymer solution to enter larger pores and thus liberate more trapped oil. The resistance factor (RF) and residual resistance factor (RRF) values were 7.34 and 1.43 respectively. It means that there was a very small reduction in permeability after polymer flooding and viscosity of the polymer solution was high during the experiment.

Table 15 – Core properties and saturation results

Core #	V_p, cc	L, cm	A, cm^2	k(abs), mD	k(eff), mD	S_{oi}, %	S_{wi}, %
1	15.36	7.15	11.413	25.03	15.24	80.26	19.74

Table 16 – Results of recovery test

Injected fluid	Volume of displaced oil, ml	Recovery factor, %	Total recovery, %
Brine	7.89	63.96	**75.59**
Polymer	1.431	11.62	
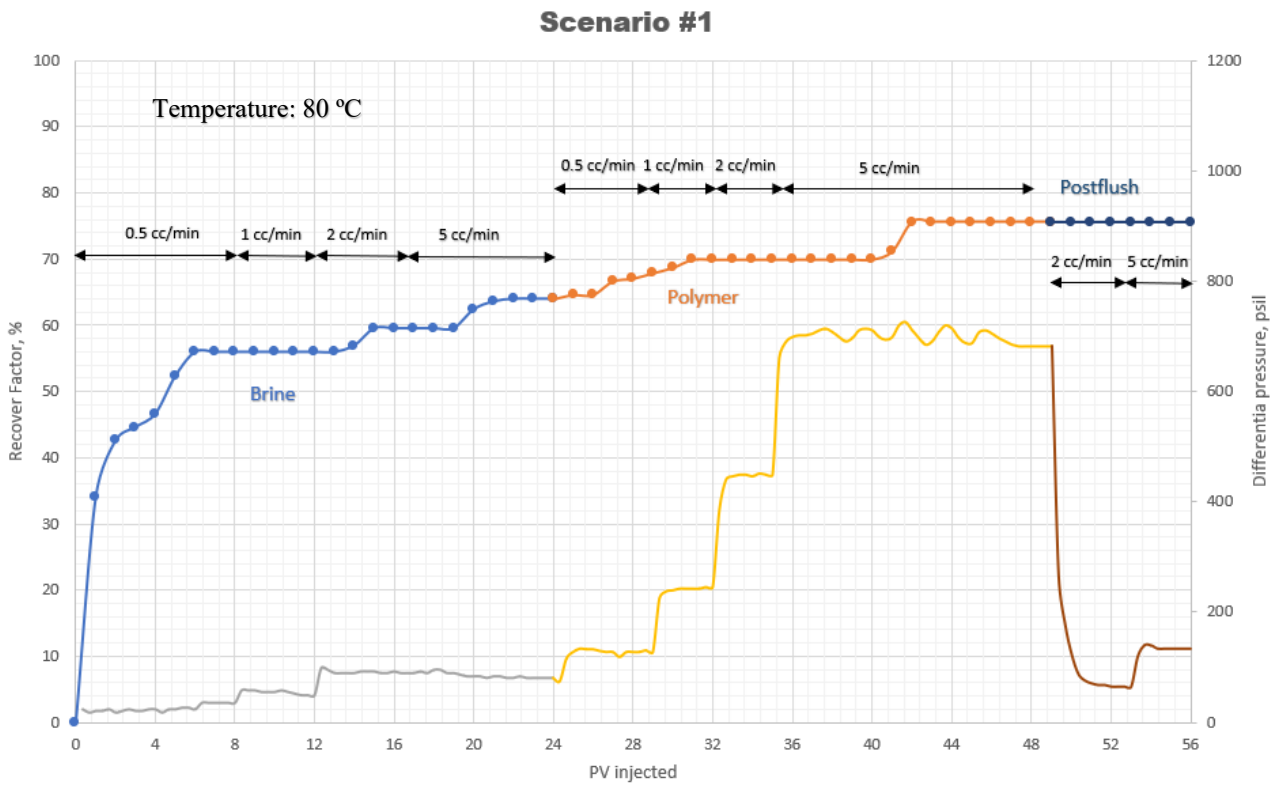
Figure 55 - Recovery factor vs PV injected

