Investigation of Nanoparticles Dispersion for Enhanced Oil Recovery (EOR) Applications

by

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16701

Dissertation submitted in partial fulfillment of

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

INVESTIGATION OF NANOPARTICLES DISPERSION FOR ENHANCED OIL RECOVERY (EOR) APPLICATIONS

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A project dissertation submitted to the

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BACHELOR OF ENGINEERING (Hons)

PETROLEUM ENGINEERING

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(ARIF LUQMAN ROZMAN)

ABSTRACT

With recent advancement in nanotechnology, this specific area of interest has slipped through the oil and gas industry significantly. Nanoparticle is a branch from nanotechnology which fundamentals are nano-sized particles that aids in recovering oil left behind from primary and secondary methods. Nanoparticles theoretically benefits tertiary oil recovery or enhanced oil recovery (EOR) methods by seeping through the micro cracks or low permeable zones due to the nano-sized particles characteristic. In this research, silica nanoparticles and aluminum nanoparticles were dispersed in a sandpack to displace crude oil. The dispersion of nanoparticles however is the main concern in this research. Aggregation of nanoparticles are said to be the major contributor for paralyzing nanoparticles dispersion deeper into the formation. This research also discusses the use of sodium hydroxide (NaOH) as stabilizing solvents mixed in brine or carrier fluids which are also important in enhancing the nanoparticle properties to prevent coagulation of the nanoparticles itself when mixed to create a nanofluid.

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With that, I hoped all the experiences and knowledge that I have gained from this research will be a kick-start for my future career development.

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CHAPTER 1
INTRODUCTION

1.1 Background

Nanoparticles are being used in industries in a considerable amount of time. It has been proven to give significant results that could be projected into the oil and gas industry specifically in tertiary recovery or enhanced oil recovery (EOR). With its nano-sized bits, these particles are theoretically able to disperse further into the formation covering a substantial amount of drainage area. It could also act as a stability agent for some EOR applications in example for foam flooding.

Nanotechnology was first popularized in the 1980's by a physicist named K. Eric Drexler, it was then talking about building machines on a molecular scale and even whole computers in cell sizes. Over the years, as nanotechnology became an accepted concept, the meaning of the word shifted to incorporate the simpler kinds of nanometer-scale technology in example nanoparticles. In the subject of nano-particles stream in permeable media has turned into another go for the headway in petroleum study. The development of nanotechnology application is truly sudden as of late. The disclosures of the nano-innovation potential to wind up arrangements towards a few issues in petroleum industry has ended up empowering according late research. The salient point of nanoparticles in EOR is the capacity of it to adjust certain component in the arrangement and liquid properties. Enhanced Oil Recovery (EOR) is the most theorized region for the potential improvement by this nanoparticle application. The ascent of vitality request in worldwide scale which anticipated that would happen in the oil and gas industry has made EOR the most essential devices as to meet this desire and demand from the market.

This includes presenting theories on nanoparticles dispersion into reservoir formations and concentrating on its consequences for oil recuperation. Nanoparticle study has been a sought for subject of investment particularly in investigating the EOR applications, for example, foam flooding. Foam flooding is a well-known field in EOR with substantial results in oil recuperation though its weakness is its own.

The infusion of nanoparticles is a guaranteeing and novel methodology in improving oil recuperation for drained or retired fields. Nanoparticles have one measurement that is littler than 100 nm and have numerous novel properties that are helpful concerning oil recuperation. Their tiny size and the capacity to control molecule properties are a few of the worthwhile properties. The tiny size of nanoparticle permits them to effortlessly pass through permeable media. Controlling nanoparticle properties takes into consideration wettability adjustments or controlled arrival of chemicals at an exact area in the reservoir formation.

1.2 Problem Statement

In recent times, the study on nanoparticle applications in enhanced oil recovery is growing tremendously. However, the nanoparticle dispersion in the reservoir itself is still questionable. This is due to the aggregation property of the nanoparticles after a certain amount of time. Hence, this study is focused on the ability of nanoparticles to disperse deep into the formation to avoid aggregation.

A typical yet unpredictable marvel for these nanoparticles is its aggregation. Aggregation happens when the nanoparticles coagulate and create a much larger particle compared to its original nano-size. Conglomeration makes it particularly challenging to explore the properties and applications of nanostructured materials in most cases. Numerous engineering methods for these nanoparticles, particularly without surfactant concoction responses, aggregation occurs instantly as nanoparticles are made. Aggregation has been basically attributed to the direct common fascination between particles by means of van der Waals force or compound chemical bonding (Li & Kaner, 2005). Strategies for forestalling aggregation for the most part of it originated from coating whereby the nanoparticles are ‘covered’ from the outside by coating chemicals and/or the surface charges are customized to independent them by means of electrostatic shocks making nanoparticles hydrophobic or hydrophilic. There is also the addition of solvents as stabilizing agents to prevent the direct coagulation of nanoparticles in nanofluids. These methods are suggested to enhance the dispersion of nanoparticles deeper in the formation.

1.3 Objectives & Scope of Study

There are two objectives identified in this research.

1. To evaluate the dispersion of various concentrations of hydrophilic nanoparticles for different concentrations of stabilizing fluids in brine.
2. To study the dispersion of various concentrations of metal oxide nanoparticles for different concentrations of stabilizing fluids in brine.

The scopes of study with regards to this research would comprise;

1. The factors contributing to the dispersion of nanoparticles into the reservoir formation.
2. Experimenting on the fluid flow of nanoparticles through porous media using various concentrations of stabilizing fluids/agents.
3. EOR applications of nanoparticles to aid in enhancing EOR capabilities.
4. The study on maximizing oil recovery via tertiary methods or enhanced oil recovery (EOR).

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 Nanoparticles

Nanoparticle (NP) is characterized as a tiny particle that acts as an entire unit independently with respect to its mobility and properties which cover a reach somewhere around 2,500 and 10,000 nanometers for coarse particles, 100 and 2,500 nanometers for fine particles, and 1 and 100 nanometers for ultrafine particles. These nanoparticles are utilized as an additive towards enhancing the effect of oil recovery in EOR. Moreover, even the current available technologies still lack the needed resolution and the ability to deeply penetrate reservoir lithologies (Kong & Ohadi, 2010). A nanofluid on the other hand refers to a fluid that contains particles of nano-size ranging to 100 nm (Rao, 2010). Nanoparticles have an extensive variety of interesting applications as essential building blocks in catalytic processes, magnetic devices, polymer composites and adhesives (Pranami, 2009).

2.1.1 Nanofluids

The nano-fluids are made by the addition of nanoparticles to fluids for amplification and development of some properties at low volume concentrations of the dispersing medium (Suleimanov *et al.*, 2011). Nanofluids can be delegated as a strong nanofluid and weak nanofluid as to the quantity of nanoparticles added into the liquid. Strong nanofluids are the liquids with more than one NP added into the substance whereas the basic nanofluid is the liquid with only one NP added. Nanoparticles can remain with multifunctional or single use of sort. Developing applications of nanotechnology in the industry involve new types of these nanofluids for various applications, particularly for EOR purposes (Kong & Ohadi, 2010).

The test conducted by Suleimanov *et al.* (2011) on Newtonian oil displacement showed a significant recovery utilizing nanofluids in oil recovery in a high pressure column filled with quartz sand of permeability 1 Darcy and porosity of 26%. Concentration of nanofluids derive an essential key factor in optimizing EOR of low permeability water wet Berea sandstone by reducing contact angle as nanofluid concentration increases resulting in a desired nanofluid concentration of 0.01, 0.03 and 0.05 wt. % (Torsaeter *et al.*, 2013).

