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Enhanced Oil Recovery of Medium Crude Oil (31^0 Api) Using Nanoparticles and Polymer

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Abstract

The aim of enhanced oil recovery (EOR) is to influence the fluid-fluid properties and fluid-rock properties between the injected fluid and the residual oil phase to improve recovery efficiency. New methods of improving recoveries have been investigated since they provide lower risks, costs and uncertainty as compared to exploring for new reserves. Water enhanced with nanoparticles (nano-fluid) has recently gained research interest for enhanced oil recovery because of the possible physical and chemical properties imparted by the nanoparticles. The purpose of this research was to investigate and improve oil recovery after water flooding by nanofluid flooding. Nanoparticle used was silica nanoparticles (SiO_2) suspended in deionized water at 0.05wt% concentrations. The results from the core samples show an additional oil recovery of 4.29%, 2.022% and 1.86% respectively from three (3) cores (core 2, core 5 and core 6) at nano flooding rate of 0.5cc/min. Core 7 gave a recovery of 33% during water flooding and 38.2% during nano-fluid flooding thus giving an incremental recovery of 5.2%. These results have validated the effectiveness of chemical flooding especially nanoparticles to successfully recover crude oil from reservoirs after water flooding usefulness has declined.

INTRODUCTION

There is an increasing demand for energy, even after hydrocarbon reserves all around the world has been depleted using primary or natural recovery schemes. Primary recovery which is the initial stage involves the use of the reservoir natural energy to drive or produce the oil from the reservoir. Secondary recovery is activated when the natural energy has been depleted and the supposed oil recovery has significantly dropped. When this happens, it is necessary to augment the natural energy with an external source. The traditional secondary recovery methods include the basic water flooding, immiscible gas injection and pressure maintenance. The application of tertiary recovery processes was developed in case secondary processes become ineffective.

Improved methods of water flooding such as surfactant, alkaline, polymer or a combination of the alkaline, surfactant and polymer flooding (ASP) has been developed to effectively sweep and recovery more residual oil. The ASP flooding works through by altering the wettability of the rock formation and also reduction in interfacial tension. Polymer flooding can be classified under chemical flooding and sub-classified under water flooding. Polymers applied to water flooding increases the viscosity of the fluid injected and reduces its mobility ratio.

Since the polymer process is a well proven technology by earlier onshore applications, especially in China, it has high potential for medium oil (22.3–31.1°API) and even for heavier oil recovery. Polymer flood has proved to be successful in many enhanced oil recovery projects globally with increased recoveries of 12-15% (Wang and Dong, 2009; Sheng, 2011; Wang *et al*., 2002). From data gathered in a Chinese oil-field, polymer flooding was found to be less costly than waterflooding due to the additional oil recovered and low costs of water injection treatments. In oil field applications, Xanthan gums and Hydrolyzed Polyacrylamides are mostly used. The Hydrolyzed Polyacrylamides is soluble in water. Xanthan gums show outstanding ability to increase the viscosity of the fluid (Guo *et al*., 1999). Polymers currently in use such as above fail to meet up to expectations. Energy consumption and demand has been projected to increase in the coming years and oil industries are faced with issues with respect to environmental processes that are safe. Finding new oil prospects are getting more difficult, thus processes to improve production and oil recovery from existing fields are been daily investigated and exploited. It is therefore paramount to use improved oil recovery mechanisms to recover large amount of residual oil.

According to U.S. Energy Information Administration; (2013), the demand and use of energy would increase by 50% when compared to the current status before the year 2030. - Therefore, there is an increased need for petroleum as a major source of energy. Conventional recovery methods usually produce about 15–30% of initial oil in place. Large quantities of oil in reservoirs are unswept, and can be produced using enhanced-oil-recovery (EOR) processes.

Nanoparticles, are usually between 1 and 100 nanometers. Nanotechnology, defines a particles as a minute object that acts or performs as a complete unit with respect to its properties and transport. They have been studied for use in various applications, namely; polymer composites (Matteo *et al*., 2012), drug delivery (Kumar *et al*., 2013), solar cells

(Qian, 2016), lipase immobilization, metal ion removal, imaging, and EOR (Lu *et al*. 2007) and hydrocarbon detection and estimation. They are surface active and are used to alter surface properties. Nanoparticles have been shown to stabilize foams and emulsions or change the wettability of rock, but their successful implementation requires considerations that are beyond interfacial properties. They can be employed for use in the quest to maximize recovery, improve the nature of water, breakdown emulsion, alter hydrophilic and hydrophobic characteristics of waterflood processes and also help maintain reservoir pressure above bubble point (Fletcher and David, 2010).

Nanoparticles have been used and verified in various scientific researches and its usefulness has been highlighted in medicine, agriculture and some other aspect of petroleum engineering such as drilling engineering. In its various forms, it has been used extensively in enhanced oil recovery processes especially with heavy oil crude reservoirs. They have been combined with surfactants and polymer to improve recovery of low API crude oils. Due to their ultra-small sizes, nanoparticles have been able to combat some important challenges facing chemical processes such as plugging and injectant trapping in the porous media which normally results in increasing injection cost and reduction in formation permeability (Ahmadi *et al*., 2011).

Frequently used nanoparticles such as the oxides of Silicon, Titanium and Aluminum which are in the rank of 1nm-100nm are smaller compared to the pore and throat sizes of the media (Alomair *et al*., 2014). This makes them flow easily without severe permeability reduction and trapping which increases the effectiveness of EOR injected fluids. Also, owing to its very small sizes, they can penetrate pore spaces where previously used or usual injection fluids cannot access leading to increase in macroscopic sweep efficiencies.