4.5.2 Second coreflooding scenario

Figure 56 illustrates recovery and differential pressure values against PV injected of second scenario. The brine was injected until no more recovery of oil was recorded. Here, also flow rates were 0.5, 1, 2 and 5 cc/min. Nanofluid and nano-assisted polymer were utilized as an EOR technique after waterflooding. After 24 PV of injected brine, oil production stopped at

high flow rates. Nanofluid was injected after waterflooding process. Additional oil recovery by injecting nanofluid comprised 9.15 %. The concentration of the silica nanofluid comprised 0.1 wt %. The main mechanism during nanofluid injection probably was wettability alteration of the system, therefore, some amount trapped oil produced. Oil production stopped after injecting 20 PV of nanofluid. Afterwards, nano-assisted polymer was injected into the core to increase the oil recovery. Concentrations of silica nanoparticles and polymer included 0.1 wt % and 2000 ppm, respectively. Recovery factor of oil enhanced significantly up to 17.7 % by injecting nano-polymer solution. The reason is, silica nanoparticles affect on microscopic sweep efficiency, while polymer impacts on macroscopic sweep efficiency. It indicates that nano-assisted polymers have a great impact on capillary and viscous forces. In the end, brine was injected as a postflush to preserve the core properties and there were no significant oil recoveries. The core properties and saturation results are presented in Table 14, while the results of flood test illustrated in Table 15.

The differential pressures of brine and nanofluid were approximately the same at different flow rates. The maximum value of differential pressure for brine and nanofluid was about 160 psi at high flow rates. As discussed in rheology experiments, addition of silica nanoparticles increases the polymer viscosity. Accordingly, nano-assisted polymer solution has a higher viscosity than pure polymer. Consequently, differential pressure of nano-polymer was higher than differential pressure of pure polymer. The differential pressure of nano-polymer solution reached 916 psi at higher flow rates as illustrated in Figure 56. The resistance factor (RF) was calculated after nano-assisted polymer flooding and it was 6.83, while residual resistance factor (RRF) comprised 1.04. According to the resistance factor, it shows great enhancement of nano-assisted polymer viscosity in the porous media. There is no permeability reduction as RRF illustrated. It seems that an addition of silica nanoparticles to polymer solution decreases polymer retention in carbonate rock.

Table 17 – Core properties and saturation results

Core #	V_p, cc	L, cm	A, cm^2	k(abs), mD	k(eff), mD	S_{oi}, %	S_{wi}, %
2	15.09	7.13	11.413	43.43	24.05	79.5	20.5