2.1.2 Nanoparticles Selection

Table 0.1: Nanoparticle Selection

Nanoparticles	**Findings**
Silicon Oxide	Dispersed in ethanol improved recovery through change in rock wettability. (Ogolo *et al.*, 2012)
	Homogeneous and heterogeneous water free-oil recovery increased better with surfactant dispersing agent. (Suleimanov *et al.*, 2011)
	Reduction of interfacial tension and wettability alteration using polymer coated SiO2. (Ragab, 2014)
	Adjusting the surface charge density of the nanoparticles, stable fluids can be employed to more effectively displace oil from flow impaired locations. (McElfresh *et al.*, 2012)
	Lower IFT was observed with increasing nanofluid concentration from 0.01 to 0.05 wt. % and reduces oil saturation by 13%. (Torsaeter *et al.*, 2013)
Aluminum Oxide	Reduce viscosity of the oil. (Bennetzen & Mogensen, 2014; Ogolo *et al.*, 2012)
	Results demonstrate that the wettability alteration plays a more dominant role in the oil displacement mechanism using nano-EOR using PVP as stabilizing agent. (Hendraningrat & Torsaeter, 2014)
	Produced oil lighter than injected oil in terms of viscosity reduction. (Ogolo *et al.*, 2012)

In this study, silica nanoparticles for hydrophilic NP and aluminum oxide as metal oxide NP are chosen to be utilized. Silicon dioxide, otherwise called silica, is an oxide compound that of silicon with the chemical formulae SiO_2. Silica nanoparticles possess a noticeable position in systematic research, in view of their simple readiness and their wide range of uses in different applications, for example, catalysis, electrics and electronics, pharmaceutical and various sensors (Rao *et al.,* 2005). Silica nanoparticles are also ventured for in enhanced oil recovery applications. These are due to the main component of sandstone comprises primarily of silica which directly makes silica nanoparticles an environmental friendly substance. Silica nanoparticle dispersion is said to have good stability due to its properties in the ability to counterbalance the gravity force effect (Li & Torsaeter, 2015). The study conducted by Torsaeter, *et al.* (2013) showed that an increase in hydrophilic silica nanofluid concentration will increase water-wetness in a low-permeability Berea sandstone core plug due to the electrostatic repulsion force between particles will be higher with an increased amount of nanoparticles. The nanofluids will spread along the solid surface and adsorption may be occurred, decreases contact angle and displace most of the trapped oil that remains after secondary flooding with brine (Torsater *et al.*, 2013). Torsaeter *et al.* also concluded that the concentration of the nanoparticles comprised in the nanofluid affects the effectiveness in displacing oil as a tertiary recovery method. However, nanoparticles have a tendency to block pore network at higher concentration (e.g. > 0.06 wt%) in low-permeability Berea cores.

Aluminum oxide was chosen as the other nanoparticle for this specific project. Aluminum oxide, a metal oxide NP, in brine is able to reduce the viscous properties of the displacing fluid in this aspect, oil (Bennetzen & Mogensen, 2014; Ogolo *et al.*, 2012).

According to a research done by Ogolo *et al.* (2012) on enhanced oil recovery using nanoparticles, silicon oxide NP dispersed in ethanol tends to enhance oil recovery through a change in rock wettability from water wet to oil wet and aluminum oxide NP are able to reduce the oil viscosity.

This means, silica and aluminum oxide NP could very well alter the rock wettability from oil wet rock to water wet rock and reduce the oil viscosity respectively hence, increasing the mobility of oil flow form the reservoir formation.

2.2 Nanoparticle Dispersion

At the point when nanoparticles are scattered in a base liquid, the state of the nanoparticles is controlled by the attraction between the nanoparticles and between the nanoparticle and base liquid (Rao, 2010). Colloidal particles transportation in porous media are governed by the retention of itself. Aluminum oxide and silicon oxide particles were the best options for enhanced oil recovery. The aluminum nanoparticles reduced oil viscosity and the silicon particles altered rock wettability. It was also indicated that by using ethanol as a dispersing agent in the experiments could alter the outcome in improving recovery. This was because ethanol reduces the oil-water interfacial tension, which would help to recover more oil. A high recovery was noted when using silica nanoparticles in brine and using particles in brine was extremely important because when these particles are injected into the reservoir it will interact and mix with reservoir brine (Bramer & Christopher, 2014).

2.2.1 Retention and Aggregation

The major retention mechanism is the irreversible attraction to the rock grain surfaces (Caldelas *et al.*, 2011). The paper predicted a rock grain surface retention with the colloids, a constant first order rate coefficient is preferably used. On the other hand, it was also specified that when the colloids and rock grain have repulsive force, the coefficient have been found to be underestimated. Retention and aggregation of nanoparticles are the major factors governing the dispersion of nanoparticles through the reservoir formation, hence, affecting drastically the recuperation of oil. Retention time indicates the time taken for any suspended particles to settle down or sediment in the bottom of the container. Theoretically, as the retention time is longer, more particles are left suspended within a certain fluid which indicates a more stable nanofluid. Transport in reservoir rock has two major components which comprises the nanoparticle retention which quantifies the fraction of injected nanoparticles that reach the target zone and the mobility of the nanoparticle dispersion through the porous media under operating conditions to bring the injected nanoparticles through the desired path and time to the target location (Rodriguez *et al.*, 2011).

Carrier fluid or brine was used to aid the flow of nanoparticles into the formation. In the presence of high ionic quality (1 wt% or 0.13 KCl) and multivalent particles

($Ca^{2+}$and Mg^{2+}) altogether influenced the nanoparticles transport or dispersion into the reservoir formation which is said to be because of the charge collaboration between the nanoparticles in suspension and the communication between the nanoparticles and the permeable medium itself (Caldelas et al., 2011; Yu et al., 2010). The electrostatic forces between the nanoparticles, and between the nanoparticle and the rock surface, govern the main reason of aggregation of nanoparticles or attraction to the reservoir rock surfaces. Electrostatic forces however are highly dependent on ionic strength which reduce or compress the size of the electrical double layer of particles thus decreasing the repulsive forces between particles as shown in Figure 2.1. These repulsive forces affects the aggregation of particles and particle attachment to surfaces, large ionic strengths therefore allow the attractive van der Waals forces to dominate (Rodriguez Pin *et al.*, 2011). Nanofluid mixtures are also an important criteria in avoiding agregations. The pH of a nanofluid affects the adhesive forces between the nanoparticles. In a study done, an adhesive intraction between nanoparticles and glass surface in water was objectified and when the pH of the solution was kept at 8.5 – 9 by adding sodium hydroxide, the adhesive force between the nanoparticles decreased hence avoiding aggregation (Pranami, 2009). As for the dispersion stability and the transportability in the reservoir rock, the reservoir brine salinity and pH are an important design parameter in controlling not only the electrostatic repulsion between the particles and between the particle and the pore wall, but also the hydrogen-bonding capability of the coating layer on the nanoparticle surface (Yu *et al*., 2010).

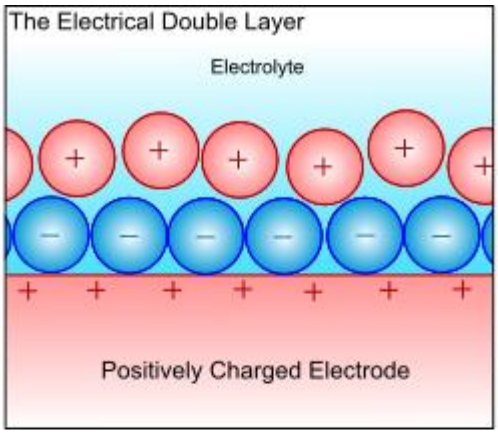

Figure 0.1: Electric Double Layer (DoITPoMS, n.d.)

The flow of nanoparticles through a permeable medium up to a several meters in single phase fluid and a mixture of crushed sedimentary rocks and clay which represents a reservoir rock is possible (Caldelas *et al.*, 2011). According to the research done by Caldelas *et al.*, the specific surface area of the permeable formation has a significant effect on nanoparticle retention whilst the composition of the grains within the formation has a secondary effect on it. Four different lithologies (Boise sandstone, Texas Cream limestone, kaolinite clay, and illite clay) were chosen in assessing the effect of NP retention and a range of various specific surface areas. The grain size effects linearly with surface area in terms of smaller grain size resulting in smaller surface area. Some variety in the estimation of recovery was observed for tests with comparable surface areas. This variety is steady with retention being controlled by the effect between van der Waals force, Brownian motion, and hydrodynamic drag.

2.3 Enhanced Oil Recovery

With the expanding interest and utilization of energy worldwide, the need to fully recover hydrocarbon from the current oilfield has become a point of interest. Only around 35% to half of the unrefined petroleum in stores has been recovered through traditional oil recovery routines. Several tertiary or enhanced oil recovery (EOR) methods have as of now been embraced to endeavor the buildup oil in reservoirs (Ogolo *et al.*, 2012; Sun *et al.*, 2014). Enhanced oil recovery (EOR) techniques are getting to be progressively imperative as energy interest climbs. Methods presently used to recover crude oil from reservoirs generally concentrating on 15-30% of that accessible.