Nanoparticles have high surface to volume ratio. Nanoparticle usage in EOR of heavy oil reservoirs helps to overcome the challenges such as heat loss to the formation, gravity overriding of steam, heat loss to aquifer or bottom water, corrosion and scale development to well bore, formation of black coke that reduces permeability just to mention a few that thermal recovery.

The effect of nanotechnologies in the oil industry is significantly increasing because of its ability to improve some of the factors that have a positive influence on oil recovery (Babadagli, 2017). Nanoparticles can be used in oil industry to deal with problems that result from conventional recovery mechanisms such as adsorption and chemical thermal degradation etc (Choi and Eastman, 1999).

Nanoparticles on field scale level are always injected into the formation with a desired solution, considering the nature of the reservoir and fluid properties. For proper displacement of heavy oil using nanoparticles it is advisable to use a solution with low mobility and high viscosity. Polymer increases the viscosity of water to decrease the mobility ratio. The study of nanoparticles and its application to EOR have been extensive, however, nanoparticles with polymer chains joined to its surface - popularly known as polymer-coated nanoparticles — are an evolving type of materials that can be better to nanoparticles for enhanced oil recovery due to increased stability and ability to dissolve in a medium, ability to stabilize foams and emulsions. Nano-fluids can help solve these challenges because their addition helps to increase the viscosities of the injected fluids. Shah; (2009) discovered that a CO_2 nano fluid (1% CuO NPs in gas phase CO_2) was 140 times greater than that of CO_2. Also, Molnes *et al*., (2016) discovered that the shear viscosity of aqueous medium was increased when cellulose nano-crystals were dispersed in de-ionized water.

There are two (2) key mechanisms at play that make the use of nanoparticles effective for increased oil recovery. The first is through mobility control by using polymer and surfactant-coated nanoparticles and wettability operations. The mechanism of oil recovery by nanoparticles was investigated by (Wasan, 2003) referred to as the "*structural disjoining pressure*". It was claimed that the pressure increases with reducing nanoparticle sizes. The pressure creates a wedge/film scenario and will separate the fluid from the formation.

Currently, there are three (3) main experimental methods that are commonly used by researchers for wettability measurement: the contact angle method, the Amott test and the core displacement test (Giraldo *et al*., 2103; Anderson, 1987; Amott, 1959; Anderson, 1986). Of the above mentioned, only the contact angle method is the universally used approach for wettability determination.

Laboratory works are the first step towards analyzing the performances of nanoparticles in recovery before a full scale application is made. The analysis made in this study was to verify and ascertain the effect of polymer and nanofluid flooding on oil recovery. Also, laboratory core flooding experiments will be performed with and without nanoparticles to verify the percentage recovery and their applicability on field scale to improve recovery from heavy oil reservoir. Nanoparticle prices are normally cheaper than chemicals thus reducing injection costs thus making them to be widely applied for EORs at oilfields. On field applications, the process is relatively cheap, does not pollute the environment, has higher oil recovery, does not corrode well equipment and it is easier to handle as compared to EOR methods that are alternative means for heavy oil recoveries.

The need to recover more residual and also reduce damages and operational costs has led to the evolution of chemical enhanced oil recoveries because conventional secondary recoveries (mainly water and gas injection), gave recoveries that are low. The aim of this work is to improve recovery from medium oil reservoirs (after water flooding) by injecting nano-fluids (silica oxide) in core samples to investigate incremental recoveries per time. The objectives are thus to perform a laboratory core flooding on core samples to investigate the recovery efficiencies of water flooding, polymer flooding and nano-fluid injection for a medium oil crude using core samples.

METHODOLOGY

Materials

The materials used in this project includes: four (4) core plugs (3 cores for nano-fluid flooding and 1 core for polymer flooding), 10 liters of crude oil sample with API ^{0}31, polymer (Gum Arabic/Poly acrid), nanoparticles (silicon oxide), produced water (Brine) which was used as the based fluid, and acetone.

Equipments

Reservoir Permeability Tester: The reservoir permeability tester is equipment originally meant for testing core samples to measure their permeability. A further extension of its function is its use as a core flooding equipment. Core samples can be water flooded or gas injected depending on the nature of the work. Parameters such as water and oil saturations, residual oil and water saturations, oil recoveries and permeability changes may be measured and calculated while using the RPT. For this work oil recoveries after (water, polymer and nano-fluid flooding was measured), permeability impairment, porosity, water and oil saturations and residual oil saturations were measured. Figure 1 below shows the diagram of RPT and its features.

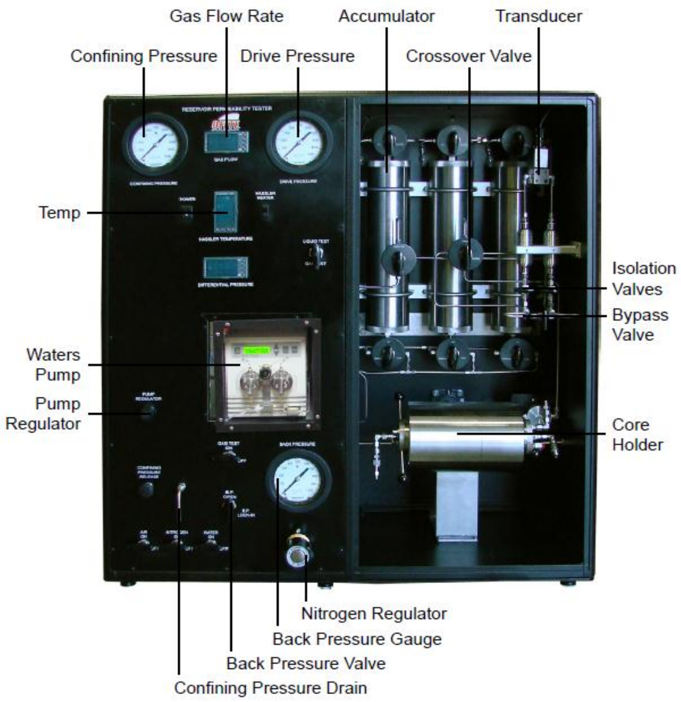

Figure 1: Reservoir Permeability Tester (Ofite - Reservoir Permeability Tester, 2015)

