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Experimental Study of Permeability Alteration due to Nanoparticle Retention in Porous Media in Nanotechnology Assisted Enhanced Oil Recovery:

by

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CHAPTER ONE

1 INTRODUCTION

Many oil producing fields in different regions of the world are nearing their decline phase. Some of which have more than 50% of their Original Oil in Place unproduced. The unsolved puzzle becomes how to extract more oil economically and extend the lifespan of a well, thereby delaying abandonment. Primary oil recovery which uses the natural drive of the reservoir recovers just about 15% of the original oil in place. While secondary oil recovery involving gas injection, water injection, etc. recovers an additional 30% of the reservoir oil, leaving about 55% of the original oil in place still unrecovered, because the traps caused by capillary forces or oil may be bypassed in these process for some reasons (Afeez et al 2019). Because of the estimated increase in energy demand in the coming years, the oil industry is expected to venture into other methods of improving oil recovery.

The next line of action becomes Enhanced oil recovery. Different methods of Enhanced oil recovery include:

Thermal recovery: i.e. heating the oil to reduce viscosity by injecting steam into the reservoir. This method of Enhanced Oil Recovery is unsuitable for very deep reservoirs.

Chemical injection: this is the least common method. Chemicals are injected into the reservoir to free trapped oil in the well by lowering surface tension. With the current decline in oil price, chemical Enhanced oil recovery has become a very expensive means of Enhanced Oil Recovery.

Nano particle injection: this is another method of Enhanced Oil Recovery, which involves injecting nanoparticles into a reservoir to enhance oil production. Nano particles due to their small size can produce higher penetration and dispersion rates than other Enhanced Oil Recovery techniques.

1.1 BACKGROUND TO THE STUDY:

Nano particles or ultra-fine particles are defined particles of matter between 1-100 nanometers in diameter. They can be used in enhanced oil recovery because of their small nature.
Permeability alteration can be defined as a change in the permeability of a rock due to retained substances.
Nanoparticle retention is the ability of a reservoir rock to absorb and keep some amounts of the nanoparticles injected into it thereby reducing its permeability. Enhanced oil recovery is the third method of oil recovery used after the primary and secondary oil recovery processes have been used.
Nano particles injection is a type of enhanced oil recovery which involves injection nanoparticles into a reservoir rock.

In previous times, different works have been published on the effects of nanoparticles when used for enhanced oil recovery. But the researcher will focus on how nanoparticles are retained in the pore spaces of reservoir rocks, and how it affects the rock permeability.

Nanoparticles have been observed to have different advantages for the oil industry, which includes; Increased oil recovery, improved water disposition, maintaining the reservoir pressure above the bubble point pressure. Etc.

We have different types of nanoparticles which include organic and inorganic nanoparticles. Liposomes are organic nanoparticles composed of amphiphilic lipids that form a self-assembly induced by layer with an internal aqueous layer. They are used in encapsulation of drugs to be delivered to different areas of the body. This occurs when lipids are added to a solution of those drugs. Magnetic nanoparticles exhibit paramagnetic properties. Metallic nanoparticles exhibit specific adsorption/ emission properties. The reservoir conditions are usually harsh, hence the thermal stability of nanoparticles make them suitable in withstanding harsh temperature conditions when injected into the reservoir. Their super paramagnetic properties aid in magnetic separation when coming out of the production well.

Different technologies provide information from near well bore areas. Nano particles can be used to gather information from deeper areas because of their high penetrating abilities. They can be adjusted to detect changes in temperature, share rate, pressure etc. in the reservoir environment. Their relatively small sizes aid their unhindered passage through pore spaces of reservoir rocks. Their uses include:

- Location of residual oil
- Deducing inter-well connectivity by analyzing concentration curves.
- Estimating the distribution of pore sizes in reservoir rocks.
- Location of fractures and high permeability streaks.
- There are different methods by which nanoparticles can be used for enhanced oil recovery. They include:

- Recovery of trapped oil or reduction of residual oil saturation.
- Reduction of viscosity leading to recovery of bypassed oil.
- Stabilization of foam.
- Wettability alteration. Etc.

Different properties of the nanoparticles make them advantageous in enhanced oil recovery. Their properties include:

- Their ability to move freely on porous media without plugging pore throats.
- Ability to modify their surfaces to match different reservoir properties.
- Their interfacial tension modification properties between oil and water.
- Their ability to modify the viscosity of the displacing phase.
- They can be designed for targeting definite locations through surface modifications.
- Their ability to be collected on production sites through n magnetic separation.
- Their ability to encapsulate chemicals, send then to specific areas in the reservoir before triggering their release. (Bennetzen 2014)

1.2 STATEMENT OF PROBLEM

The researcher focuses on reservoir studies and enhanced oil recovery using nanoparticles. When nanoparticles are injected into the reservoir rocks, they sometimes get absorbed into the rock's pore spaces which lead to reduction in pore volume and hence permeability alteration of the reservoir rock.

The researcher also checks the ratio of injected fluid to that of produced fluid.

The goal is to curb permeability alteration when using nanoparticles for enhanced oil recovery.

1.3 AIMS AND OBJECTIVES

- To review the application of nanotechnology in enhanced oil recovery.
- To decode the ratio of nanoparticle produced to that injected in low permeability systems.
- To understand reasons for increased nanoparticles retention in high temperature reservoirs.
- To study the adsorption and straining of nanoparticles which in turn reduces permeability in porous media.
- Study of maximum retention concentration of nanoparticles as a function of injected particle concentration.
- Analyzing oil recovery factor as a function of nanoparticles concentration.
- Methods of preparation of Nano fluids.
- Study the alteration of rock wettability due to surface reactivity of nanoparticles.
- Selection of the particular type of nanoparticle that is suitable for a particular rock type.

1.4 SCOPE AND LIMITATIONS

The study is limited to the use of nanoparticles as a means of enhanced oil recovery. Other enhanced oil recovery processes like thermal injection, chemical injection, etc. are not considered in the course of this study.

We will be considering how nanoparticles can be used to enhance oil recovery. Also the disadvantages of using nanoparticles as a means of enhanced oil recovery.

The effects of using the different types of nanoparticles will be considered and how each of them enhances oil recovery. Their effect on the individual rock samples will also be considered.

1.5 SIGNIFICANCE OF STUDY

This work is expected to benefit oil companies in the upstream sector in their bid to maximize oil recovery from reservoir rocks to be able to maximize their profit.

The findings will help exploration and production industries to be able to meet the increasing demand in world’s energy sources.

We will also be able to generate the ratio of nanoparticles to be injected in a particular rock sample during enhanced oil recovery to prevent reduction in the rock permeability.

We will find out the types of nanoparticles suitable for different rock types.