2.3.1 Nanoparticles in Enhanced Oil Recovery

Although the use of nanoparticles in EOR is very recently ventured, there are extensive researches done on the ability of nanoparticles to aid in EOR applications. Foam flooding is an advancement in EOR. Foams have been proposed for utilization as mobility control and to enhance oil recovery in several secondary recovery and EOR, for example, steam, CO_2 and nitrogen flooding. Distinctive surfactants are obliged to create foams that are tolerant to oil, electrolyte and steady at downhole demanding conditions. Sodium dodecyl sulfate (SDS) foam was used in a specific experiment where the foam stability was increased with the aid of SiO_2 nanoparticles. It also shows a better tolerance to downhole temperature whereby the foam bubbles are able to maintain a spherical shape with time through the permeable media (Sun *et al.*, 2014). Findings indicated how dispersed nanoparticles in a fluid mixture can alter the interfacial properties of the fluid/fluid frameworks (Hendraningrat & Shidong, 2012; Suleimanov *et al.*, 2011). The study indicate that the surface of the whole formation can be altered in a sense of ionic changeability or nanofluid coating.

A reduction in IFT was one of the potential applications by which nanoparticles may aid in enhanced oil recovery due to less energy required to mobilize and remove oil trapped in the formation (Bramer & Christopher, 2014; Hendraningrat & Shidong, 2012). In the study done, it was observed that the interfacial tension (IFT) between the crude oil and nanofluids decreases as the nanofluid concentration increases (Alomair, Matar, & Alsaeed, 2014). On top of that, aluminum nanoparticles have a tendency to displace oil through their capability in reducing oil viscosity when used with fresh water and brine as dispersing fluids (Alomair *et al.*, 2014; Ogolo *et al.*, 2012). In a research conducted using a spinning drop to observe a decrease in the interfacial tension between synthetic oil and a brine/nanofluid, a 0.01 wt% silica nanoparticle solution in brine will decrease the interfacial tension from 14.7 mN/m to 9.3 mN/m and when silica NP concentration increased to 0.05 wt% a further reduction of the interfacial tension to 5.2 mN/m was observed.

CHAPTER 3
METHODOLOGY/PROJECT WORK

3.1 Project work overview

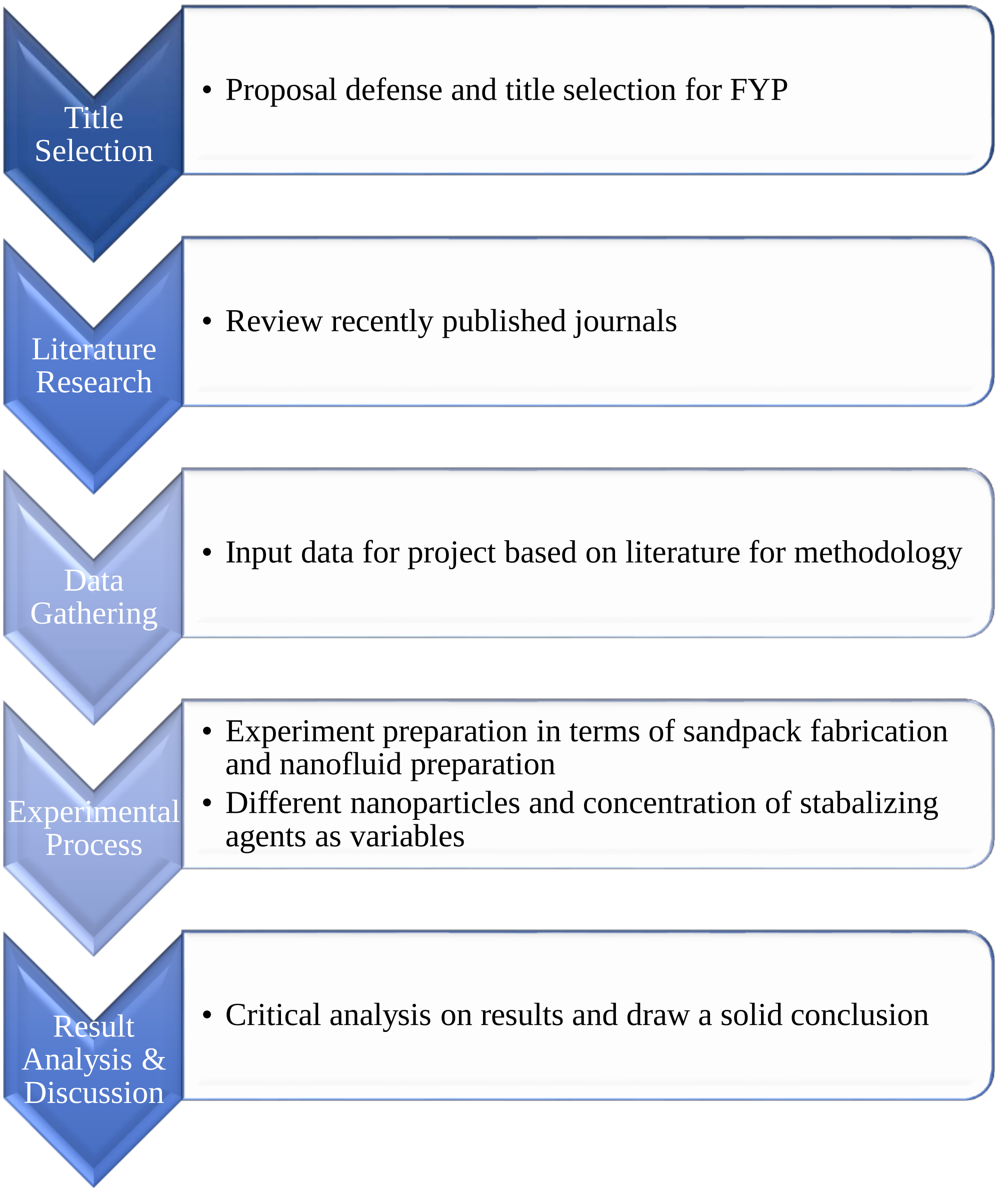

Figure 0.1: Methodology Overview

The first part of the project was the literature review. This part focusses on previous papers recently published by qualified journals as the basis of study. The aim of this stage was to increase understanding on the idea of nanoparticles and subsequently structuring solid fundamental information to support the future study. To develop the problem statement and gather as much information possible for experiment methodology. This part was also crucial in understanding fundamental concepts behind nanoparticles itself.

The inputs gained from the various sources, for example, *Universiti Teknologi* PETRONAS (UTP) researches, lecturers and experts additionally have contributed a significant point towards accomplishing this stage.

Following the readiness of the sandpack holder and chemicals, accommodated apparatuses and supplies, the experimental stage of this study was constructed. Nanoparticles and sandpack preparation will be the key elements in performing this stage. All the data will be analyzed through several techniques available including the use of equipment in the laboratory. Successively, the cultivated analysis of the outcomes were drawn and the conclusion derived.

3.2 Procedures

With a specific end goal to effectively finish the project, arrangement of steps and methodology are distinguished beforehand. The following are the derived techniques with depiction of each of the stages in the undertaking.

3.2.1 Creating a sandpack

The sandpack preparation gives an option to create a permeable medium for performing EOR applications replacing a core sample from the reservoir. The structure utilizes a sand pack which is essentially an acrylic tube topped off with stuffed quartz sand inside. This sandpack will be utilized for the injection of nanoparticles in order to investigate the dispersion under controlled conditions.

The sandpack holder was sent for fabrication using acrylic as the main material and thick rubber as a mean to hold pressure and avoid leaks. Figure 3.2 shows the fabricated acrylic sandpack holder.

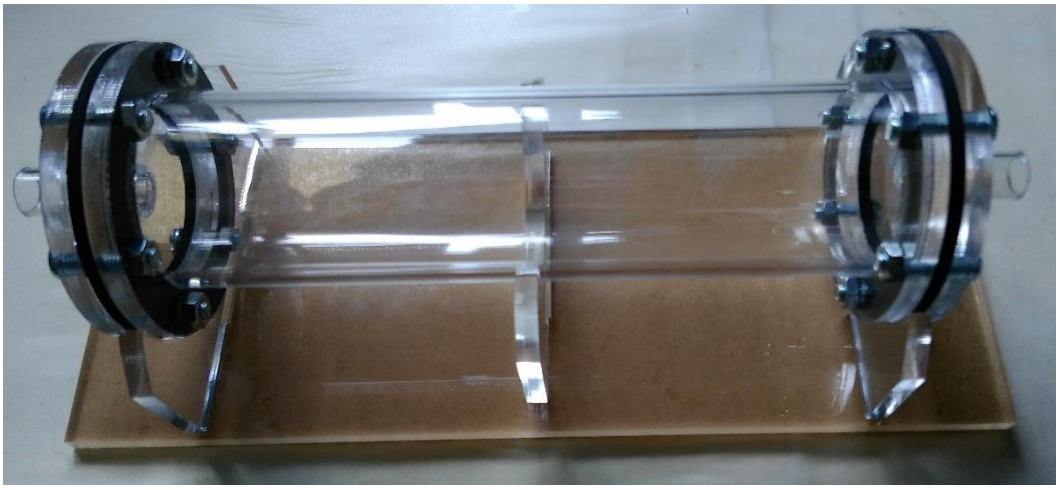

Figure 0.2: Acrylic Sandpack Holder

The sand used for this research is beach sand from the shores of Lumut, Perak. Beach sand has a cementing property which enables the sand to be packed into the sandpack holder. The rubber element at each end of the sandpack holder avoids leakage while injecting fluids. The beach sand was sieved to obtain a well sorted grain size, cleaned with water and dried in the oven at 150°C for at least 8 hours or left overnight. The sand was sieved to a range of 600 µm to 150 µm using a mechanical sieve as shown in the Figures 3.3 and 3.4. The most amount of sand was collected at a range of 425 µm to 300 µm. Collected sand was washed and dried in the oven overnight prior to the sieving process.