Table 18 – Results of recovery test

Injected fluid	Volume of displaced oil, ml	Recovery factor, %	Total recovery, %
Brine	7.2208	60.16	
Nanofluid	1.099	9.15	**87.045**
Nano-polymer	2.126	17.7	
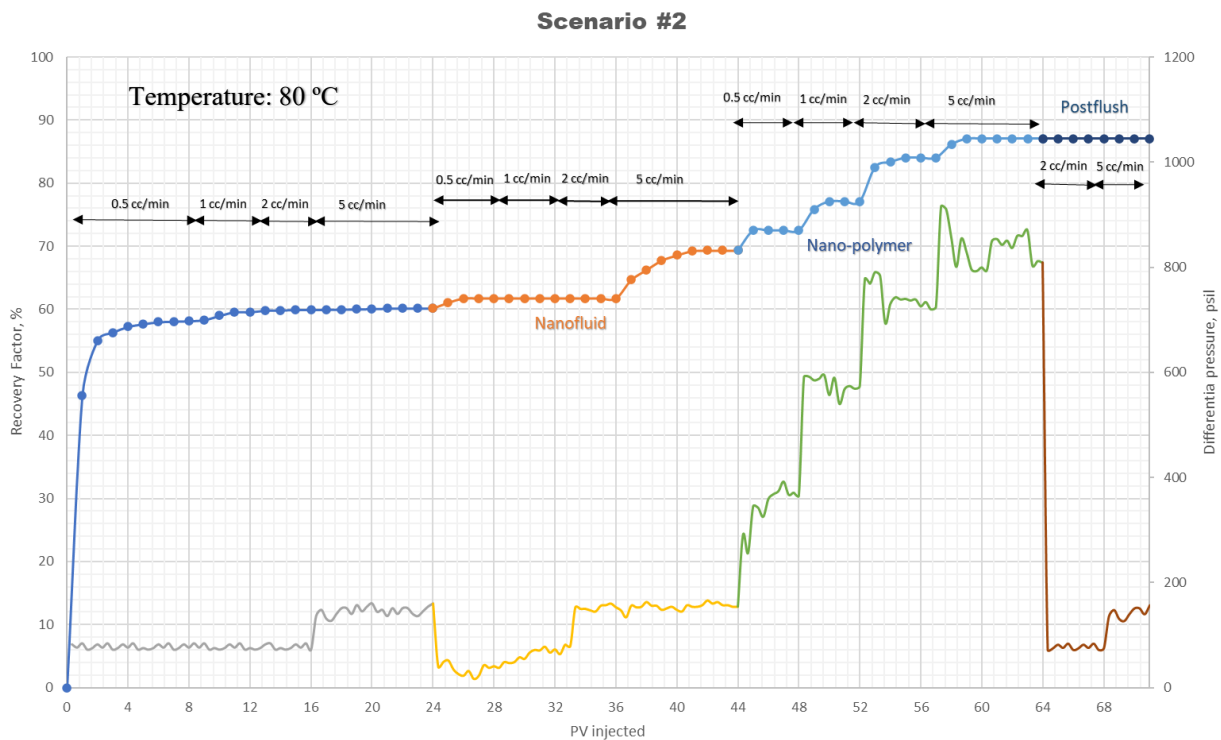
Figure 56 - Recovery factor vs PV injected

4.5.3 Third coreflooding scenario

Figure 57 depicts recovery and differential pressure values against PV injected of second scenario. The brine was injected until no more recovery of oil was recorded. The flow rates ranged from 0.5 cc/min to 5 cc/min. Oil production stopped after 25 pore volumes (PV) of brine injection. In this experiment, nanofluid and polymer were used as a tertiary recovery. Silica nanoparticles and polymer concentrations were 0.1 wt % and 2000 ppm, respectively. Initial oil recovery by waterflooding comprised 67.35 %. According to the study, silica nanoparticles probably decrease mobility ratio, causing polymer solution to move to unswept regions and improving oil recovery. In oil displacement mechanisms and on wettability alteration,

nanoparticles play a significant role. However, additional oil recovery by nanofluid solution comprised only 1.47 % injecting 20 PV, while by polymer flooding it was 14.71 % injecting 25 PV. Finally, brine was injected as a postflush to preserve the core properties and there were no significant oil recoveries. The core properties and saturation results are presented in Table 16, while the results of flood test illustrated in Table 17.

Figure 57 also shows differential pressure values of each injected fluid. Average differential pressure for brine and nanofluid was 80-90 psi at high flow rates. A more viscous polymer solution requires higher differential pressure to displace trapped oil from the core. Thus, by polymer flooding differential pressure reached 719 psi at high flow rates. Resistance factor (RF) was 7.56, while residual resistance factor (RRF) comprised 1.24. Approximately the same as the first scenario. The viscosity of the polymer solution in porous media was high enough to displace the oil with favorable mobility and only a minimal reduction in permeability.