CHAPTER 2

2 LITERATURE REVIEW

2.1 ENHANCED OIL RECOVERY OVERVIEW

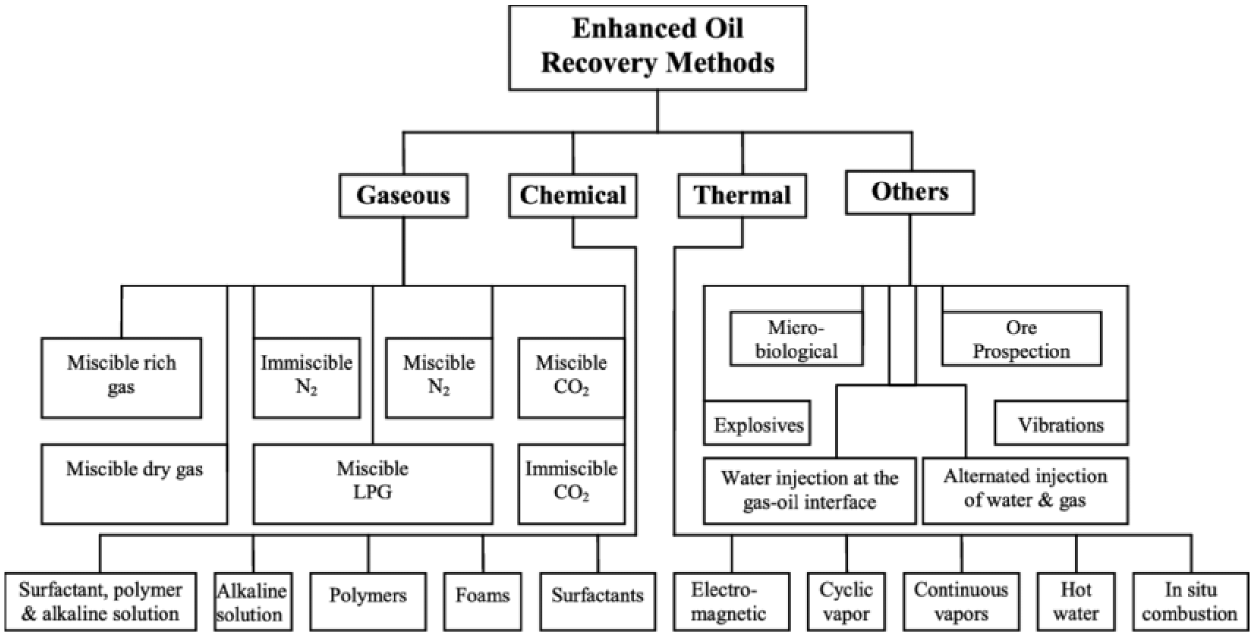


Figure 1 Organogram For Enhanced Oil Recovery Methods.

In the primary recovery process, water drive gives the highest recovery because pressure is constant. All under saturated reservoirs are water drive reservoirs.

For secondary process, a well that produces under water flooding, at the end of its productive life is bound to have water encroachment. We also need to have a uniform permeability. If the permeability is not uniform, you increase the injection pressure to avoid one part absorbing the water. Gas flooding is basically the same as water flooding, just that gas is used as the driving force.

ENHANCED OIL RECOVERY: This is essentially approved to reduce the hydrostatic pressure and viscous forces. The commonly used methods are

THERMAL COMBUSTION: which includes hot water injection (where water is boiled outside and injected) and Steam injection (where steam is used to soak and clean the well). This is especially suitable for heavy oil reservoirs to avoid catalytic cracking.

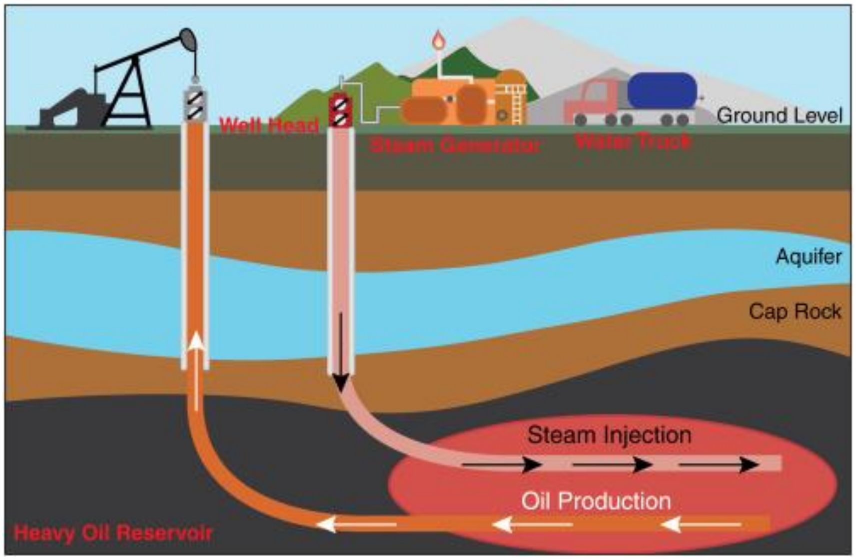


Figure 2 Thermal Combustion

MISCIBLE FLOODING: This includes the displacement of oil by non-aqueous injection of H.C solvents (LPG and alcohols), lean hydrocarbon gases (methane, ethane, etc.) or high pressure non hydrocarbon gases e.g. CO_2, and Nitrogen. The displacement efficiency is largely a function of interfacial forces acting among the oil, rock and displacing fluid. If the interfacial tension between the trapped oil and displacing fluid could be lowered to 10^{-2} or 10^{-3} dyn/cm. A miscible process is one in which the interfacial tension is zero.ie the residual oil and the displacing fluid combine to form one phase. If the interfacial tension is zero, the displacement efficiency is maximized.

CHEMICAL FLOODING: It involves the injection of chemicals to wash out oil from the pore rock. E.g. surfactant and detergent. The three main forces withholding the residual oil in the reservoir are: capillary forces, viscous forces, interfacial tension. Examples of chemical EOR processes are: Polymer flooding, Surfactant flooding, Alkaline flooding, Foam flooding, CO_2 flooding, Nano technology EOR.

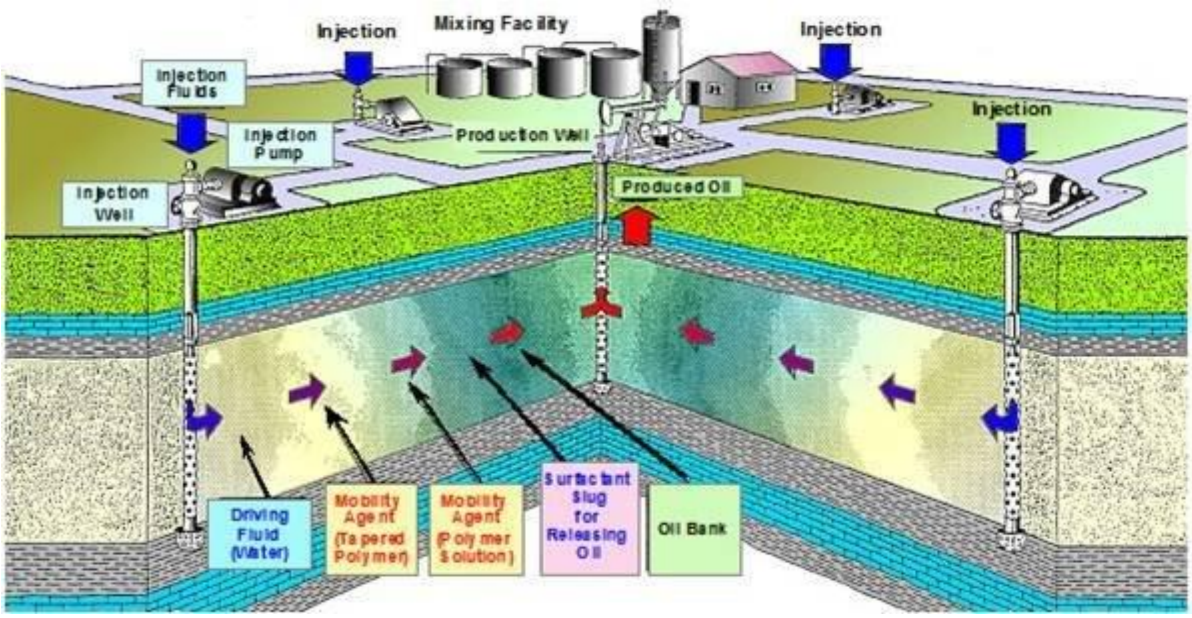


Figure 3 Chemical Flooding

2.2 NANO TECHNOLOGY:

This involves the use of fine scale nanoparticles in the Enhanced oil recovery process. When they are injected, the help to free the trapped oil that had been bypassed during the primary and secondary recovery process.