Figure 0.3: Sand Sieve Arrangement

Figure 0.4: Mechanical Sieve

The sand was then washed with tap water in a basin then dried in the oven to 150°C to remove water and any organic materials left behind.

The dispersion test will be done by observing the gain after injection of the nanoparticles through the sandpack. The sandpack's porosity and permeability was calculated by utilizing the equations below. Porosity will be calculated by the difference of volume injected and displaced by the total volume of the sandpack. Whereas, permeability will be calculated using a correlation suggested by Timur which relates the water saturation with permeability. Timur utilized a database of 155 sandstone tests from three varying oil fields. The three sandstones display varying degrees of sorting, consolidation, and arrays of porosity. Timur measured irreducible water saturation (S_{wi}) using a centrifuge and then equated permeability (k) relative to S_{wi}^{-2} as indicated in Eq. 2 (Timur, 1968).

Figure 0.5: Schematic diagram of a sandpack

(from left: Automated syringe pump, sandpack and collecting beaker)

$$\Phi = \frac{V_p}{V_b} \qquad \text{(Eq. 1)}$$

V_p = Sand pore volume

V_b = Total bulk volume of sandpack

Ultimately, the porosity of the sandpack itself was determined by utilizing the volume of an object via water displacement in a cylindrical measuring glass. Dry sand is first poured into the measuring glass and its volume was recorded. Then a fixed volume water is introduced into the dry sand volume and a volume of wet sand (water + dry sand) was recorded. The difference in wet sand volume and dry sand volume indicates the total air space volume occupied by the sand. Initial water saturation was determined by subtracting the volume of brine injected by the volume of brine displaced by crude oil.

$$k = a\Phi^b S_{wi}^{-2} \quad \text{(Eq. 2)}$$

k = Permeability

Φ = Porosity

b = 4.4

a = 0.136 (Φ, S_{wi} in percentage); 8581 (Φ, S_{wi} in fraction)

S_{wi} = Initial water saturation or connate water saturation

3.2.2 Nanofluid preparation

Silica oxide (SiO_2) and aluminium oxide (Al_2O_3) are used for this study. These nanoparticles was prepared by mixing them in carrier fluids or 3 wt% brine (NaCl) to investigate the effect of dispersion due to different concentrations of nanoparticles and stabilizing agent (NaOH). Silica and aluminium nanofluids was prepared by mixing different concentrations of each nanoparticles in various concentrations of stabilizing agents (NaOH) as showb in Table 3.1. The prepared nanofluid was based on the total volume of sandpack holder itself. These arrangements were then blended with a magnetic stirrer bar at various velocities for 4 hours (Li & Kaner, 2005).

Table 0.1: Nanofluid Preparation

Nanoparticles	**NP wt.%**	**NaOH wt.%**
SiO_2 + 3 wt.% Brine (NaCl)	0.01	1.00
		5.00
	0.05	1.00
		5.00
Al_2O_3 + 3 wt.% Brine (NaCl)	0.01	1.00
		5.00
	0.05	1.00
		5.00

3.2.3 Nanofluid stability and injection

A turbidity meter will be used to confirm the aggregation effects for each sample prepared prior to injection into the sandpack. Prior to inserting the nanofluids into the turbidity meter, the nanofluids are stirred with a magnetic stirrer for another 4 hours in total of 8 hours. The turbidity meter reading was recorded every 10 minutes for a one hour period in order to analyse the stability for each nanofluid mixtures.

Prior to injecting the sandpack with brine, a brine mixture was prepared with 3 wt% of sodium chloride (NaCl) mixed with boiled distilled water. The distilled water was boiled to remove all the dissloved air bubbles that might be present within the water itself. Once the brine is prepared, the sandpack holder is packed with sand grains by pouring the sand into the sandpack in small amounts until the brim of the holder to ensure a good packing is obtained. Brine was then injected into the sandpack vertically as seen in the figure below to remove all the air within the sandpack and to avoid the brine to channel only through certain paths instead of saturating the sandpack. Volume injected and first water droplet out from the sandpack was recorded to calculate the volume of brine within the sandpack. Injection rate for all injection done to the sandpack was at 0.5 ml/min.

Tapis crude oil was prepared by filtering using a filter funnel to remove all large organic particles prior to injecting into the sandpack. Tapis crude was injected at a rate of 0.5 ml/min until the first drop of oil is displaced out. The collected volume of brine in the collecting tank as seen in the arrangement from the Figure 3.5 was recorded and deducted from the initial volume of brine in the sandpack. The difference in volume of brine brings about the initial water saturation or connate water saturation in the sandpack. Volume of crude injected was also recorded.

Nanofluids prepared earlier was then injected after crude oil was saturated in the sandpack as per arrangement in the Figure 3.5. The volume of crude displaced for each nanofluids was recorded and tabulated.

3.3 Gantt chart

Table 3.2 shows a description of the Final Year Project (FYP) 1 which starts from January up till April 2015.

Table 0.2: FYP 1 Milestone

Milestone	**Week**										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
FYP 1 briefing	■										
Selection of project	■	■	■								
Literature research on Nanoparticles			■	■	■	■	■	■	■	■	
IRC briefing				■	■						
Submission of extended proposal						■					
Proposal defence									■		
Interim report submission											■
Key Milestone											
Gathering data about the nanoparticles and its dispersion under various conditions and carrier fluids	●										
Derive the methodology for the research which includes the use of sandpack and ordering nanoparticles					●						
Continue the research about methodology and seek aid from postgraduates on sandpack									●		
Update materials and equipment to be used after feedback from proposal defence									●		

Table 3.3 shows a description of the Final Year Project (FYP) 2 which starts from May up till September 2015.

Table 0.3: FYP 2 Milestones

MILESTONE	**WEEK**														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Continuation of project work															
Submission of progress report															
More research done on project work															
Pre- SEDEX															
Submission of final report (draft)															
Dissertation submission (softcopy)															
Submission of technical paper															
Viva and hard bound submission															
Key milestone															
Preparation of np samples to be run to get optimum np condition before injecting into sandpack															
Fabricate sandpack and determine porosity and permeability based on timur relation															
Inject nanofluids into sandpack and record gain of saturated oil															

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Nanofluid Stability

The presence of nanoparticles changes rheological properties of any liquids mixed creating a nanofluid. These nanofluids mixtures were prepared according to respective concentrations of nanoparticles and solvents. In this case, the solvent used was sodium hydroxide (NaOH).

Once prepared, the nanofluids were then tested on stability via Nephelometric Turbidity Unit (NTU) readings on a turbidity meter. Theoretically, a higher NTU reading shows more particles suspended within a liquid hence showing a more stable nanofluid. Although, the high readings must retain its value throughout a certain time period, in this case one hour, to show that the suspended particles stay suspended instead of just settling down.

As seen in the Figures 4.1 through 4.4, a much stable nanofluid represent by a small or no deflection on the graph of NTU against time. Although aluminum oxide nanoparticles at 0.05 wt% have a much higher initial value of NTU, the NP was not able to retain that value within the one hour period instead most of the particles settled down. A pH meter was also used to measure each nanofluids pH reading as shown in the table 4.1.

Figures 4.1 and 4.2 show the stability of aluminum oxide nanofluid in different concentrations of solvents and NP. As discussed a higher NTU value results in more suspended particles within the fluid. Aluminum oxide nanofluid of 0.05 wt% mixed in 1 wt% NaOH resulted in the highest NTU value. The value was not stable and declined rapidly after 20 minutes and fluctuated 30 to 15 NTU. These values proves that the nanofluids prepared has more suspended aluminum oxide nanoparticles and stabilizes after 20 minutes.