Soxhlet Extractor: The Soxhlet Extractor extracts lipids from a solid material but is used extensively in core analysis to remove water and oil from core samples. This is necessary to restore the core sample back to its original state or to prepare a core for a certain injection purpose so as to estimate certain reservoir or core parameters as shown in figure 2 below.

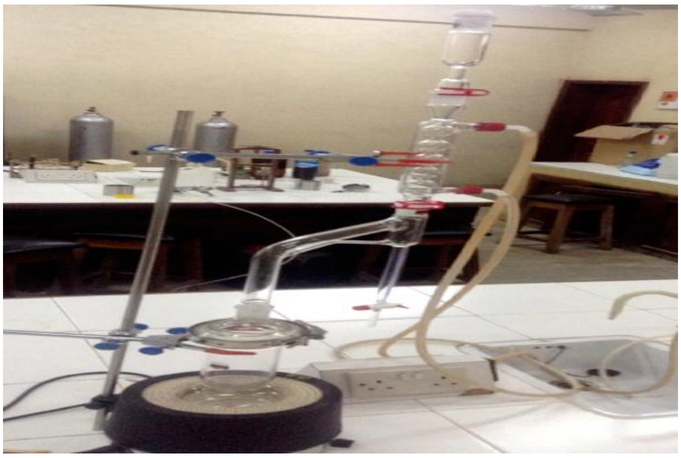

Figure 2: Soxhlet Extractor

Manual Saturator: This is used to obtain saturation of cleaned and dry core samples by a simple process. It consists of a saturation pressure cell, hand operator pressure pump, liquid tank and moisture trap and a vacuum pump as seen in figure 3 below. The saturation pump is used to inject additional saturated liquid into the cell.

Figure 3: Manual Saturator

Glass Capillary Viscometer: This equipment was used in measuring the viscosity of the crude oil used in this experiment. Figure 4 below shows the diagram of Glass Capillary Viscometer.

Figure 4: Glass Capillary Viscometer

Desiccator: The Vacuum Desiccator's sole purpose is to simultaneously dry multiple core samples in a vacuum. This is shown in figure 5 below.

Figure 5: Dessicator

Procedure:

Core cleaning: Acetone is slowly boiled in a Pyrex flask, and its vapors move upwards as the core is swamped in the acetone vapors (at 110°C). The acetone and water vapor enters the inside compartment of the condenser and the water flowing in the inner compartment condenses both vapors to immiscible liquids. Afterwards the core samples were dried and placed in a Desiccator.The crude oil sample viscosity was measure using the viscometer. Core samples used in research work are shown in figure 6 below.

Figure 6: Core samples used

Preparation of Brine: The concentration of brine to be used was about 3.0wt%- (30000ppm or 0.03g/ml). 30g of salt was measured using the weighing balance and 750ml of water was poured into the measuring cylinder.

Porosity: The cores were cleaned and measurements were taking on the length, diameter, and the weight for each core before inserting into the manual saturator. The cores were set into the core holder and the brine sample was filled into the saturation tank about lesser than half the height to avoid damaging the pump. The saturated cores were weighed using the weighing balance for pore volume determination (v_p) and porosity ($\emptyset$).

Permeability: In obtaining permeability of the core plugs the relative permeability tester was used where the fluid was pumped, passing through the cores. This procedure was done for few hours and measurements (permeability) were recorded.

Density: The Pycnometer was used to measure both the oil and the water density.

Viscosity: In order to measure the viscosity of the fluids a glass capillary viscometer was used.

Preparation of Nanoparticles and Polymer (Gum Arabic): The nano-fluid was prepared by diluting the highly concentrated nano suspensions with a dispersion agent, (deionized water). The nanoparticle in use was SiO_2 (20-70nm, purity - 98-99.5% and specific area 140m^2/gr.). 50mg of SiO_2 was spread in 1 liter of deionized water to make nano-fluid suspensions. The suspensions were diluted to a concentration of 0.005wt%, 0.025wt% and 0.075wt% for testing concentration. The gum Arabic (polymer) was mixed with deionized water at a concentration of 3wt% but before it was used, the viscosity of the injected fluid was calculated by using the mobility ratio.

Core flood Setup: This consists of three (3) different vessels, filled with brine, crude oil or nano-fluid. All vessels had valves on the inlets and outlets in order to regulate the fluid flow. A replica of the schematic diagram of the Coreflood setup is shown in Figure 7 below.