Fines are tiny particles which can easily detach from the rock and cause formation damage. Nanoparticles have been found with the ability to prevent formation damage and detach skin damages as a result of polymer based simulation fluids and blockages caused by paraffin.(Habibi & Heidari, 2012)

Nano particles have the ability to precipitate in the pore spaces of a reservoir rock thereby clogging the pore spaces. By so doing, it reduces the reservoir permeability. Quartz and soil have and their reactions to the passage of nanoparticles have previously been studied while little work has been done to see the effect of the passage of nanoparticles on other rock types. E.g. limestone, dolomite, sandstone.(Bayat et al., 2015)

Injection of metal nanoparticles may deteriorate the recovery process due to the attractive Vander Waals and electrostatic forces between the metallic particles and the porous media which could cause damage in the porous media. A dispersive agent is used to neutralize the attractive forces and prevent further agglomeration. This agent could affect the viscosity of the solution, so its concentration should be checked to yield the highest injection and lowest retention. The viscous force is affected by the nanoparticle injection rate. It supplies momentum for particle distribution in porous media. From an injectivity test carried out, nanoparticles have lower retention and better injectivity when you compare them to micron sized particles. The injection of metal nanoparticles has been used for different reasons such as: location of the bypassed oil in the oil reservoir and oil mobilization etc.(Shokrlu & Babadagli, 2013).

Nano sized particles can be deposited and they form a blockage on the reservoir rocks. The surface charge of the particles will decrease the agglomeration of the dispersed particles in water to increase their stability during transport. The surface charges can also affect this adsorption on the rock surface because the particles will be attracted to surfaces with opposite charges.(Almahfood & Bai, 2021)

We can actually check how surface treated nanoparticles (Iron oxide) are transported in sedimentary rocks by injecting different aqueous dispersions of this particular nanoparticle into a core sample. Those dispersions should have different ionic strengths and ph. From the experiment, nanoparticles with relatively low negative charges will greatly reduce the retention in reservoir rocks; hence little or no permeability reduction is noticed. Although nanoparticles have a wide range of application across different fields of study, we should always remember the basic use of nanoparticles as regards the exploration and production industry, which remains: as sensors in the observation of certain reservoir properties, and for enhanced oil recovery.

2.3 NANOPARTICLES SPECIFICATIONS:

- Uniform dispersion in the solvent to prevent aggregate formation.
- Ability to penetrate a long distance depth into the reservoir without a large amount of retention.
- An ability to attach themselves at some specified places in the reservoir. For example, at the oil-water contact of the reservoir to be able to detach the two fluids, and hence, enhance oil recovery.

The first condition has actually been met by using a specific polymer to coat the surface of the nanoparticles. For the second condition, it has also been found out that when a perfect surface coating was used, the nanoparticles remained dispersed in the solvent without agglomeration, and the rate of retention of the nanoparticles even in low permeability reservoirs was relatively low. Hence, both conditions have been met by the polymer coating. And the process of meeting the third condition is still a research in progress.(Yu et al., 2010)

Research has shown that a mixed Nano fluid of silicon and aluminum oxide gave the highest oil recovery as compared to other nanoparticles.

2.3.1 DISJOINING PRESSURE:

This is the ability of a fluid to spread along the surface. The disjoining pressure will be greater when the nanoparticles are less, and it will be lower when the nanoparticles are more. Nanoparticles have the ability to mobilize immobile oil through the reduction of the interfacial tension, which is the force separating two immiscible fluids. Nanoparticles like aluminum oxide have the ability to destabilize the water drops, thereby reducing the viscosity of the crude oil. (Alomair et al., 2015)

2.3.2 WETTABILITY ALTERATION:

Altering the wetting phase of a reservoir rock can be useful in changing the permeability of that particular reservoir and hence enhancing oil recovery. The different methods of enhancing oil recovery include:

Organosilanes treatment: the chemical formula for organosilane is $(CH_4)_nSiCl_x$. Organosilanes are hydrophobic (oil wetting agents) which can be used to alter rock wettability from oil to Water.

Naphthenic acid treatment: all carboxylic acids present in crude oil are called naphthenic acids. They cannot be dissolved in water, but can be dissolved in organic solvents. They are harmful to the environment and can only be used in laboratory measurements. They also change the wetting phase of a reservoir rock from oil to water

Thermal: Reservoir rocks are believed to be originally water wet, and changed to oil wet during migration of oil. The heavy oil penetrated the water films and got deposited on the rock surface. Hence, becoming the wetting phase. A reversal can be made for this process by heating the rock. When heat is applied, the absorbed agents are desorbed, and the rock returns to its original water wet state.

Use of Nano materials: This is the most recent of all the means of wettability alteration. In a study to detect the effect of Nano silica particles on wettability alteration and recovery factor, maghzi et al used glass model initially saturated with heavy oil. The flooding process was performed with distilled water and dispersed silica nanoparticles in water (DSNW) and the results of these flooding scenarios were compared. It is reported the wettability of the micro model was altered to partially water wet while flooding with distilled water and strongly water wet while flooding with (DSNW). The reason for this change can be traced to the hydrophilic nature of the silica nanoparticles and the hydrogen bond between silica nanoparticles and water which lead to a high surface free energy. The increase in ultimate recovery is said to have a direct relationship with the percentage of silica nanoparticles in water.)

Nano silica particles and Nano poly silicone are the most effective nanoparticles used for wettability alteration of reservoir rocks. The former makes the system more water wet, while the later can make it either water wet or oil wet, depending on the particular type used.(Sheshdeh, 2015)

CuO nanoparticles have the tendency to alter the rock wettability, reduce the viscosity of the oil and enhance oil recovery. The core sample to be used should preferably be an oil wet core where zero percent of the original oil in place can be recovered. When wettability alteration is studied using the relative permeability curve, we can see that nanoparticles cause a rightward shift in the critical saturation of water and oil, thereby causing wettability alteration, and improving oil recovery. When the nanoparticle concentration is low, the viscosity decreases. The reason being traced to the catalytic reaction of nanoparticles on breaking of bonds between carbon and sulfur.(Tajmiri & Ehsani, 2016)

2.4 NANO PARTICLES TRANSPORTATION IN RESERVOIR ROCKS:

Elna Rogriduez et al in October 2009 experimented on the Enhanced migration of surface treated nanoparticles on low permeability rocks. He used silica nanoparticles. When nanoparticles are treated on the surface, they can be navigated through even low permeability rocks. This is because of their small size and most especially their surface coating which prevents the coagulation of the particles and enables them stay dispersed in water. The surface coating also prevents the electrostatic interaction between the nanoparticles and the pore throats in both sandstone and limestone reservoir.

Two factors determine the effective transportation of nanoparticles in reservoir rocks.