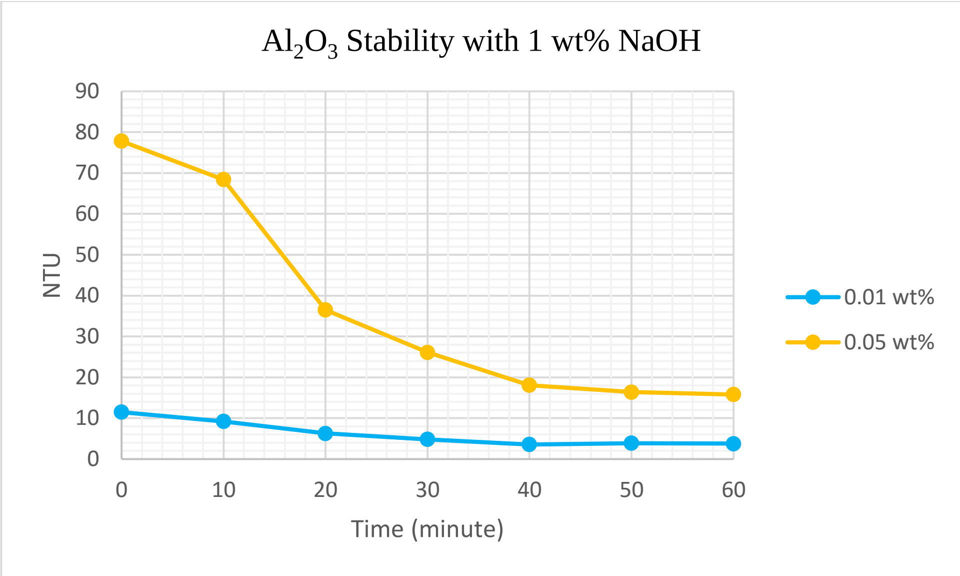

Figure 0.1: Aluminum Oxide NP stability in 1 wt% sodium hydroxide (NaOH)

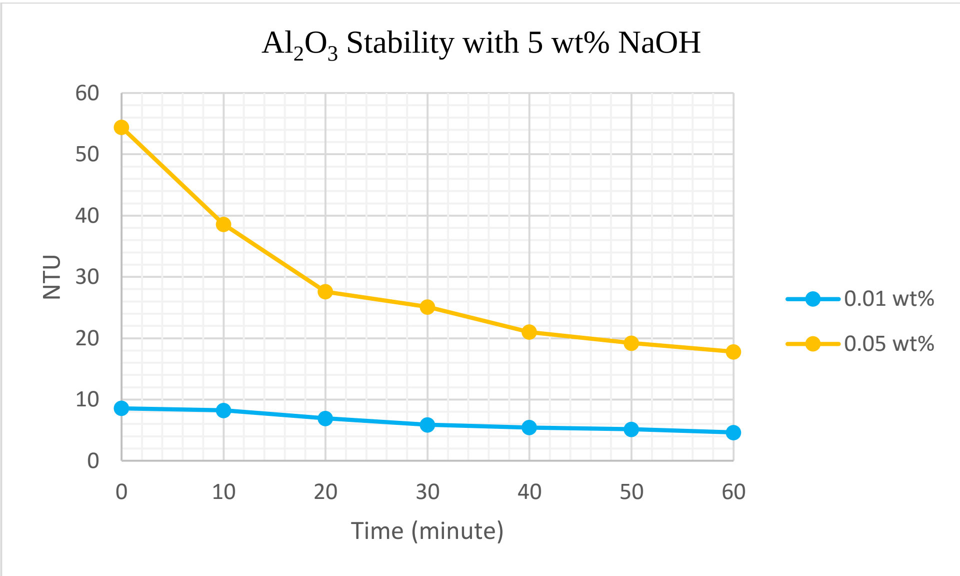

Figure 0.2: Aluminum Oxide NP stability in 5 wt% sodium hydroxide (NaOH)

Figures 4.3 and 4.4 illustrate silicon dioxide nanofluids in different concentrations of NP and NaOH solvent. The NTU values for silicon dioxide nanofluids are low resulting in a much lower amount of suspended particles within the fluid. Although displaying low values ranging at highest 11 NTU, these nanofluids are stable from the start until the end of a one hour period. These results indicate that silicon dioxide nanoparticles were able to retain a longer retention time as compared to aluminum oxide nanoparticles.

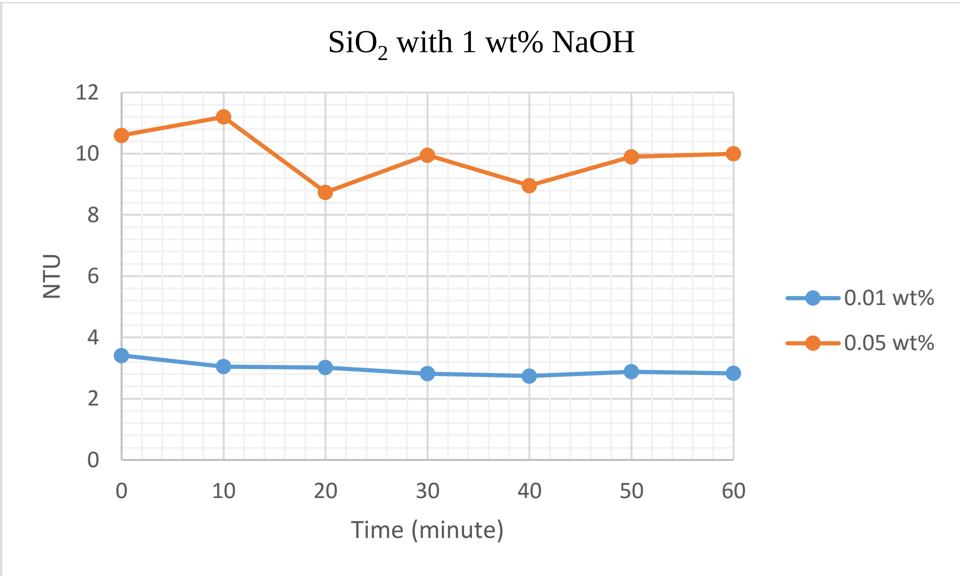

Figure 0.3: Silicon Oxide NP stability in 1 wt% sodium hydroxide (NaOH)

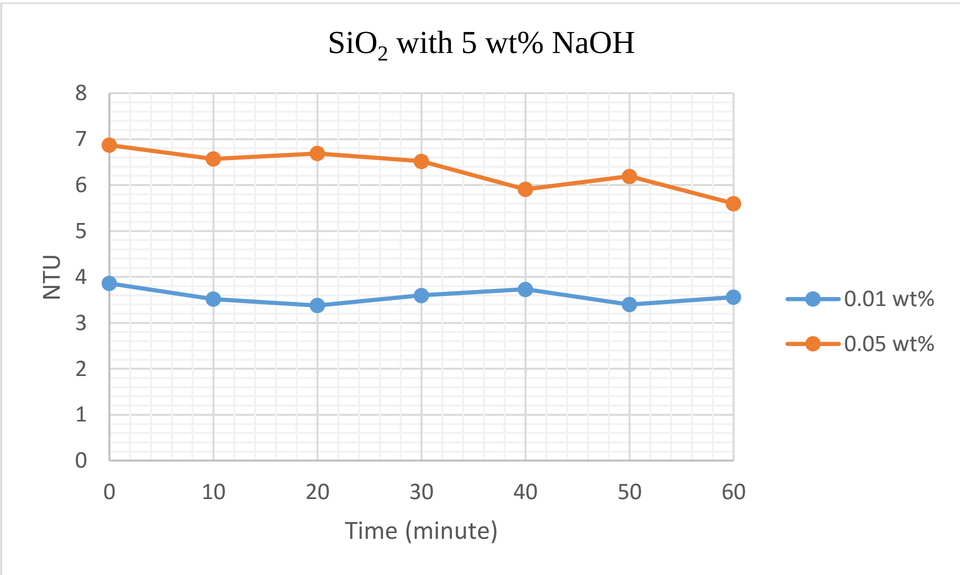

Figure 0.4: Silicon Oxide NP stability in 5 wt% sodium hydroxide (NaOH)

Table 0.1: Nanofluids pH Reading

NP wt%	Aluminum Oxide				Silicon Dioxide			
	0.01	**0.05**	**0.01**	**0.05**	**0.01**	**0.05**	**0.01**	**0.05**
NaOH	**1 wt%**		**5 wt%**		**1 wt%**		**5 wt%**	
pH	12.9	12.88	13.29	13.17	12.93	12.97	13.36	13.16

According to literatures, a nanofluid pH affects the stability of the nanoparticles within the fluid. A pH meter was used to measure the pH for each nanofluid and resulted in the same values of around pH 13 as shown in Table 4.1, which shows all the nanofluids are alkaline. The pH test was done as a control step in ensuring the pH consistency of the nanofluids prepared.