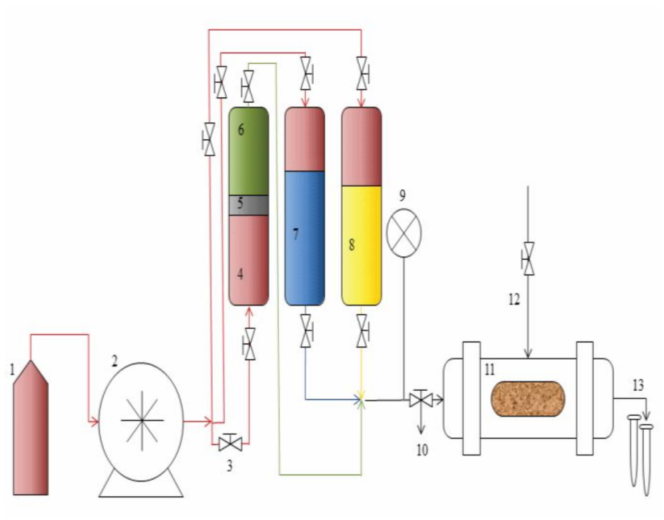

Figure 7: Experimental setup of the core flooding apparatus. (1) pump fluid, (2) pump, (3) valves, (4) displacing reservoir fluid, (5) piston to separate the oils, (6) crude oil, (7) NSB, (8) Nano-fluid, (9) pressure gauge, (10) bypass valve, (11) Hassler cell holder with core (12) sleeve pressure, (13) effluent into test tubes (Aurand et al., 2014).

Core flood Scheme: After the cores were cleaned and initially saturated with 100% brine, they were placed in the core holder with the aid of rubber sleeves and metallic plates for firm packing. The flooding experiments had to start with a primary drainage process. Oil was injected into the core plugs at 5mL/min until brine was no longer produced. This process enabled us to estimate the irreducible water saturation, and oil saturation. Water was injected into the core plugs at 3mL/min until oil was no longer produced for secondary recovery (water flooding). The residual oil saturation can be estimated after proper water flooding. The core samples were further treated with nano fluid flooding immediately after water flooding, to estimate additional oil recovered. This same process was implemented for polymer flooding.

SEM Analysis: After the cores were flooded, they were sent for SEM analysis.

RESULTS AND DISCUSSION

The cores were flooded with only water (single fluid) to know the absolute permeability of the core plugs. Flooding continued until the graph lines/plots of differential pressure against time displayed a straight line. This depicts steady state condition of fluid that flow through the core. Then permeability values were recorded for each core sample as stated in the Table 1 below.

Table 1: Determination of porosity for all the cores

Core Samples	Length (cm)	Diameter (cm)	Bulk volume (ml)	Wet weight (g)	Dry weight (g)	Pore volume (ml)	Porosity %	Absolute K (mD)
Core 2	5.5	3.7	59.14	149	137	11.11	0.1879	247.3
Core 5	6.6	3.5	63.51	175	162	12.04	0.1895	278.8
Core 6	6.0	3.6	61.08	141	126	13.89	0.2274	582.0
Core 7	6.1	5.5	58.69	154	138	14.81	0.2523	245.0

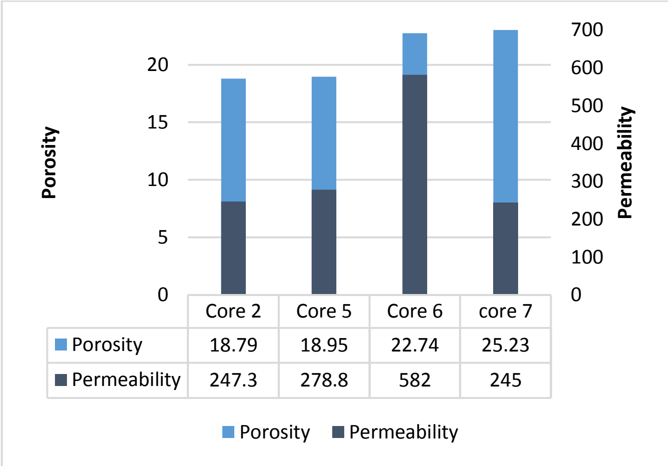

Figure 8: Permeability and Porosity

The porosity (light blue) and Permeability (dark blue) are presented for the four (4) cores used. The porosities of the cores are 18.79%, 18.95%, 22.74% and 25.23% while the permeability are 247.3 md, 278.8 md, 582 md, and 245 md respectively as shown in figure 8 above. Core 6 has the highest permeability while core 7 has the lowest.

Viscosity and Density Measurements: The measurements of the fluid properties where performed at room temperature 20 °C to 23 °C. A Pycnometer was used for density measurements and a glass capillary viscometer for measuring the viscosities. A summary of the fluid properties is given in Table 2.

Table 2: Density and Viscosity

Fluid	Density(g/ml)	Viscosity (cP)
Nanofluid (silica oxide)	1.08	0.89
Crude Oil	0.88	4.62
Water	1.08	0.89
Polymer	1.104	1.94

Silicon oxide is a very hard substance with a very high melting point of 1,610 ^{0}C and a boiling point of 2,230 ^{0}C. It is insoluble in water and does not conduct electricity. The Table 3 below shows the properties of silicon oxide.

Table 3: Properties of SiO_2

Surface Area	140 m^2/g
Size	20–70 nm
Purity	More than 99.5 %
Wettability	Hydrophilic
Dispersible in Phase	Water
Bulk density	0.15 g/mL

Core Flooding: A particular type of silica nanoparticles was tested with core flooding. First water was used to displace the till the residual oil saturation was attained. Subsequently, nano-fluid was used to see if the remaining oil will flow. This continued until there was no more recovery.