Table 19 – Core properties and saturation results

Core #	V_p, cc	L, cm	A, cm^2	k(abs), mD	k(eff), mD	S_{oi}, %	S_{wi}, %
3	16.13	7.27	11.413	39.23	23.92	79.9	20.1

Table 20 – Results of recovery test

Injected fluid	Volume of displaced oil, ml	Recovery factor, %	Total recovery, %
Brine	8.6814	67.35	
Nanofluid	0.1454	1.47	**83.53**
Polymer	1.8955	14.71	
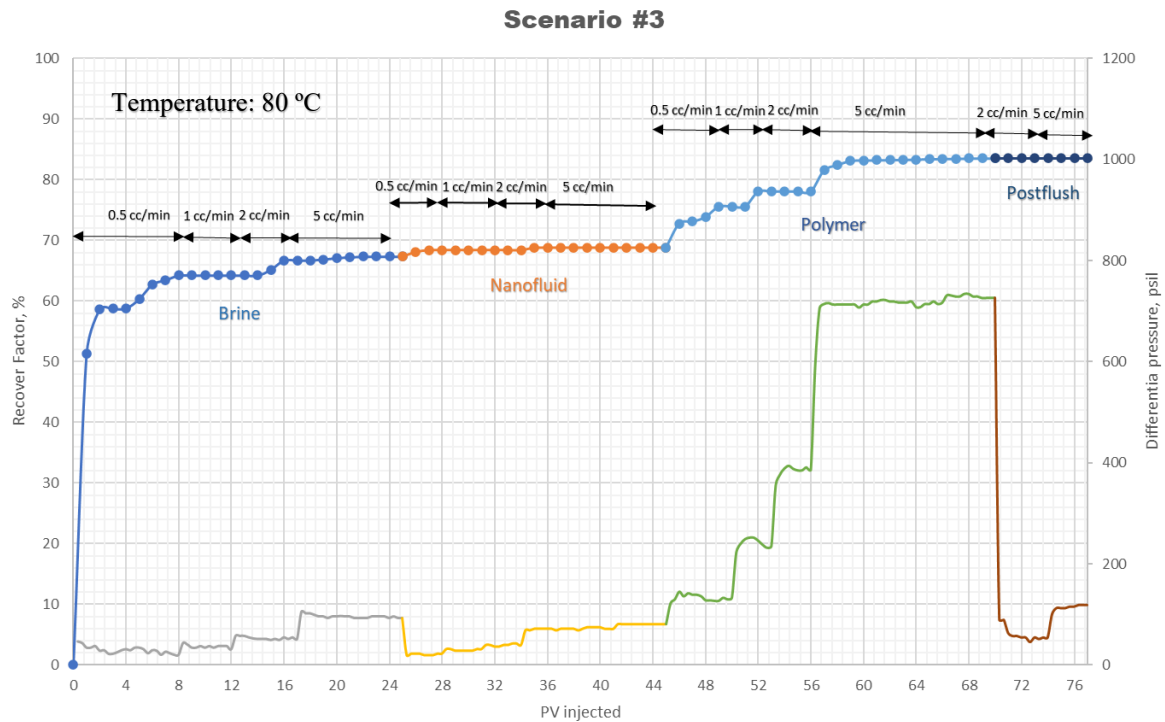
Figure 57 - Recovery factor vs PV injected

4.5.4 Fourth coreflooding scenario

Core displacement study was conducted using carbonate sample in order to investigate the effectiveness of chemical slug of silica nanoparticles-polymer mixture (2000 ppm SAV 10 polymer + 0.2 wt % silica nanoparticles). Initially, water was injected up to 24 pore volumes (PV) to recover the crude oil until the water cut reached above 95 %. Brine was used as a secondary recovery mode. Results illustrated that 61.046 % of oil was recovered by waterflooding. Then, 21 PVs nano-polymer slug is injected to recover additional oil in EOR mode. The additional oil recovery by nano-polymer flooding was found to be 19.01 %. In the end, brine was injected as a postflush to preserve the core properties and there were no significant oil recoveries. As the chemical injection process begins, the recovery of oil increases suddenly. Injection fluids with high viscosity, such as modified synthetic polymer and silica nanoparticles, lead to increased sweep efficiency and allow more oil to be pushed towards the production lines. In addition, silica nanoparticles presented in the chemical slug, altered the wettability of the system, thus accelerating oil recovery. Table 18 summaries core properties and saturation values and Table 19 shows additional oil recovery obtained by nano-polymer slug.