4.2 Nanofluid Injection

Brine at 3 wt% concentration of sodium chloride (NaCl) was injected into the sandpack vertically as seen in figure 4.5. This is done to emit the air bubbles within the sandpack itself. These air bubbles contribute to an error in calculating connate water saturation. The brine was injected at low rates of 0.5ml/min to fully fill all the pore spaces within the sandpack. Porosity calculations were done by methods of water and sand volume displacement (Appendix IV).

Figure 0.5: Brine (3 wt% NaCl) Injected into the Sandpack

Figure 4.6 shows the brine being displaced by crude oil (Tapis blend) until the sandpack was fully saturated with crude oil. Once the sandpack was visibly fully saturated with crude oil, the amount of brine displaced was recorded and connate water saturation was obtained by subtracting injected brine by brine collected as discussed earlier in the methodology. Nanofluids was then injected into the sand pack (Figure 4.7). The recovery of crude oil post injection process was tabulated in Table 4.2.

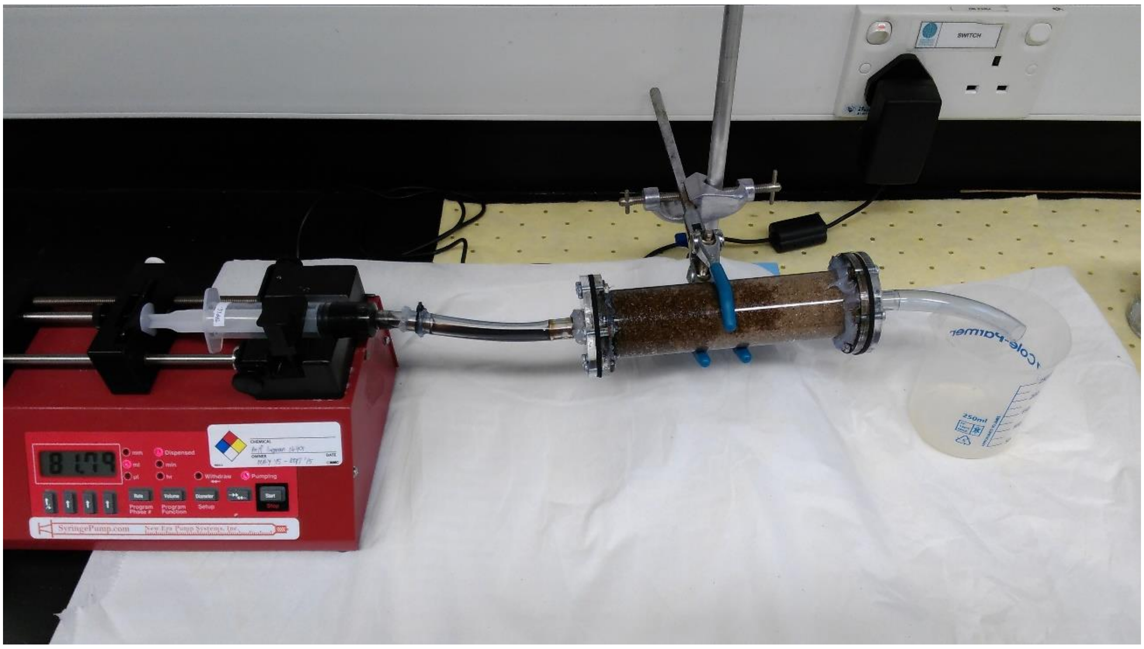

Figure 0.6: Tapis Crude Oil Injected into Sandpack

Figure 0.7: Nanofluid Injected into Sandpack

Table 0.2: Crude Oil Recovery by Various Nanofluids into the Sandpack

NP wt%	Aluminum Oxide				Silicon Dioxide				Brine 3 wt%
	0.01	0.05	0.01	0.05	0.01	0.05	0.01	0.05	
NaOH	1 wt%		5 wt%		1 wt%		5 wt%		
Injected Fluids									
Brine 3wt% (ml)	68.00	68.00	68.00	68.00	68.00	68.00	68.00	68.00	68.00
Crude (ml)	38.00	38.00	37.00	37.50	38.00	38.00	38.00	38.00	36.50
Nanofluid (ml)	32.00	30.00	35.00	35.00	25.00	24.00	38.00	20.00	-
Crude Displaced (ml)	28.00	30.00	29.00	27.00	25.00	20.00	28.00	22.8.	15.00 @41%
Crude Displaced due to NP (%)	74.00	79.00	78.00	72.00	66.00	53.00	74.00	60.00	-
Porosity	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Permeability (mD)	1313.60	1507.90	1322.40	1279.20	1322.40	1279.20	1313.60	1322.40	1322.40
Initial Water Saturation (ml)	30.00	28.00	29.90	30.40	29.90	30.40	30.00	29.90	29.90

Permeability calculations were done by utilizing a correlation by Timur as discussed in the literature (Appendix I-III). Permeability ranges around 1.3 D for the sandpack arrangements. Porosity on the other hand was calculated using volume displacing methods (Appendix IV). Porosity and permeability are two key elements in determining effectiveness of each nanofluids in displacing crude oil. In secondary drive mechanism, water injection deemed the most vastly used methods. In accordance to this research, water injection was simulated by displacing the crude oil within the sandpack with brine itself. As seen in Table 4.2, when only brine was used to displace crude oil, only 41% recovery was achieved. Aluminum oxide nanofluids reckoned the best recovery reaching 79% crude oil displaced at maximum. As shown in Table 4.2, 0.05 wt% aluminum NP mixed with 1 wt% NaOH recovered the most crude oil at 79%. While displaying a high value, the NTU for this nanofluid averaged out at around 16 NTU which is considerably high as compared to the other nanofluids. The high permeability value from this specific sandpack arrangement for the nanofluid at 1.5 D and high NTU value as compared to the rest were the factors to its highest recovery. However, when 0.01 wt% aluminum NP in 5 wt% NaOH was injected through a sandpack with permeability value of around 1.3 D, the recovery was the second highest at 78%. The NTU value for this nanofluid was only averaged around 4 NTU which is considered low. Although recording a low value in the NTU, the recovery was significant and the permeability was averagely the same as the other sandpack arrangements.

When injecting 0.05 wt% silica dioxide NP mixed in 1 wt% NaOH, the recovery was at 53% which showed the lowest value as compared to the other injection done. The NTU value for this nanofluid was around 10 which was higher than 0.01 wt% aluminum oxide NP in 5 wt% NaOH that recorded NTU value of 4. While displaying a higher NTU as compared earlier, the recovery deemed the lowest from the batch. The permeability value from this nanofluid's sandpack arrangement was also the lowest at 1.2 D as compared to the other sandpack arrangements which was the factor to its low crude oil recovery.

4.3 Discussion

Nanoparticles of higher concentrations in the respected nanofluids mixture will be well dispersed as compared to a much concentrated mixture. This is due to the aggregation effects of nanoparticles itself. A murkier mixture shows the nanoparticles retention in the nanofluids. A much longer time of retention leads to a better result ultimately. Although, recent findings have concluded that the nanoparticles concentration should not exceed a certain limit (ex: >0.6 wt%) with respect to its mixture due to the coagulation of the particles between itself. As seen from Table 4.2, two types of nanofluids which have the tendency to improve recovery were identified. These were 0.01 wt% aluminum oxide in 5 wt% NaOH and silica dioxide nanoparticles in 5 wt% NaOH. It is likely that aluminum oxide and silica dioxide nanoparticles improved recovery due to reduction of oil viscosity and change of formation wettability respectively. While aluminum oxide has been reported to reduce oil viscosity, silica dioxide has been known for its ability to change wettability.

In regards to interfacial tension (IFT) reduction, nanoparticles were able to reduce IFT due to less energy required to mobilize and remove oil trapped in the formation. This is a useful mechanism in recovering trapped oil in dead end pores by making the hydrocarbon mobile.

Porosity and permeability were the key factors in nanoparticles dispersion through a porous media. The aim in utilizing nanoparticles is to redirect trapped crude in micro pores enabling it to flow. However, this research utilizes a sandpack arrangement which yields a much larger porosity and permeability value of 0.45 and around 1.3 D respectively. The higher values lead to a greater recovery of crude post injection of nanofludis into the sandpack. Similarly, the volume of nanofluid injected into the sandpack varied which leads to understanding an early fingering of nanoparticles through the sandpack despite the large value of porosity and permeability.