Core 2: From the experimental results, it was discovered that after the injection of almost 3PV of water, for core 2 (at an injection rate of 3cc/min) oil recovery ceased and water breakthrough commenced thereby leaving some residual oil which could still be recovered. This necessitated the injection of Core 2 at 0.5cc/min with nano-fluid. The nano-fluid flooding gave an additional recovery of 4.29% of oil. The experimental results are shown in the tables and graph (see Tables 4, 5, 6 and Figure 9).

Table 4: Oil injection to determine the residual oil saturation

Total Pore Volume of the Core	Total Volume of Recovered Oil	Residual Oil (Volume)	Total Oil in Place	Sor	Sw
50.4321	23	11.89	34.89	0.3407853	0.659215

Table 5: Waterflooding to determine the residual oil saturation

Total Pore Volume of the Core	Total Volume of Water Recovered	Residual Volume of Water	Swi	So
50.4321	34.89	15.5421	0.30817872	0.6918213

Table 6: Nanofliud flooding to determine the residual oil saturation

Total Pore Volume of the Core	Total Volume of Recovered Oil	Residual Oil (Volume)	Sor	Sw
50.4321	1.5	10.39	0.206019579	0.7939804

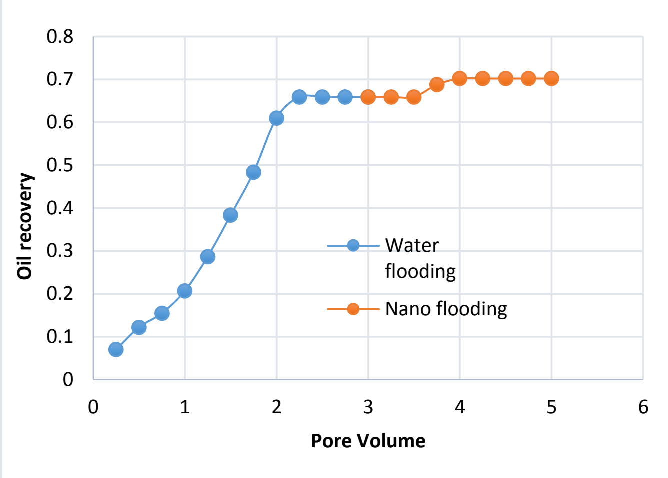

Figure 9: Increased Oil recovery using 0.05 %wt SiO_2 (Core 2)

Core 5: From the experimental results as shown in Figure 10 below, it was discovered that after the injection of almost 3PV of water, for core 5 (at an injection rate of 5cc/min) oil recovery ceased and water breakthrough commenced thereby leaving some residual oil which could still be recovered. This also necessitated the injection of Core 5 at 0.5cc/min with nano-fluid. The nano-fluid an additional recovery of 2.022% of oil.

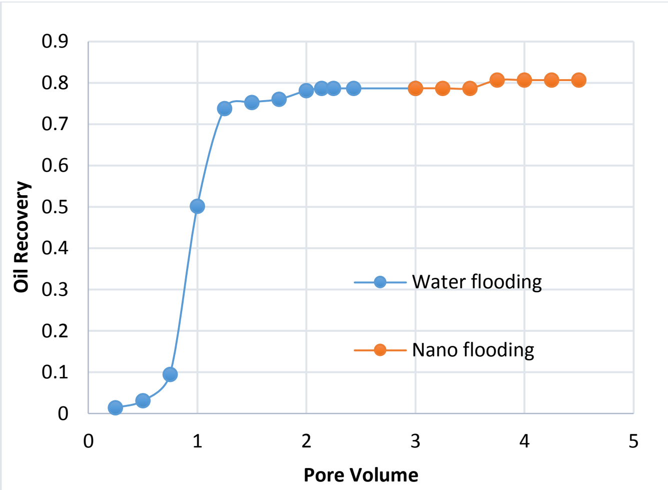

Figure 30: Increased Oil recovery using 0.05 %wt SiO_2 (Core 5)

Core 6: From the experimental results as shown in Figure 11 below, it was discovered that after the injection of almost 3PV of water, for core 6 (at an injection rate of 5cc/min) oil recovery ceased and water breakthrough commenced thereby leaving some residual oil which could still be recovered. This necessitated the injection of Core 6 at 0.5cc/min with nano-fluid. The nano-fluid an additional recovery of 1.86% of oil.

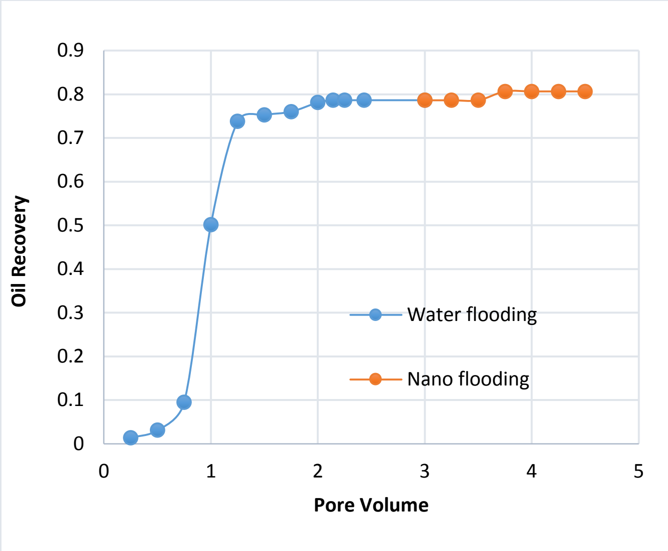

Figure 41: Increased Oil recovery using 0.05 %wt SiO_2 (Core 6)

After a successful nanoparticle flooding, a different core sample (Core 7) was then used to perform water and polymer flooding to examine the effectiveness of polymer flooding compared with water flooding. A pump rate of 5.0cc/min for water flooding and polymer flooding was used and it was kept constant as shown in Figure 12a.