- The retention of nanoparticles.
- The mobility of the dispersion of the nanoparticles.

The retention of nanoparticles determines the percentage of the injected particles that scale through to the targeted depth. While the mobility of their dispersion will determine the conditions like flow rate or particle injection pressure in which the nanoparticles will navigate the chosen path and the amount of time it takes to reach the destination.

Some factors that affect nanoparticles retention in pore throats include:

Vander Waals attraction: it is also a factor that is responsible for the nanoparticles at surface conditions not forming aggregates.

Electrostatic forces: they exist between the nanoparticles and between the nanoparticles and the surface of the reservoir rock. Electrostatic forces depend on ionic strength. When the ionic strength is high, the size of the electrical double layer of the particles becomes lowered. Hence the repulsive force between the particles reduces drastically. Recall that the repulsive forces prevent particle aggregation or the attachment of the particles to the surface of the reservoir rock. We can deduce that when the ionic strength is large, the repulsive strength is lowered. Hence, the particles tend to be deposited more, and get retained on the pore spaces. This doesn’t apply in unsaturated areas, because non Vander Waals forces are dominant there, and it thus affects particle retention.

Ph. value of the nanoparticle or the rock surface: when the ph. of the nanoparticles or rock surface is close to zero, the aggregation or attachment of the particle increases. Even the electrostatic forces will be reduced when the ph. is close to zero. We should always note the charges of the pore wall and nanoparticles at the surface.

Finally, the method applicable in the preparation of the nano suspension fluids can affect their retention and aggregation.

The concentration of the particle is a factor that affects the mobility of nanoparticles. Since the particles are solid, the migration may be a function of the shear- induced migration. I.e. at the boundary of the rocks, some slippages occur between the particles and the rock and it improves the rate of transportation of those particles. Due to reduction of friction, smaller nanoparticles are in the dispersed phase to enable them stay dispersed in the solvent without coagulating.(Rodriguez et al., 2009)

2.5 CLASSIFICATIONS IN NANOTECHNOLOGY

Nanoparticles contain two parts: the core, and the shell. The chemical component of the shell determines the solubility of those particles. E.g. lipophobic and hydrophilic nanoparticles that get dissolved in polar solvents e.g. water, hydrophobic and lipophilic nanoparticles that can dissolve in non-polar solvents. The electrostatic repulsive force between the nanoparticles is inversely proportional to the size of the particles but with an increase in electrostatic repulsive force.

(Hendraningrat, Li, & Torsæter, 2013) deduced that when LHP nanoparticles were injected into the core, it decreased the interfacial tension so much that more oil was produced. For the viscosity of oil, no significant change was observed.

2.5.1 SIZE OF THE PARTICLE:

They observed that the size of the nanoparticle is inversely proportional to the amount of oil recovered. When small sizes of nanoparticles were used, a larger volume of oil was recovered as opposed to a large size of nanoparticles being used with the same amount of residual oil present.

2.5.2 ROCK PERMEABILITY:

It was observed that the permeability of the rock did not affect the amount of oil recovered when the nanoparticles were injected. The particles still functioned properly in low permeability rocks. So, we can deduce that nano technology assisted enhanced oil recovery can work in a large range of rock permeability.

2.5.3 EFFECT ON INITIAL ROCK WETTABILTY:

It was also deduced that the initial wetting fluid in each core affected the amount of oil that was recovered from each core. The highest amount of oil recovery was discovered in intermediate wet core. Even though they had lower residual oil as compared to other cores when nanotechnology was applied, they had the highest oil recovery.

Effect of nano solution injection rate: it was also observed that the rate of injection of nanofluid did not increase or reduce the amount of oil recovered. We should note that nanoparticles have a tendency to coagulate. Hence, increasing the injection rate may improve this potential. In conclusion, the particles were observed to form cakes at the core inlets when higher injection rates were applied.

2.5.4 EFFECT OF TEMPERATURE:

It was observed that when temperature was increased, more oil was recovered. Therefore, we can conclude that nanotechnology EOR is a great technique to employ in high temperature zones like the reservoir area. (Hendraningrat, Li, Torsæter, et al., 2013)

2.6 NANOFLUIDS

Different suspension fluids can be used in the dissolution of the nanoparticles, e.g. Water for hydrophilic particles, and ethanol or oil for hydrophobic nanoparticles. When nanofluids are injected into a porous media, some phenomena occur, namely: desorption, adsorption, blocking, transportation and aggregation of the particles. Nanoparticles are Brownian particles, hence, five different forces dominate the interaction between nanoparticles and the pore walls, namely: Van der Waals attractive potential force, electric double layer repulsion force, born repulsion, interaction between acid and base and hydrodynamics. When the forces are summed, if the net force is negative, we can deduce that the force of attraction exceeds the repulsive force between the nanoparticles and the pore walls. Hence, the particles get adsorbed on the walls. When particle diameter is bigger than the pore throat, blocking will occur. The nanoparticles will form aggregates if the system of dispersion departs from equilibrium. They begin to cluster up, hence blocking some pore channels.

The alteration of rock wettability by nanoparticle is observed to be because the interface between the nanofluid and the rock is replaced by hydrophilic nanoparticles adsorption layers and liquids. Nano structured particles (NSP) were also found out to have better adsorption properties than colloidal nano particles (CNP). High concentration of Nano structured particles can block the core, leading to reduction in permeability. While high concentration of colloidal nano particles nano fluids can make the core more permeable. (Li et al., 2015)

2.6.1 NANO FLUID CONCENTRATION:

The rate of nanoparticle adsorption and straining is directly proportional to the concentration of injected nanoparticles. Adsorption rate is higher than the rate of the straining of the nanoparticle. When there is high concentration of injected nanoparticle fluid, it increases the formation damage which affects the pressure drop. When the amount of nano structured particles injected is high, there will be a larger pressure drop.

We can detach the formerly adsorbed nanoparticles by flushing the core with brine after injection. The higher the concentration of the nanoparticle fluid, the higher the amount of nanoparticles that can be desorbed during the post brine flushing. (Wang et al., 2016)

At lower nanoparticle fluid concentration, the rock wettability could tend towards water wet, thereby improving the amount of oil recovered. While at high nanoparticle fluid concentration, the nanoparticles tend to block pore throats.(Alhuraishawy et al., 2019)