Solvent mixtures are also a key in understanding the nanofluids behavior to coagulate and retain a longer retention time. This research utilizes sodium hydroxide (NaOH) as a solvent in maintaining the alkalinity of the nanofluids as discussed in the literature to avoid nanoparticles from attracting to each other. Also, literature proves that by increasing the pH of a nanofluid, aggregation was considered controllable. When nanoparticles start to coagulate, a much larger particle is formed and might risk the chance of plugging micro pores within the sand face itself. Likewise, when nanoparticles are dispersed evenly in a nanofluid together with a higher retention time, displacing hydrocarbon from micro pores is achievable.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

Fundamentally in concluding this research, the literatures resulted in a positive reaction to the renowned properties of silica dioxide and aluminum oxide nanopartices in aiding the effectiveness in EOR applications. Silica dioxide nanoparticles was chosen as a representative for hydrophilic oxides. While aluminum oxide nanoparticles represents metal oxides. This way, the difference in effectiveness from both groups could be determined. The experimental procedure of injecting through a sandpack was able to replicate a porous media in observing the nanofluids dispersion. Although, aggregation was a major factor in the dispersion criteria whereby nanoparticles tend to coagulate right after mixing in the carrier fluid in this case brine. With the aid of different concentrations of stabilizing agents in this sense, sodium hydroxide (NaOH), will opt for a better result to overcome the aggregation effect. In concluding the best option in nanofluid selection for best recovery, two nanofluids were identified, 0.01 wt% aluminum oxide in 5 wt% NaOH and silica dioxide nanoparticles in 5 wt% NaOH. Where both recorded a recovery of 78% and 74% respectively.

A sandpack was fabricated especially for this project and the parameters for porosity and permeability was manually calculated to further assure the effectiveness of these nanofluids. A further recommendation for this project is to better utilize a core plug to best represent the reservoir conditions and a much wider scope could be analyzed (example: High pressure and temperature ratings). The pressure and temperature could value a much wider result in further replicating the reservoir conditions and observe the effect of these parameters on the nanoparticles itself. Otherwise a steel sandpack can also be used instead of the acrylic material used to overcome the brittleness of the material.

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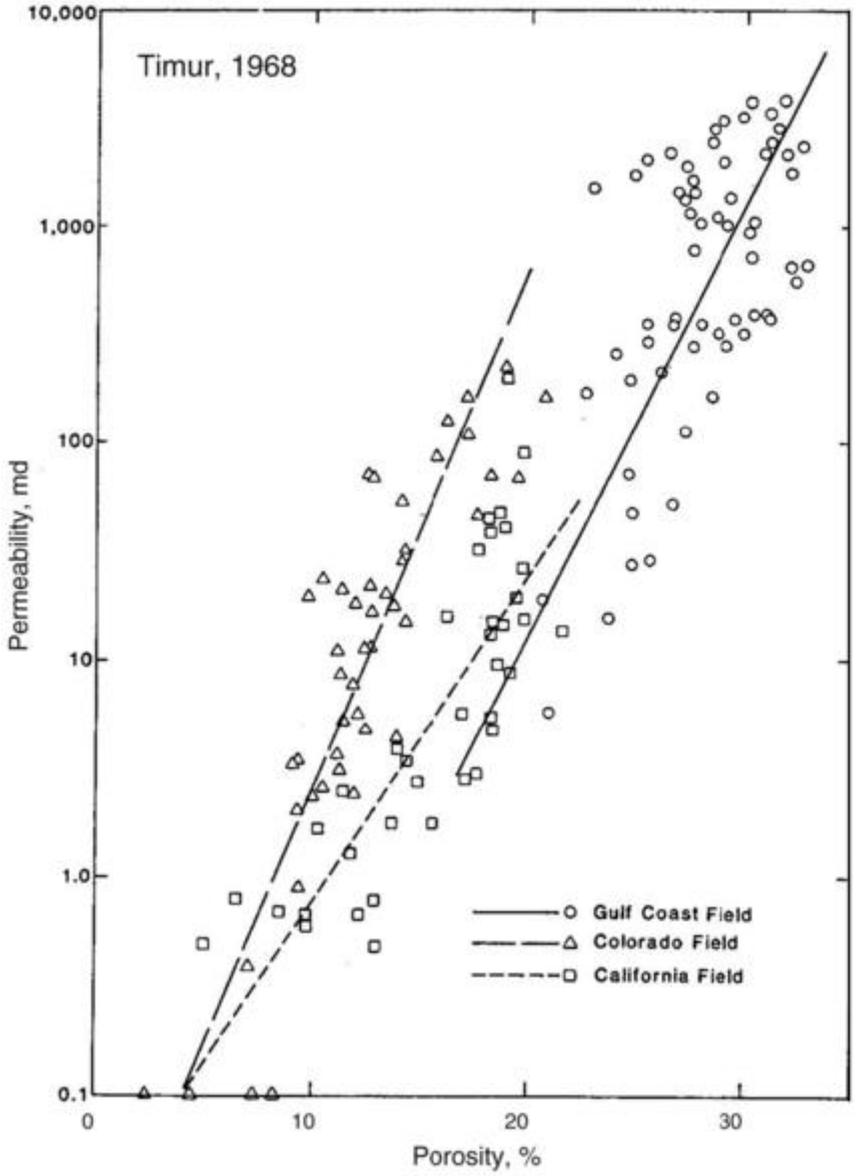
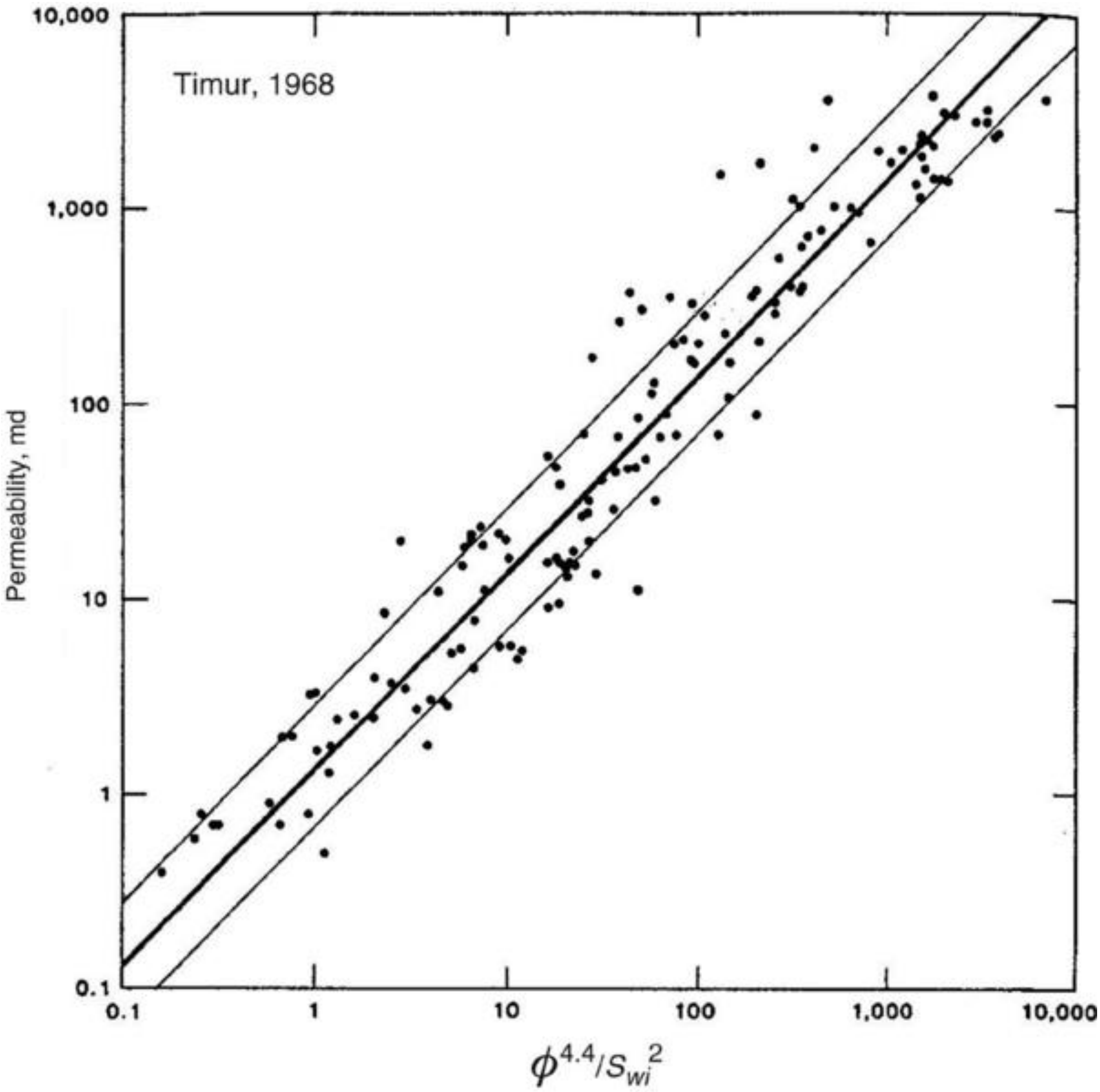
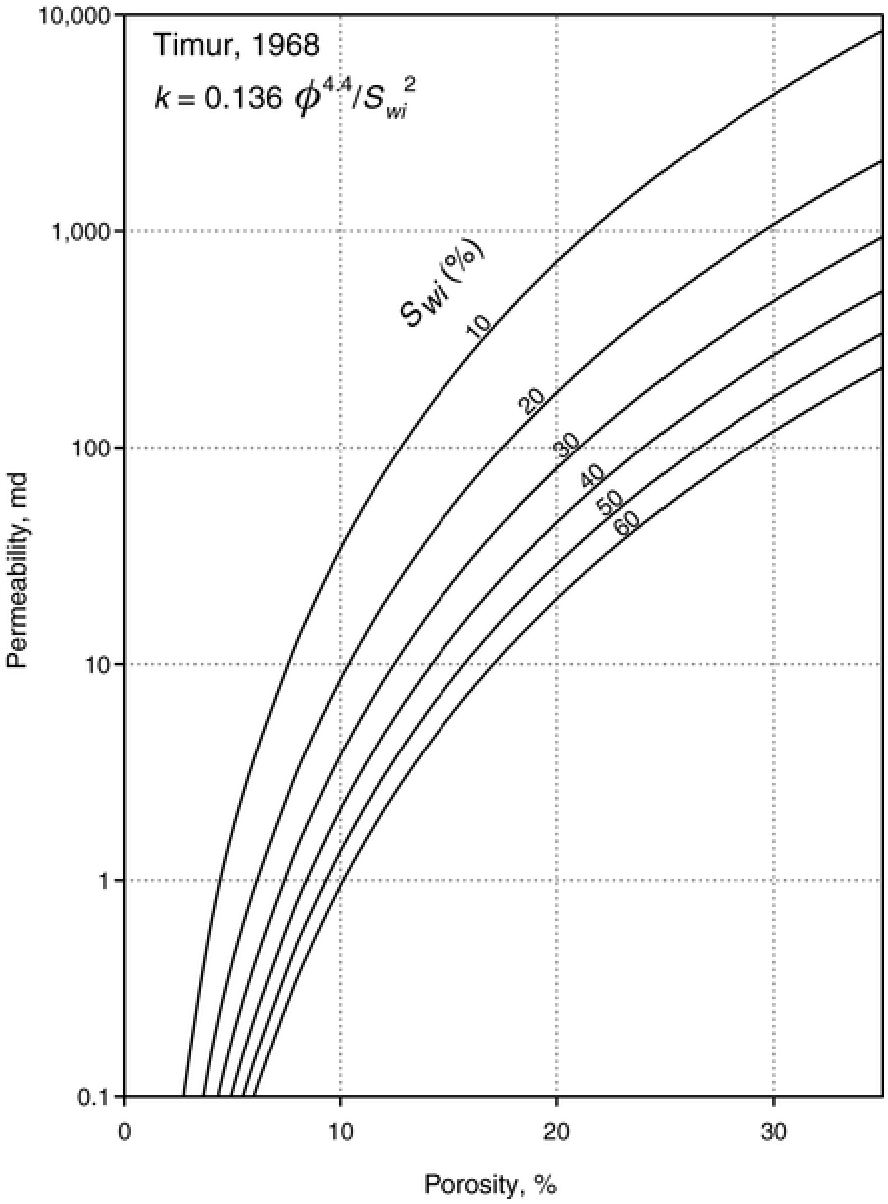
APPENDICES