The core flood tests were performed differently using the following procedures:

- Injection of Oil to the core saturated with brine
- Initial waterflood to residual oil saturation,
- Oil was injected to residual water saturation,
- Polymer flood (2 PV) injection, to irreducible oil saturation
- Alkaline (A) slug injection, or
- Extended polymer flood.

For Core 7, results showed that at a pore volume of 1.12 water and polymer flooding gave different result in percentage oil recovery water (see Figures 12a and 12b).

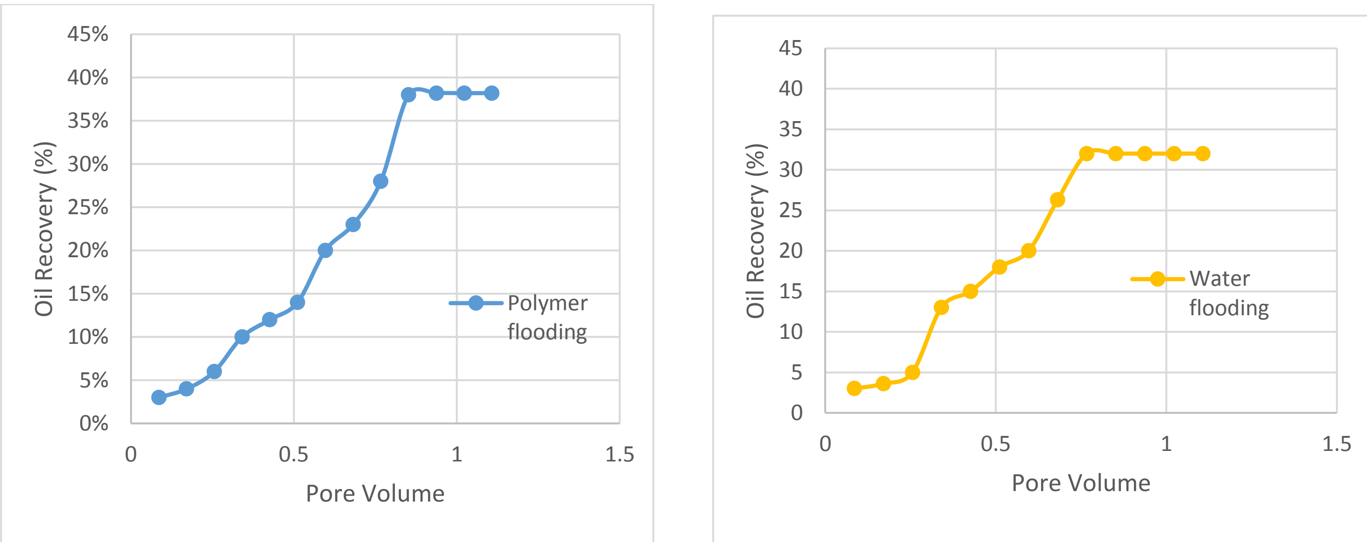

Figure 52: Oil recovery against pore volume of Core 7 (a) Polymer flooding and (b) Water flooding

An incremental recovery was observed from 33% to 38.2 % OOIP (see Figures 12a and 12b) because water had by-passed some oil and was trapped in the core plug which the polymer aided its mobility. Meanwhile at this pore volume, water and polymer flood could no longer be able to produce oil.

Core 7 was flooded at an injection rate of 5cc/min during the water flooding and at 5cc/min during the polymer flooding. The polymer flooding offered an additional recovery of 5.2%.

Permeability Impairment: The single-phase flow of water into core plugs pre and post nano-fluid injection was compared to observe permeability impairment.