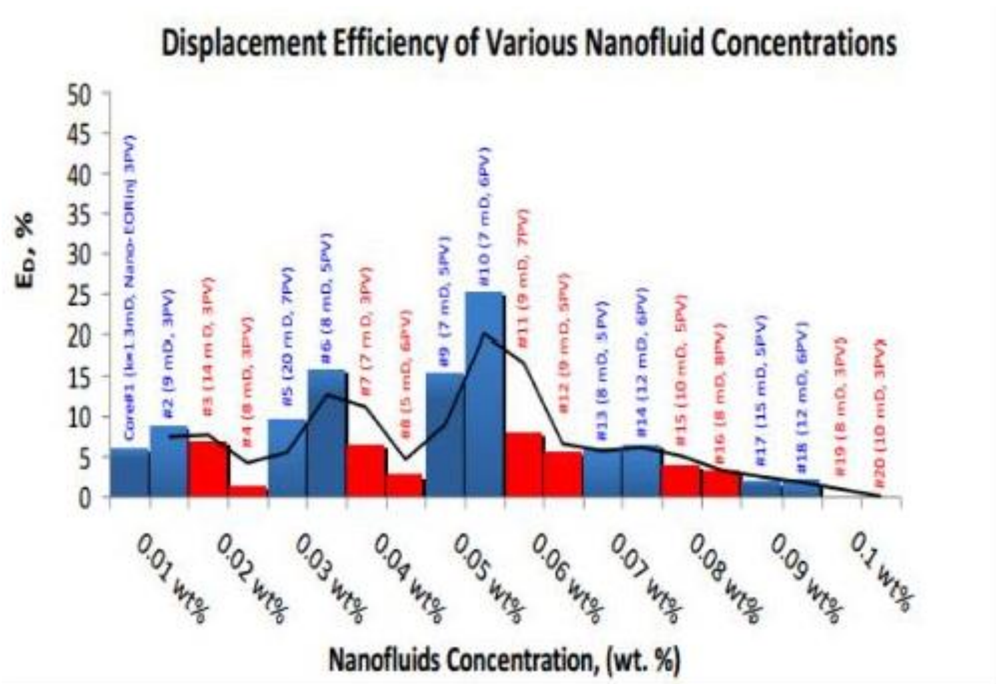


Figure 4 Displacement Efficiency Of Various Nanofluid Concentrations.

2.6.2 NANOFLUID EMULSION:

Droplets from stable emulsion are known to block the pathways in high permeability rocks, and improve flux in the pathways for low permeability rocks. Oil saturation in rocks with high permeability is higher than in low permeability rocks. The apparent viscosity of the emulsion will be high in high permeability rocks than low permeability rocks. Hence, we can deduce that the blockage effect of emulsion does not improve the flood stability or sweep efficiency. Nanoparticles with surfactants have a close mode of packing. Hence, they can enhance the effect of blockage caused by emulsion, and thus lead to a better flood stability and sweep efficiency.(Xu et al., 2016)

Apart from nanotechnology enhanced oil recovery, other methods consider three different forces, namely: capillary, gravity and viscous forces. But nanoparticles enhanced oil recovery considers disjoining forces and other nanoscale forces. Low permeability reservoirs have a large volume of oil, but they can't be produced easily, because of low productivity, poor sweep efficiency, and water flood injectivity. Nanoparticles alter these rock properties to free rapped oil. Nanoparticles reduce interfacial tension. That's one way by which they improve oil recovery.(Hendraningrat, Li, & Torsæter, 2013)

Trapping of hydrocarbons can be attributed to the capillary forces, and they are highly influenced by the rock wettability and interfacial tension. The smaller the particles used for the enhanced oil recovery process, the less the effect of gravity on them, and the more effect surface tension and van der Waals forces have on them. When nanoparticles are evenly dispersed, oil recovery increases, increases concentration of nanofluid improve oil recovery, but the particles get deposited on pore throats.

2.6.3 NANOFLUID PROPETIES:

When the injection rate was increased above 2cm3/min, no increase in oil recovery was observed, therefore, the maximum rate of injecting the nanofluids is cm3/min. the concentration rate of 0.01 – 2.0%wt/wt of silica nanofluids has been observed to be the best for sandstone reservoirs in the Niger delta.

A concentration of 2%wt/wt of silica nanofluids at maximum is best to disallow the formation of nanoskin, which in turn damages the formation by reduction in permeability. Nanoskin can be defined as a layer that reduces rock permeability, formed at the pore surface of a rock by the deposition of nanoparticles on the pore throats.

Different factors that can form a nanoskin include: the concentration of the nanofluid, the flow rate, flow pressure, grain size, temperature, salinity, clay content. Etc.(Omotosho et al., 2019)

CHAPTER 3

3 METHODOLOGY

3.1 LABORATORY EXPERIMENT:

The experiment was carried out in Laser Engineering Laboratory, Rumudara Portharcourt.

3.2 EQUIPMENTS USED

THE EQUIPMENTS USED INCLUDE:

- Weighing balance: this is the equipment used to measure the weights of the sand packs.

Figure 5 Weighing Balance

- Viscometer: this is an equipment used to measure the viscosities of different fluid samples.

Figure 6 Viscometer

- Auto Flooding System (AFS 300): This is the equipment used to flood the core with different fluid samples. Both the imbibition process and nanofluid injection process were carried out in this equipment.

Figure 7 AFS 300 Core Flooding Machine

- Oven.
- Saturator.
- Density meter: this is used to measure the densities, API and specific gravity of different liquid equipment used in the course of the project. E.g. Crude oil, brine, and nanofluid.

Figure 8 DENSITY METER

- Measuring cylinder: this is used to get the volume of different fluid samples used during the experiment.

Figure 9 Measuring Cylinder

3.3 THE MATERIALS USED INCLUDE:

- Plastering sand: this is the particular sand used to form the sand packs as a replica of reservoir core samples.

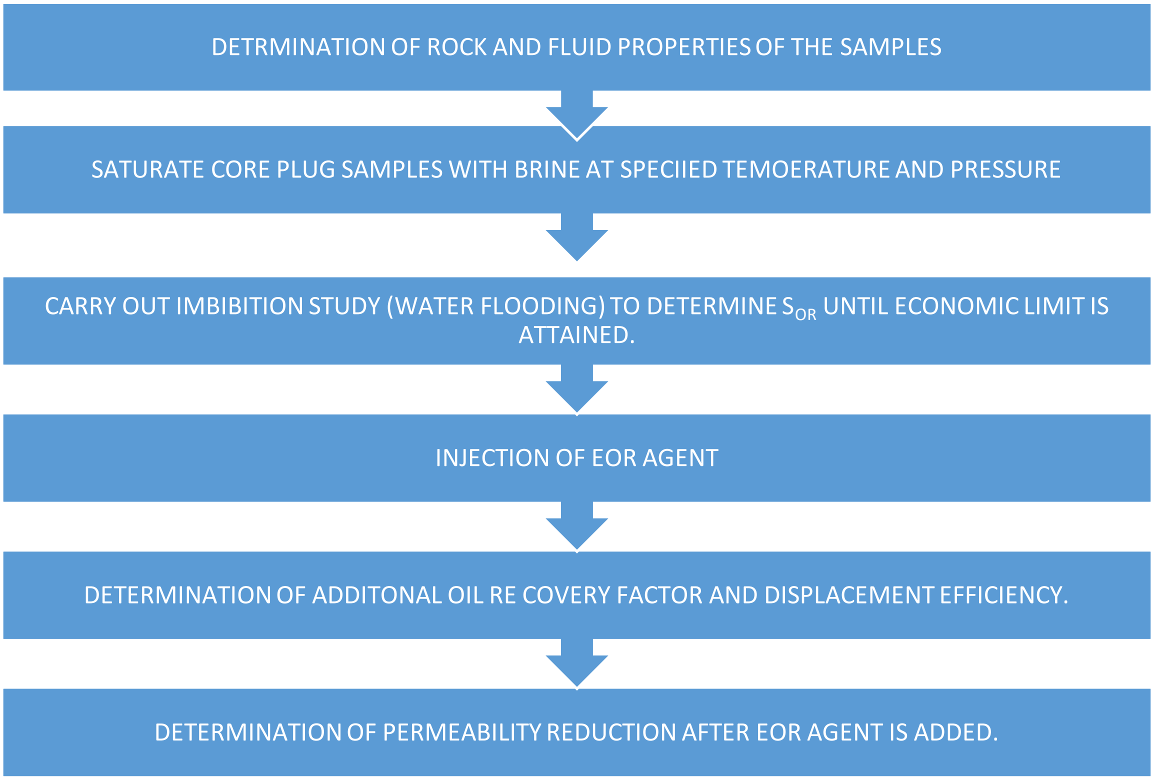
Figure 10 Plastering Sand

- Nano particles (TiO_2, ZnO, Al_2O_3).
- Industrial salt (NaCl).
- Aluminum foil: They were used in shaping the sand packs. It formed the mold into which the sand was poured.