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The nano-assisted polymer solution has a higher viscosity than pure polymer. Therefore, differential pressure of nano-polymer was higher than differential pressure of pure polymer. The differential pressure of nano-polymer solution reached 856 psi at higher flow rates as illustrated in Figure 58. Resistance factor (RF) in this scenario comprised 7.6 and residual resistance factor (RRF) showed 1.02. In porous media, the nano-polymer had a viscosity sufficient to displace oil and no reduction in permeability was observed.

Table 21 – Core properties and saturation results

Core #	V_p, cc	L, cm	A, cm^2	k(abs), mD	k(eff), mD	S_{oi}, %	S_{wi}, %
4	17.096	7.95	11.413	30.27	14.92	72.3	27.7

Table 22 – Results of recovery test

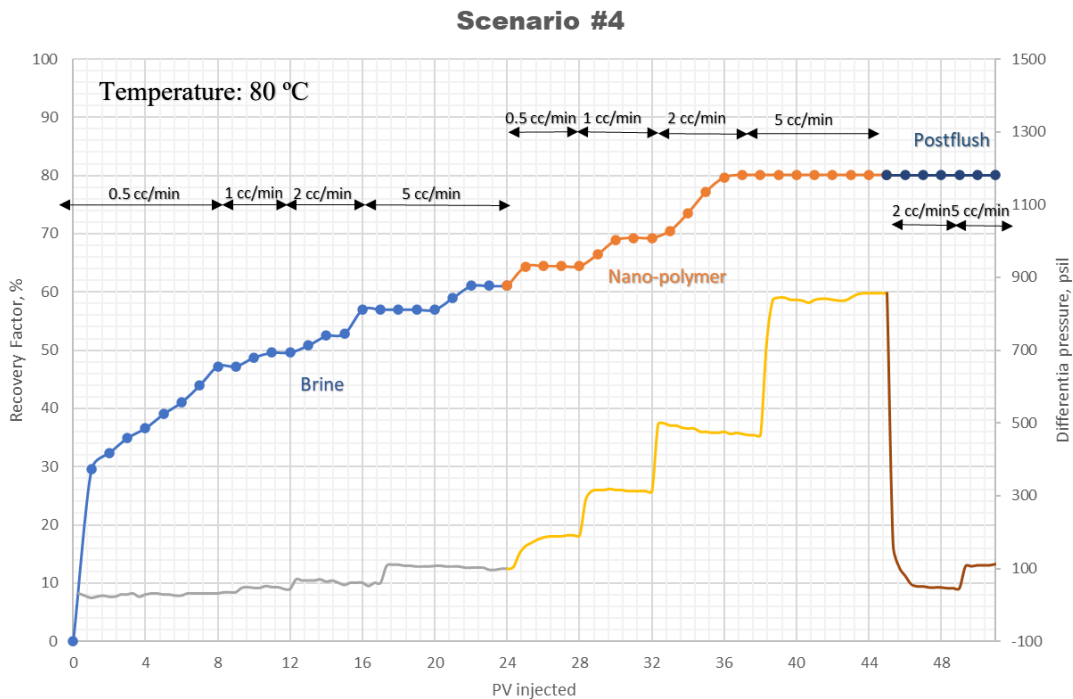| Injected fluid	Volume of displaced oil, ml	Recovery factor, %	Total recovery, %
Brine	7.545	61.046	80.056
Nano-polymer	2.35	19.01	

Figure 58 - Recovery factor vs PV injected

4.5.5 Resistance factor (RF) and residual resistance factor (RRF)

A measurement of polymer solution mobility reduction in relation to brine is performed using RF. The RRF represents the reduction in permeability caused by the polymer solution and observed after a postflush brine. Formulas (9) and (10) define the RF and RRF, respectively:

$$RF = \frac{\Delta p_p}{\Delta p_w^{before}} \qquad (9)$$

$$RRF = \frac{\Delta p_w^{after}}{\Delta p_w^{before}} \qquad (10)$$

where Δp_p is differential pressure of polymer, Δp_w is differential pressure of brine, "before" and "after" superscripts are relative to the polymer flooding.