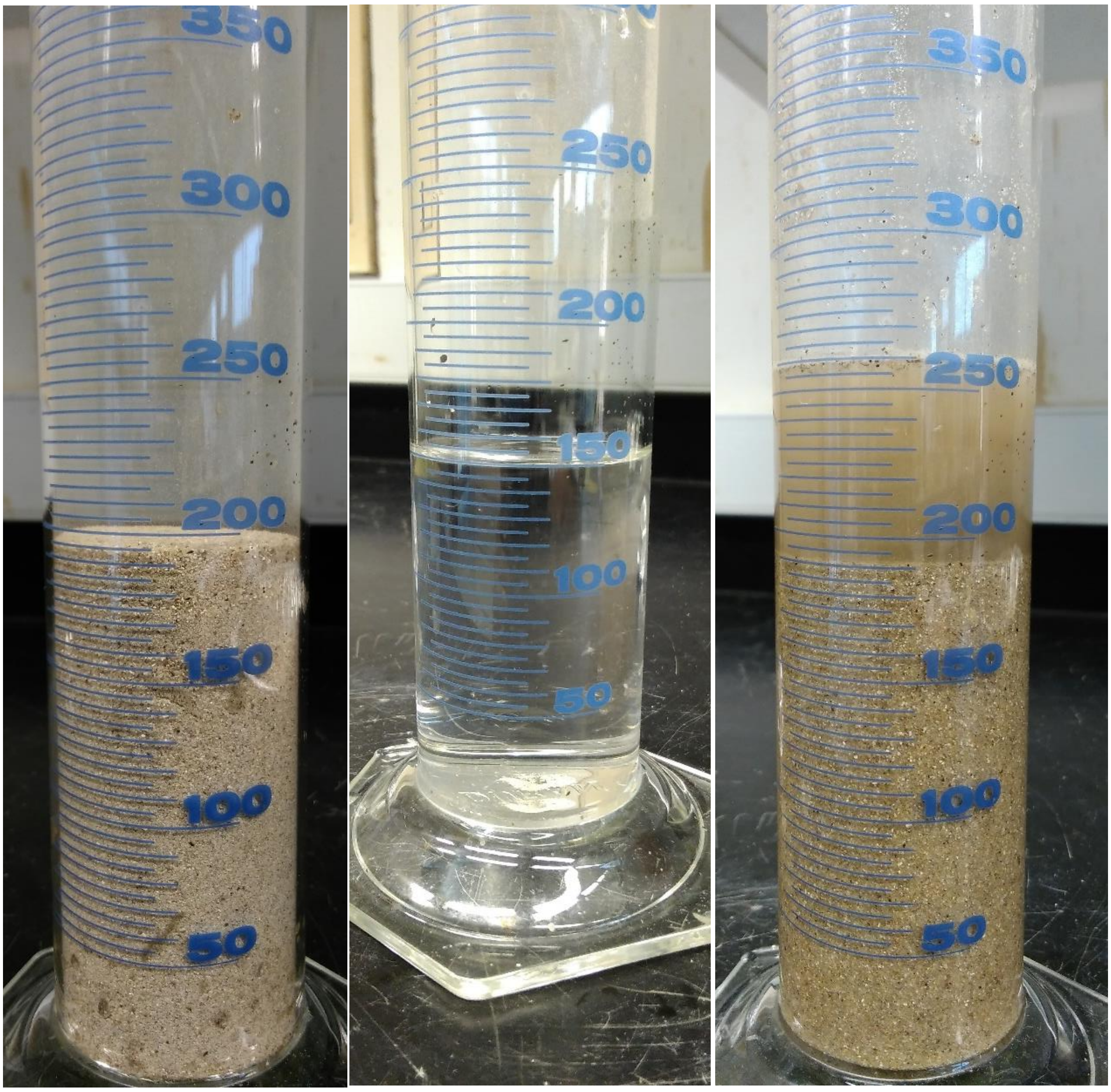
Appendix I: Permeability/porosity data from three US oil fields by Timur. (Timur, 1968)



Appendix II: Permeability data from three US oil fields as a function of $\phi^{4.4}/S_{wi}^{2}$, after Timur. Two bounding lines represent the standard error band that includes 68% of the sample points. (Timur, 1968)



Appendix III: Permeability/porosity relationship with irreducible water saturation as a parameter, after Timur. (Timur, 1968)



Appendix IV: Volume measurement via water displacement method to calculate pore volume of sand (From left: dry sand 188ml, water 150ml and wet sand 250ml).