

Non-thermal Recovery of Heavy oil and Oil Sands Using Nanoparticle

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DEDICATION

I want to dedicate this work to every individual who helped human beings and lost their lives during the COVID-19 pandemic, all the doctors, nurses, and every person that helped another person until science can overcome this novel virus.

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I like to express my sincere gratitude towards Dr. Konstantinos Kostarelos for his great support of my research, his patience, knowledge, and all of his unconditional help. I am really grateful and honored for having the chance to work under him during this research.

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Abstract

Heavy oils and oil sand resources are considered the largest portion of known energy resources, comprising 70% of total resources. Still, there is potential to increase oil production from these resources to fulfill future global energy needs. There have long been serious critiques of the methods and processes that are currently used to extract oil from these reservoirs because of their low efficiency and negative effects on the environment, particularly with respect to oil sands; there is room to improve efficiency and using new methods. A more efficient method that improves the recovery from heavy oil reservoirs with a smaller carbon footprint would benefit regions with extensive heavy oil resources like Venezuela, Canada, and several states in the USA. Sodium nanomaterial has the potential to be an alternative method for heavy oil resources because it initiates a series of reactions, has low surface energy consumption, and has low waste production.

In this study, we employed sodium nanoparticles to investigate the recovery improvement relying on the unique reactions that produce heat, gas, and in-situ surfactant (“soap”). Next, we applied this method to extract oil from Athabasca oil sand samples. We flooded a heavy oil-saturated sand pack in a core holder with nanofluid suspended in a dispersant fluid to see the incremental recovery that can be realized after an initial brine flood process and compared it to a baseline experiment using only dispersant fluid. We also conducted a series of static and dynamic tests to investigate the efficiency of nanomaterial, and alkali fluid generated by a nanofluid, on total oil extraction. This project concluded that sodium nanofluid can affect recovery from heavy

oil resources based on our results, which extracted a significant amount of oil from oil sands.

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Nomenclature

Acronyms

API	American Petroleum Institute
bbls	Barrels
BPR	Backpressure regulator
CHOPS	Cold Heavy Oil Production with Sand
cm	Centimeters
DI	De-ionized water
EOR	Enhanced oil recovery
g	Grams
GC	Gas chromatography
GC-MS	Gas chromatography and mass spectrometry
GOR	Gas oil ratio
IFT	Interfacial tension, dynes/cm
IOR	Improved oil recovery
L	Liters
M	Mole per liter
ml	Milliliter
mm	Millimeter
OOIP	Original oil in place
psig	Pounds per square inch, gauge
psia	Pounds per square inch, absolute
PV	Pore volume
ROIP	Residual oil in place
SAGD	Steam Assisted Gravity Drainage
TAN	Total acid number
TDS	Total dissolved solids

WAG	Water Alternating Gas
wt.	Weight

Symbols

A	Area, cm ²
C	Concentration, wt% or ppm
cP	Centipoise
k	permeability, md
L	Length, inch or cm
p	pressure, psia or psig
Δp	pressure gradient, psi
q	rate, cm ³ /min
RF	Recovery Factor

Greek

λ	Mobility, md/cp
μ	viscosity, cp
ρ	density, g/cm ³

Chapter 1

Introduction

This study applies an innovative method of nanofluid injection for its unique properties and reactions for the purpose of enhanced oil recovery (EOR) in heavy oil and oil sand reservoirs.

1.1 Background and Motivation

Heavy oil and extra heavy oil comprise nearly 40% of world oil reserves. The terms “heavy” and “extra heavy” oil are used for oils with low API gravity (high specific gravity) and low viscosity. Specifically, heavy oil is defined as oil that having 22.3 API or less, and oil of 10 API or less are known as extra-heavy, ultra-heavy, or super heavy because they are denser than water. In comparison, conventional oils such as Brent or West Texas Intermediate crudes have densities from 38 to 40 API (Alboudwarej and Shawn, 2006; Dusseault, 2001).

The economic value of heavy oil reservoirs is currently difficult to assess due to current oil market instability. These reservoirs comprise a large share of hydrocarbon reserves that could help meet future energy demand. Heavy oil promises to play a major role in the future of the energy industry. Many countries are mobilizing now to increase their production, revise reserve estimates, test new technologies, and invest in infrastructure to ensure that their heavy oil resources are available when the market demand increases (Alboudwarej and Shawn, 2006).

Most of the 6 to 9 trillion barrels of heavy oil, extra-heavy oil, and bitumen that exist in the world are accumulated in similar geologic settings (Alboudwarej and Shawn, 2006). These are super-giant, shallow deposits trapped on flanks of basins and normally unconsolidated, high porosity and permeability sand deposits (Alboudwarej and Shawn, 2006; Bryan and Kantzas, 2008). Significant deposits have been found in countries like the United States, Canada, China, Venezuela, and Albania (AEUB, 2007; Bryan and Kantzas, 2008).

The methods for recovery of heavy oil is divided into two main groups according to temperature and whether thermal energy addition is required. Non-thermal methods can be used when the viscosity of the oil is low enough to allow the oil to flow and be produced at reservoir temperatures. Thermal methods are used when a temperature increase is required for the hydrocarbon to flow (Alboudwarej and Shawn, 2006).