Figure 11 Aluminium foil

- Sieve.
- water

3.4 EXPERIMENTAL WORK FLOW



3.5 PROCEDURE:

To make the sand packs, aluminum foils were soaked in water for about 10 hours and allowed to dry. The wooden part is pulled out and the congealed aluminum foil is cut into lengths of 7cm.

We should note that the sand packs were made as a replica of the cores from the reservoir. 63-250 micro meter grain sizes were chosen because those were the sand sizes found at the reservoir pay-zone.

3.6 PREPARATION OF SAND PACKS:

- Cutting and washing of cloth sieve.
- Wash the sand and sun drying it.
- Oven dry the sand at 60of or fry to ensure it is very dry.
- Sieve the sand with sieves of different mesh sizes (63- 250micro meters) grain sizes.
- Mix the different sand ranges.
- Fix the sieve and masking tape at one end of the the 7cm long foils.
- Fill in sand from the other end of the foil and shake to make it compacted.
- Cover the other end with a sieve and paper tape.
- Weigh the cores (dry weight).

Figure 12 Washing of Sand

- Mix the brine solution. (3% or 30g of NaCl for 1 liter of water)
- Drop the consolidated sand packs into the brine solution and soak for 48hours to get the wet weight.

Pore volume = (Wet weight – Dry weight) / density of brine

Alternatively, instead of waiting for 48 hours to saturate the core, we used a saturator to saturate the core with brine under pressure.

(39% is the porosity of clean sand)

- Using a core flooder, inject oil into the brine saturated core.
- Measure the volume of brine displaced by the oil, and that becomes the original oil in place.
- The residual brine in the sand packs becomes the connate water saturation.

Aluminum foil --- 0.56g
Industrial salt --- 30g/1000ml of water.
TiO_2 --- 12g/ 400ml of water
ZnO --- 12g / 400ml of water.
Bulk volume = volume of core.

A total of 7 sand packs were made with dimensions as follows:

Table 1 Sand Pack Properties

Synthetic plug I.D	Dry weight (g)	Length(inches)	Diameter (inches)	Length (cm)	Diameter (cm)
Group 3-C	125.8	2.685	1.373	6.82	3.487
Group 3-D	126.7	2.692	1.437	6.838	3.65
Group 3-E	130.4	2.735	1.481	6.947	3.762
Group 3-F	129	2.789	1.395	7.084	3.543
Group 3-G	125	2.703	1.439	6.866	3.655
Group 3-H	124.7	2.717	1.46	6.901	3.708
Group 3-I	129.2	2.801	1.5	7.115	3.81

A weighing balance was used to measure the dry weight, and a vernier caliper was used to measure the diameter and length of the sand packs.

3.7 Preparation of the nanofluid:

Here we measure 30g of each of the nano particles and add into 1000ml of water. We stir thoroughly and allow it to mix for 3 days to get a homogenous mixture. The particles are not fully water soluble, so after the stipulated time, we collect the solution formed, and use them as our nano fluid for each of the particle.

Figure 13 Nanofluids

- Get the properties of the crude oil sample given to us. We used a density meter to get the density, API, and specific gravity of the crude oil sample given to us. We also use a viscometer tube to measure the crude oil viscosity at different temperatures. We do the measurements at ambient temperature of 15^{o}c, and at elevated temperature of 50^{o}C Crude oil.

Brine and EOR reagents properties at ambient temperature:

Table 2 Brine and EOR reagents properties at ambient temperature:

Properties	Brine 3% NaCl	Crude oil	EOR reagents:		
			3% ensiAl_2O_3suspon	3% TiO_2 suspension	3% ZnO suspension
Specific gravity	1.0198	0.8838	1.0005	1.0004	1.0004
Density (g/cm^3)	1.0162	0.8786	0.9966	0.9965	0.9967

Viscosity (cP)	0.90	12.1539	0.83	0.87	0.88
API @ 15^{o}C		28.15			

CRUDE OIL, BRINE AND EOR REAGENT PROPERTIES AT AN ELEVATED TEMPERATURE OF 50^{O}C

Table 3 Crude Oil and Brine Properties At Elevated Temperature Of 50oc

Properties	Brine 3% NaCl	Crude oil	EOR Reagents		
			3% Al_2O_3 suspension	3% TiO_2 suspension	3% ZnO suspension
Specific gravity	1.0175	0.882	1.0005	1.0004	1.0006
Density (g/cm^3)	1.0061	0.8613	0.9918	0.9917	0.9898
Viscosity (cP)	0.68	5.9108	0.47	0.54	0.59
Api @15^{o}c		28.17			

We also vary the concentrations at different temperature and measure the different densities at each of the temperatures.

Table 4 Nanofluid Densities at Different Concentration

NANOPARTICLES	CONCENTRATION	DENSITY @28^{O}C	DENSITY @60^{O}C
Al_2O_3	0.01wt%	1.0162	1.0110
	0.5wt%	1.0162	1.0110

	3.0wt%	1.0163	1.0113
TiO_2	0.01wt%	1.0165	1.0100
	0.5wt%	1.0165	1.0100
	3.0wt%	1.0165	1.0100
ZnO	0.01wt%	1.0165	1.0115
	0.5wt%	1.0165	1.0115
	3.0wt%	1.0165	1.0115

- Place the cores into a core flooder and inject the different EOR reagents.
- Measure the additional oil recovered from the cores.
- Measure the permeability of the cores after the EOR reagent is injected into the core.

3.8 REVIEW:

The two different pressures acting on the reservoir rock are the over burden pressure and the pore pressure.

We use the pump section of the core flooding equipment to stimulate the two pressures on the core samples to replicate what's happening in the reservoir. We use Nitrogen to stimulate the pore pressure. We select an overburden pressure of 5000 psi, and temperature of 50^{o}c. the back pressure regulator is responsible for the pore pressure in the core sample.

We also have no ageing constant, so, we pack the sand to make them very consolidated and thus replicate the reservoir. The core flooding equipment used was ASM 300. It can go a max of 150^{o}c, and 15,000psi overburden. Ageing a core is the process of returning a core to its original wetting phase. Capillary pressure accounts for the flow or production of fluid from a reservoir rock sample.

Since we made the sand packs ourselves, we do not account for depth.

CHAPTER 4

4 RESULTS AND DISCUSSIONS

Table 5 Experimental Results

Properties	Sample ID: Group 3-E (Al_2O_3)	Sample ID: Group 3-F (TiO_2)	Sample ID: Group 3-I (ZnO)
Length (cm)	6.947	7.064	7.115
Diameter (cm)	3.760	3.543	3.682
Pore volume (cm^3)	24.41	24.22	23.82
Bulk volume (cm^3)	104.25	98.46	103.52
Porosity (%)	23.5	24.6	23
Absolute permeability @5,000psi (mD)	182.22	164.49	99.57
Effective permeability after EOR flooding (mD)	102.66	83.09	137.63

From the above table, we can deduce that the injected nanoparticles got deposited in the pore spaces of the reservoir rock, thereby drastically reducing the permeability of the reservoir rock.