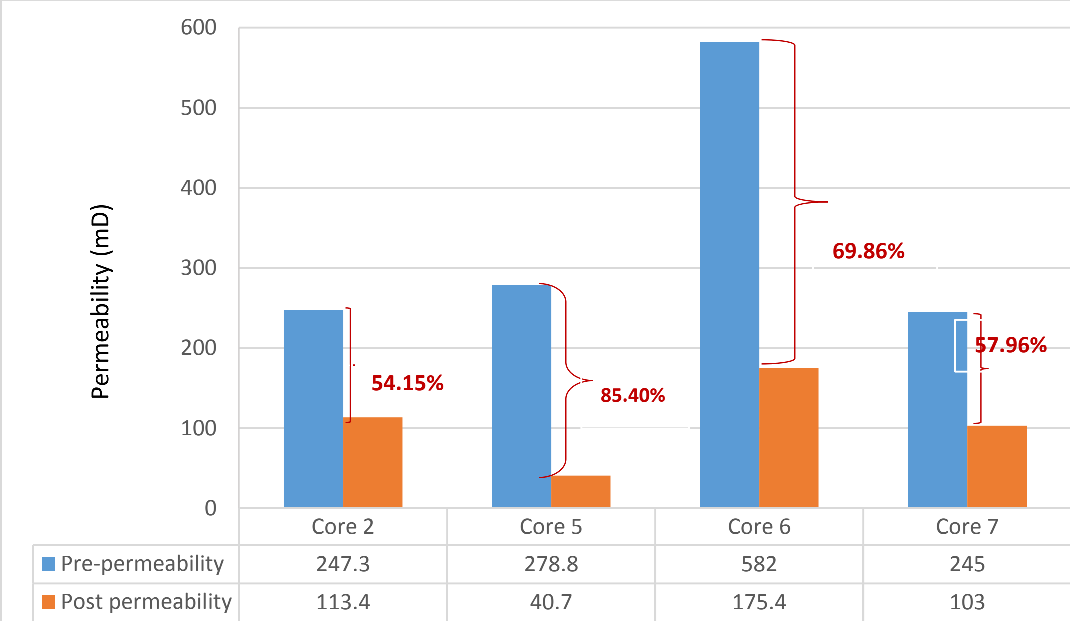

Figure 63: A bar chart showing Permeability Impairment

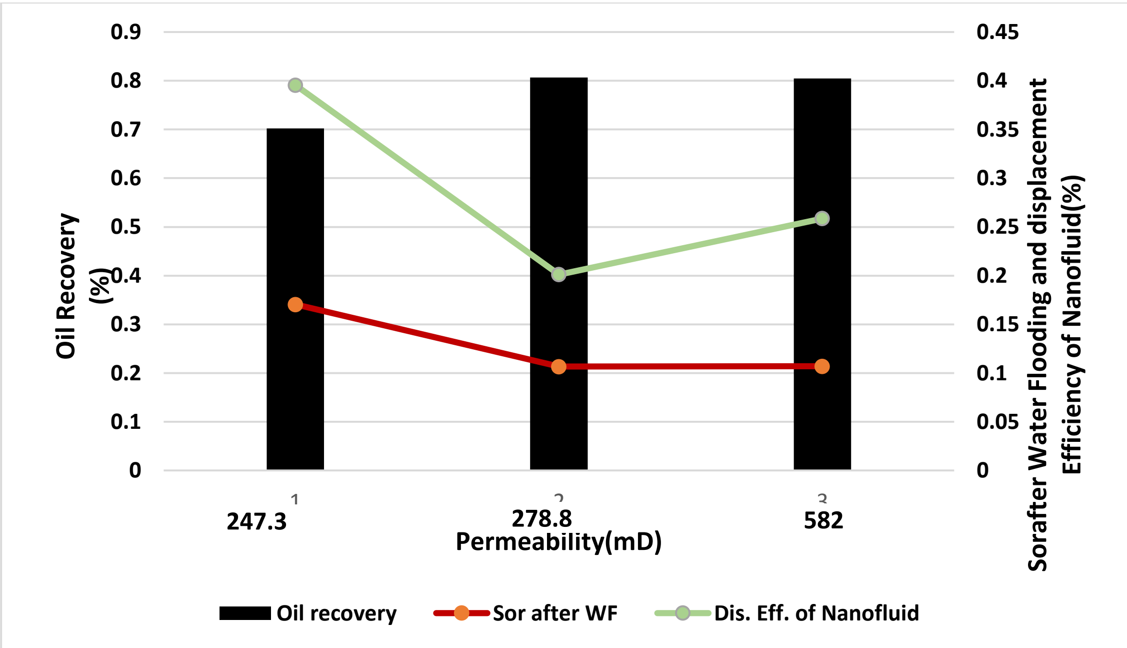

Figure 74: Effect of Permeability to Incremental oil recovery and displacement efficiency of nano-fluid.

For Core 2 permeability decreased from 247.3 md to 113.4 md having an impairment of -54.15%. For Core 5 permeability decreased from 278.8 to 40.7 having an impairment of -85.40%. For Core 6 permeability decreased from 582 to 175.4 having an impairment of -69.86%. And for Core 7 permeability decreased from 245 to 103 having an impairment of -57.96% as seen in Figure 13.

The results in Figure 14 above showed that at relatively similar residual oil recovery, increasing permeability didn't show proportional relationship to increment oil recovery. This result also shows a high Sor and high displacement efficiency for Core 2, this is because it has a low oil recovery compared to Core 5 and Core 6.

SEM Analysis: From the above analysis of nano-fluid flooding it was estimated that Core 2 which had the highest recovery or total volume of oil recovered and this may be due to the high residual oil saturation after water flooding. The Figures 15-18 are the image resolutions for the core samples after nano-fluid and polymer flooding. The SEM images show permeability impairment for both flooding scenario.

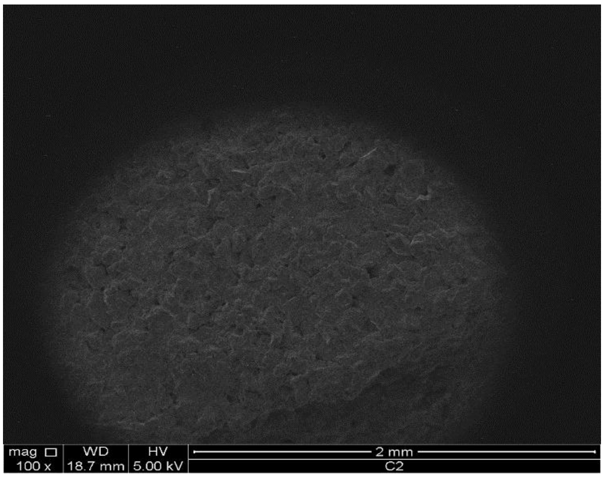

Figure 85: SEM at 100× magnification of Core 2 after nano-flooding.