In porous media, resistance factor (RF) provides a means to evaluate the development of pressure versus flow velocity considering the polymer retention. The residual resistance factor (RRF) is another important factor to consider when determining polymer injectivity. It describes the reduction in permeability of porous media because of irreversible polymer retention. In general, the RRF results for all cases were around of 1, meaning that there is a little or no permeability reduction in carbonate rock after polymer or nano-polymer flooding. Values of RF prove that during the coreflooding experiments viscosity of injected polymer or nano-polymer solutions were high enough to displace oil. In Table 20 illustrated RF and RRF values of polymers and nano-polymers utilized in all four scenarios. RRF of polymers in first and third scenarios comprised 1.43 and 1.24, respectively. At the same time, RRF values of nano-polymer solutions in second and fourth scenarios were 1.04 and 1.02. It means that addition of silica nanoparticles to polymer prevents polymer retention, therefore, there is no permeability reduction in porous media.

Table 23 – RF and RRF results

Scenario #	dP (polymer), psi	dP (nano-polymer), psi	dP (preflush), psi	dP (postflush), psi	RF	RRF
1	683	-	93	133	7.34	1.43
2	-	916	134	140	6.83	1.04
3	726	-	96	119	7.56	1.24
4	-	836	110	113	7.6	1.02

4.5.6 Selection of best flooding scenario

Figure 59 shows comparison of oil recovery in all scenarios using brine (40 000 ppm), silica nanofluid (0.1 wt %), polymer (2000 ppm) and nano-assisted polymer solutions (0.1 wt % silica nanoparticles + 2000 ppm polymer). As discussed before, in nano-assisted polymers, pressure drops gradually increased due to the viscosity of the solution. Maximum oil recovery of 87.045 % was obtained by second scenario - injecting silica nanofluid followed by nano-assisted polymer. Recovery factor for first scenario and third scenario comprised 75.59 % and 83.53 %, respectively. At the same time, last coreflooding scenario showed overall oil recovery of 83.53 %. Second scenario yield the best oil recovery due to the increased viscosity of nano-assisted polymer solution as well as ability of silica nanoparticles to change wettability of the carbonate core from oil-wet to a water-wet state. In other words, by injecting nano-assisted polymer solution silica nanoparticles impact on microscopic sweep efficiency and polymer affects on macroscopic sweep efficiency at the same time. Thus, synergy of different mechanisms such as wettability alteration, mobility control, change of disjoining pressure leads to improved oil recovery. Moreover, it was investigated that addition of silica nanoparticles prevents polymer retention in the porous media according to the RRF results presented above and RF values showed that viscosity of the injected fluid was high enough due to combination of modified synthetic polymer and silica nanoparticles, the sweep efficiency is increased, and the injected fluid can push more oil towards the production side. In summary, these mechanisms together increase the recovery factor significantly, thereby making the second scenario the best option for EOR technique.
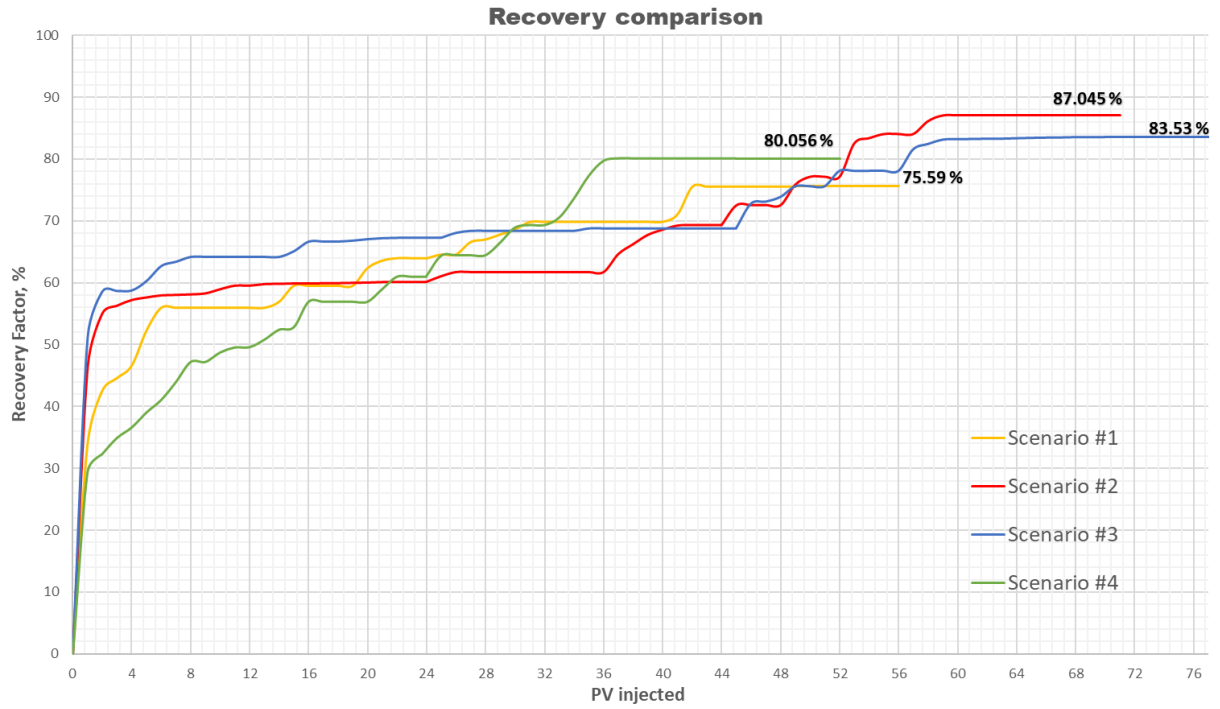
Figure 59 - Comparison of oil recovery values

5. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research was to investigate the interactions between silica nanoparticles and polymer. A variety of experiments have been conducted, and several conclusions can be drawn from the results:

- It was determined that the combination of silica nanoparticles and modified synthetic polymers was effective in achieving the objectives;
- Surface wettability is altered by silicon oxide nanofluids. Silica-based nanofluid with 0.1 wt % concentration was the most effective in altering carbonate rock wettability from oil-wet to water-wet state. Thus, it was found to be the optimal concentration for nanoparticles;
- The addition of salt has an enormous effect on the stability of silica nanofluid. 0.1 wt % of silica nanofluid was stable at 40 000 ppm salinity;
- Rheology experiments showed that silica nanoparticles addition to polymer solution increases the fluid viscosity to 18.5 %, where the viscosity of nano-assisted polymer solution was 3.8 cP at shear rate of 10 s^{-1}, 80 ºC. As a result, the combination of nanoparticles and polymer will give a better mobility ratio than a pure polymer solution. Nano-assisted polymer solution of 0.1 wt % silica nanoparticles and 2000 ppm polymer was the best choice for coreflooding applications;
- Maximum oil recovery of 87.045 % was obtained by injecting silica nanofluid followed by nano-assisted polymer as an EOR technique. Thus, combination of silica nanoparticles and polymer is more effective than pure polymer solution due to synergy of different mechanisms;
- RRF values of nano-polymer solution in second scenario comprised 1.04. It means that addition of silica nanoparticles to polymer prevents polymer retention, therefore, there is no permeability reduction in porous media;

The recommendations are to perform contact angle measurements using nano-assisted polymer solutions at different polymer concentrations to analyze the effect of polymer on wettability and investigate the effect of silica nanoparticles to interfacial tension (IFT) of the fluids. Furthermore, a detailed study of the polymer's retention in porous media can be conducted.

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