We noticed a wide gap between the rock permeability before the nanoparticle injection and after the nano fluid injection with the former being larger than the later. This observation is caused by the nanoparticles getting deposited in the pore spaces and thereby blocking the pore throats. This is one huge disadvantage of using nanoparticles for Enhanced oil recovery.

To curb this problem, we should use an optimum injection rate of $2cm^3$/min. and ensure that the nanofluid concentration does not go beyond 3%/wt.

We also recorded the additional oil recovery that was discovered after the imbibition process and after each of the EOR reagents were injected into the sand packs.

Table 6 Additional Oil Recovered

Parameter	EOR agent:		
	3% Al_2O_3	3% TiO_2	3% ZnO
Pore volume (cm^3)	24.41	24.22	23.82
Volume of crude in plugs (OOIP) at S_{WI} (cm^3)	16.5	14.5	17
Volume of water remaining in the plug samples at maximum oil saturation (cm^3)	7.91	9.72	6.82
Initial water saturation (S_{WI}) as a fraction	0.3240	0.4013	0.2863
Initial water saturation (S_{WI}) %	32.40	40.13	28.63
Initial oil saturation (%)	67.60	59.87	71.37
Volume of crude received (cm^3) after imbibition (water flooding)	12	9	9.4
Volume of residual crude left over in the sample (cm^3)	4.5	5.5	7.6
Residual oil saturation (S_{OR}) as a fraction	0.2727	0.3793	0.4471
Residual oil saturation (S_{OR}) %	27.27	37.93	44.71

Volume of crude recovered (cm^3) after tertiary recovery	1.0	0.8	1.8
Additional recovery with EOR agents (%OOIP)	6.06	5.52	10.59

From the above table, we can prove that nano particle as an Enhanced oil recovery process is a very effective one. The nanofluid injection recovered about 6times the amount of oil that was recovered after the secondary oil recovery process. The small size and chemical composition of these particles help them free trapped oil which is bypassed during the secondary recovery process.

We can also see that ZnO was the most effective nano fluid as it produced the highest quantity of recovered oil among the three nano particles.

4.1 DISCUSSION:

BULK VOLUME: This is the total volume of the core sample that is used. In this care, since the cores are cylindrical in shape, we get our bulk volume with the formula: Bulk volume= $\pi r^2 h$

PORE VOLUME: This is the volume of the pore spaces in the reservoir rock. It is calculated by: Pore volume= (Wet weight- dry weight)/ density of the brine.

POROSITY: This is the measure of the amount of pore spaces present in a particular rock sample as a ratio of the reservoir bulk volume. It is calculated with the formula. Porosity= Pore volume/ Bulk volume

PERMEABILITY: This is the volume of the interconnected pore spaces in a reservoir rocks. It is calculated by the formula: Permeability= $Q\mu L/A\Delta P$.
(Where Q= flow rate, μ= viscosity, L=length, A= area of core, ΔP= change in pressure).

VISCOSITY: This is the resistance of a fluid to flow. We have two different types of viscosity.

DYNAMIC VISCOSITY: This was measured using a u-tube viscometer.

KINEMATIC VISCOSITY: This is the ration of dynamic viscosity to the density of the fluid. It was calculated using the formula. Kinematic Viscosity= Efflux time × Viscometer constant.

4.2 COMPARING DIFFERENT NANOFLUID CONCENTRATIONS

As stated earlier, concentration of nanofluids affect the oil recovery factor in the reservoir rock.

The table below shows the recovery factor at different nanofluid concentrations.

Table 7 Oil Recovery With Varying Nanofluid Concentrations.

Water type/ nanofluid type	Concentration %	Core number	Drainage process		Water flood/ Nanofluid process			Oil Recovery	
			Swi	Soi	PVI	Swr	Sor	Oil recovery%	Incremental oil recovery%
Water Flooding		3A	0.2011	0.7989	2.825	0.5616	0.4384	45.12	
Al_2O_3	0.01	3B	0.3956	0.6044	3.410	0.7360	0.2942	51.32	6.2
	0.5	3C	0.2205	0.7795	3.350	0.6641	0.3359	56.9	11.78
	3.0	3D	0.3723	0.6277	3.520	0.7692	0.2308	63.2	18.08
TiO_2	0.01	3E	0.1050	0.8950	2.930	0.5555	0.4445	50.34	5.22
	0.5	3F	0.1412	0.8588	3.061	0.5588	0.4412	48.63	3.51
	3.0	3G	0.1305	0.8695	3.282	0.5340	0.4660	46.41	1.29
ZnO	0.01	3H	0.232	0.7680	3.211	0.5890	0.4110	46.48	1.36
	0.5	3I	0.4022	0.5978	3.048	0.6849	0.3151	47.29	2.17
	3.0	3J	0.1379	0.8621	3.501	0.5719	0.4712	45.34	0.22

We make a plot of the different nanofluid densities at different concentrations:

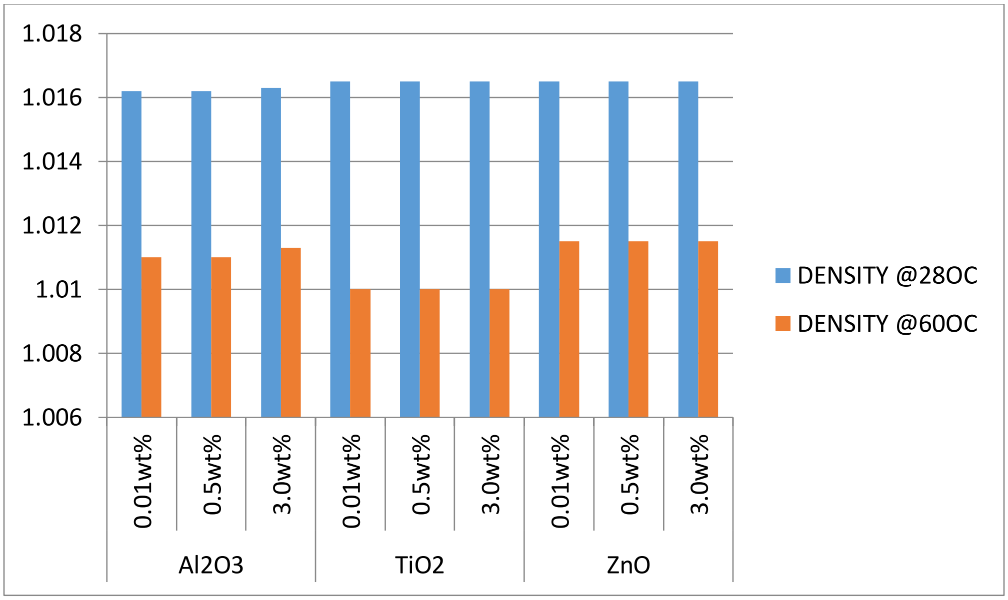


Figure 14 Nanofluid Densities at Different Concentrations

We also plot a graph or the different volumes of oil recovered at different nanofluid concentrations.