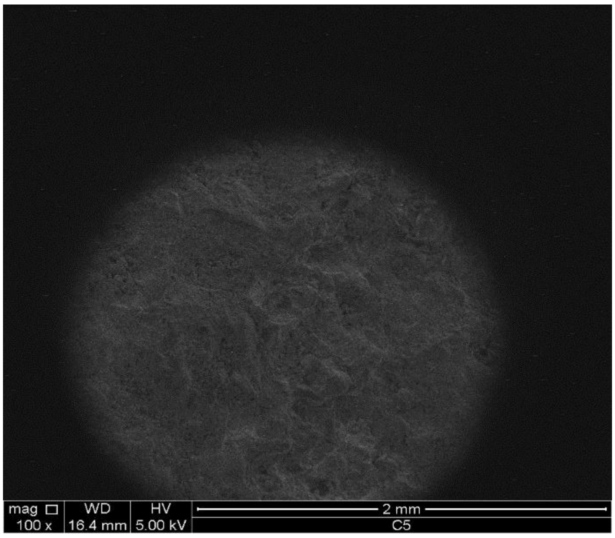

Figure 16: SEM at 100× magnification of Core 5 after nanoflooding. Core 5 after nano-flooding

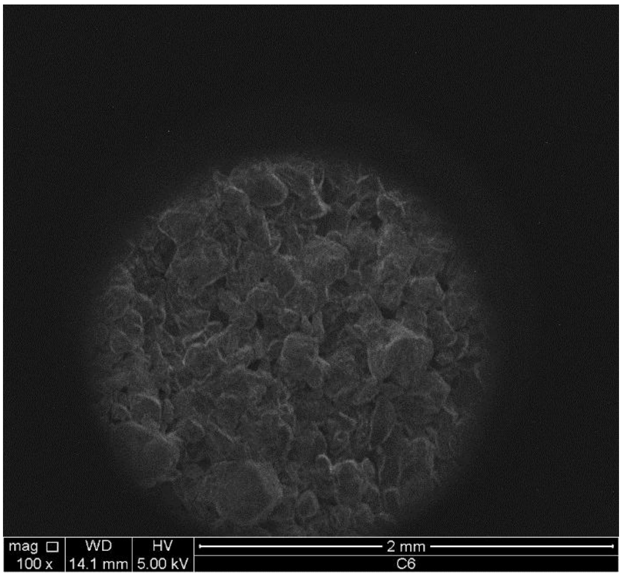

Figure 17: SEM at 100× magnification of Core 6 after nano-flooding

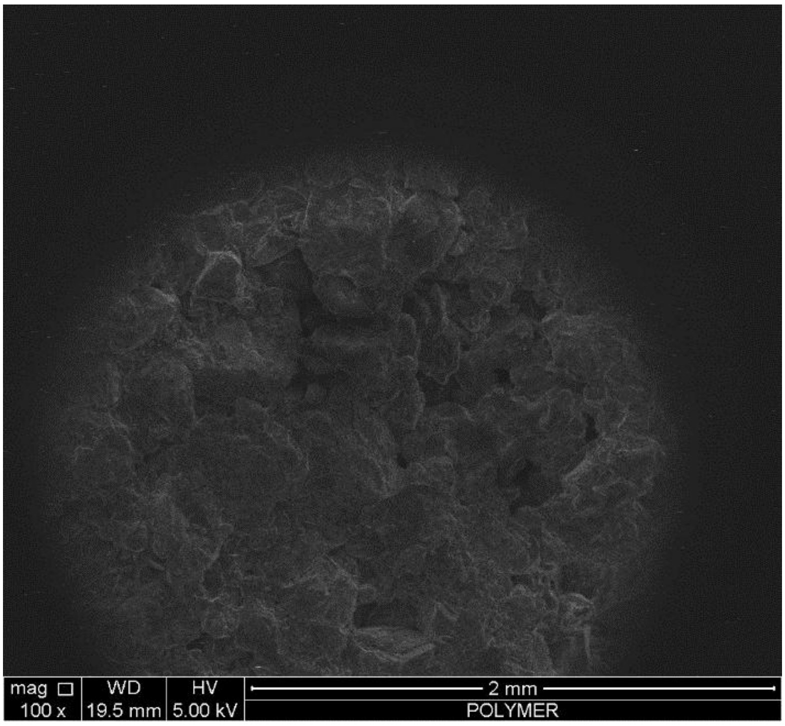

Figure 18: SEM at 100 × (2mm)) magnification of Core-Polymer after polymer flooding

Taking a closer look at each image, the whitish coloration lining the outside of the cores as vividly seen suggests retention and adsorption of nanoparticles and (since before mixing of nanoparticles with base fluid they possess a whitish color). In trying to ascertain the reason for the permeability impairment, we know that clay swelling is not responsible for this since from XRD analysis the clays are non-swelling clays. The constituents of one of the core samples are Quartz 72 %, Kaolinite 6% and Microcline 22% (Orodu *et al.*, na). Kaolinite and microcline are non-swelling clay, hence, permeability reduction is solely by adsorption of nanoparticles and polymer unto the sand grains of the rock.

CONCLUSION

This work has been able to effectively deduce that using nanoparticles (NP) and polymer as an oil recovery mechanism is able to increase oil recovery after water flooding in core plug samples. To do this, several experiments were carried out to examine the potential of NPs as an EOR. Based on these experiments, nanoparticles have the potential to mobilize trapped oil and reduced the residual oil saturation. The use of nano-fluids as an improved oil recovery process for heavy oil reservoirs resulted to a 4.29% increase of oil by altering the wettability of the formation. Polymer flooding gave an additional recovery of 5.2%. Permeability impairment was due to adsorption of nanoparticles and possibly log jamming and mechanical entrapment in the pore throat.

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