For Al2O3 at concentrations of 0.01, 0.5 and 3.0 we have:

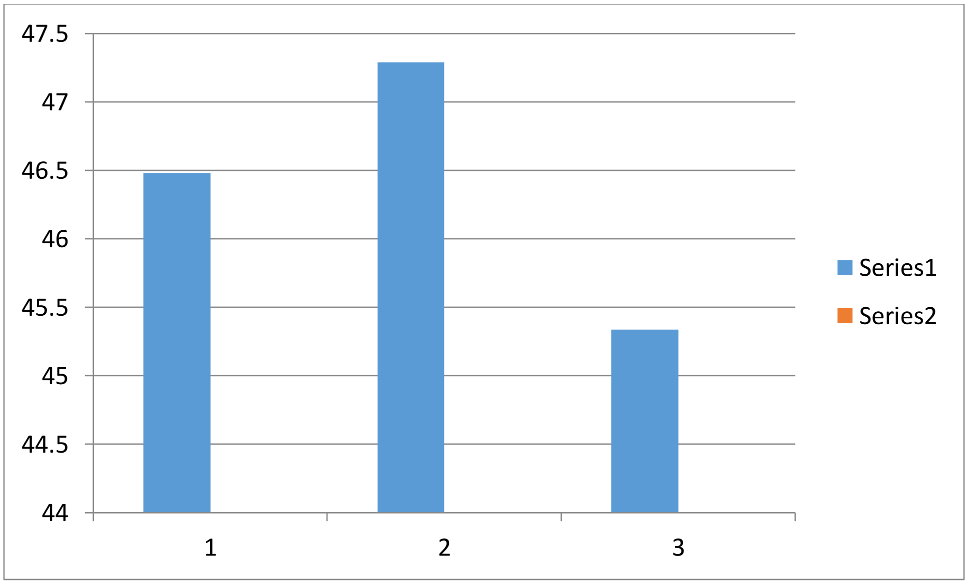


Figure 15 Al2O3,at concentrations of 0.01, 0.5 and 3.0

For TiO2, at concentrations of 0.01, 0.5 and 3.0 we have:

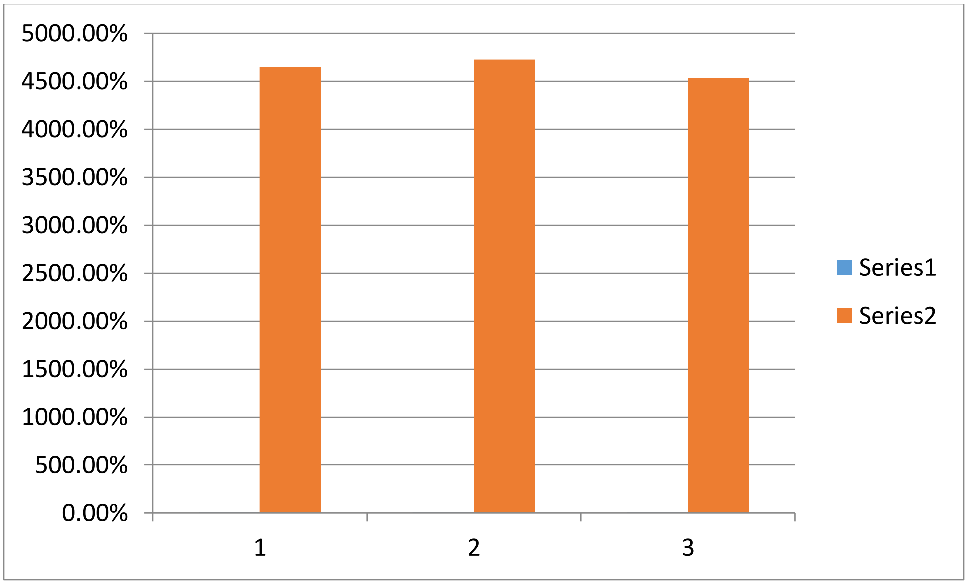
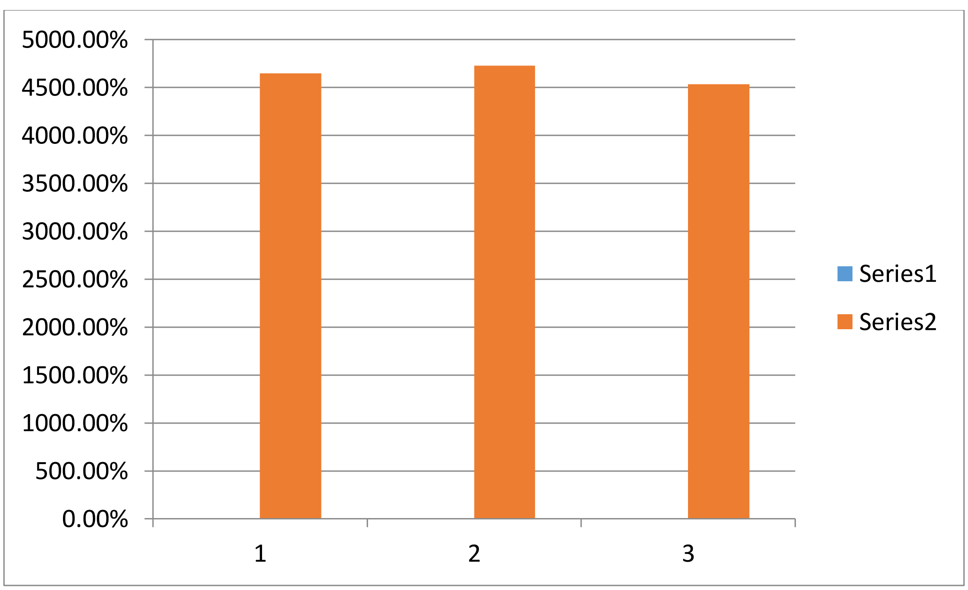


Figure 16 TiO2, at concentrations of 0.01, 0.5 and 3.0

Figure 4.17

For ZnO, at concentrations of 0.01, 0.5 and 3.0, we have:



4.3 OBSERVATIONS:

The following were observed during the course of the experiment:

- Formation of cloudy solutions during the EOR test using ZnO which indicates the occurrence of emulsification.
- The micro-powders are insoluble in water and brine.
- Wide variation in S_{WI} values despite the fact that the samples are water-wet. This could be due to sand distribution during sand packing which altered the absolute permeability of the sand packs.

CHAPTER 5

5 CONCLUSIONS:

- Zinc Oxide was more effective for the medium crude sample than Titanium and Aluminum Oxide.
- Temperature has an effect on absolute permeability due to rock fluid interactions and changes in rock matrix, though further work will need to be done on this regards.
- The emulsification process during ZnO flooding test could be the mechanism responsible for its effectiveness with medium type crude.
- The permeability reduction of 33.3% was observed between temperature 80.6^{o}f and 122^{o}f.

5.1 PROBLEMS ENCOUNTERED:

- The sand packs do not adequately give a replica of the reservoir rocks because:
- They have not undergone the ageing process
- They do not contain the properties of a carbonate reservoir,
- Since they are first saturated with brine, they do not show what happens in an oil wet reservoir rock.

5.2 RECOMMENDATION:

- The stability of the micro-powder dispersion is a major challenge. This should be addressed by identifying stabilizers like surfactants, polymers or alcohols.
- The nano fluid concentration should also be considered to avoid a great deal of permeability reduction. The nano particles should not exceed 3% wt per ml of water.
- The nano fluid injection rate should also be considered, and shouldn't be below an injection rate of 2cm^3/min to avoid particle deposition and blocking of the pore throats.
- Reservoir core plugs from the pay-zones may also be used to give an exact replica of the nano fluid dispersion in the reservoir rock pay-zone.

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