The original non-thermal method is open-pit mining. which normally has good recovery, however, the excavated material is processed using a thermal hot water method. It is also limited to resources close to the surface, typically less than 75 meters deep. Non-thermal methods include the production of heavy oil from horizontal multilateral wells located to contact as much areal extent as possible, where a diluent such as naphtha is injected to decrease fluid viscosity (Alboudwarej and Shawn, 2006). There are restrictions to this method such as drilling cost and environmental considerations regarding the use of the diluent. Technical considerations are also important. To drill horizontal sections at the shallow depths, high doglegs are required

that can lead to rod or tubing failures. In clusters where several productive layers will be drilled, there may also be a risk of collision (Villarreal and Hernández, 2013).

Thermal methods consist of the injection of fluids to increase the temperature to decrease the viscosity of the oil. The three well-known techniques are cyclic steam stimulation (CSS), steam flood, or steam-assisted gravity drainage (SAGD). These methods all have some advantages and limitations: for thermal methods, recovery is normally higher than nonthermal methods (except for open pit mining) but there are associated costs to generate steam and subsequent water treatment of the produced water. It is worth pointing out that over half of the heavy/extra heavy oil occurs in reservoirs that are not suitable for thermal methods for technical or economic reasons. This is the case when the formations are thin (<10 m), depths are large (>1000m), formation permeability is too low to permit high injection rates, or the oil saturation is low, perhaps combined with low porosity. Under such conditions, a non-thermal recovery method may be employed, which may be further modified for a viscous oil (Alboudwarej and Shawn, 2006; Selby et al., 1989).

Another method studied to increase the production of moderate and high viscosity oil is caustic injection. Caustic flooding involves the injection of alkaline fluids into reservoirs that react with naphthenic acids in crude oils, lowering the interfacial tension and forming an oil/water emulsion. The most common alkaline used is sodium hydroxide (Selby et al., 1989). Previous studies showed that oil recovery increased considerably when sodium hydroxide was added to the brine at concentrations between 0.01% and 0.1% (Scott et al., 1965; Selby et al., 1989). Some previous studies showed that

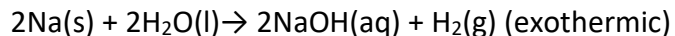
by the use of caustic fluid injection, oil recovery increased from 32% to 60% (Ali et al., 1979; Selby et al., 1989).

In recent years, nanotechnology has attracted attention for enhancing oil recovery due to increased cost-effectiveness and environmental considerations. The size of the nanoparticles that are used in EOR technologies is usually in a range of 1-100 nm (Negin et al., 2016). Nanoparticles exhibit significantly different properties compared to the bulk materials due to the much higher surface area. One of the most useful properties of these particles is to create a massive diffusion driving force due to the large surface area, especially at high temperatures (Negin et al., 2016).

The ability of nanoparticles to alter the formation and oil properties can be advantageous. Examples include shifting reservoir wettability toward water-wet and reducing interfacial tension (Negin et al., 2016; Ogolo et al., 2012).

1.2 Research Objectives

The objective of this work is to investigate a new method to increase heavy/extra heavy oil recovery that combines the attractive features of nanofluids and the proven effects of caustic fluid flooding. A sodium nanofluid was used as an alternative method to injection of caustic fluid due to the unique reactions and by-products that are triggered inside the reservoir. Sodium nanofluid produces sodium hydroxide and hydrogen in an exothermic reaction that simultaneously increases the temperature, creates a gas that acts as a propellant to mobilize oil, while also providing the benefits of caustic flooding with the advantage that the nanofluid will be consumed where the brine is located.



The goal of the work was to experimentally observe the effect of the nanofluid injection on the recovery of heavy, viscous oil to compare with previous studies. Both batch testing and core floods were conducted. Heavy, viscous oil from a field in China was used in two high permeability, unconsolidated porous media consisting of synthetic sand. The oil-saturated sand pack was initially brine flooded followed by nanofluid to examine the incremental recovery. Oil sand from the Athabasca field in Canada was also used for similar flow experiments. The produced oil and total recovery were measured in produced samples using GC/MS analysis to determine the total recovered oil from the sand packs.

Chapter 2

Background

2.1 Resources Summary and Magnitude of Resources

Heavy and extra-heavy oils are one of the largest energy reserves in the world that can fulfill future energy needs. Bitumen and heavy oil reserves occur in more than 70 countries. The global in-place bitumen and heavy oil resources are estimated to be 5.9 trillion barrels [938 billion m³], with more than 80% of these resources found in Canada, Venezuela, and the United States (Bata et al., 2019).

Comparing the magnitude of conventional resources to heavy oil resources and global oil consumption allows us to understand how significant these heavy oil deposits are. In Table 2-1, world oil consumption is compared for conventional, recoverable oil in Saudi Arabia and the heavy oil resources of Canada and Venezuela. Both countries have a heavy oil resources base (OOIP) that is about an order of magnitude larger than that of Saudi Arabia (DOE, 2019; Dusseault, 2001).

Table 2-1: Comparison of Canada and Venezuela's heavy oil resources with Saudi Arabia's recoverable resources

Comparison basis	Barrels of oil
Daily global oil consumption	100,000,000
Saudi Arabia recoverable oil	250,000,000,000
Venezuelan oil in place ¹	1,200,000,000,000 ²
Canadian oil in place	2,200,000,000,000

Total in-place reserves include both recoverable and irrecoverable reserves. These separate estimates depend upon both technology and economic conditions. Generally, recoverable heavy oil value increases with time because of innovations in technology and the reduction of conventional oil resources.

A current goal of the United States is to move towards sustained energy independence including production from known domestic oil sand deposits. Schenk et al. (2002) compiled total measured, and speculative estimates of bitumen in-place amounting to about 54 billion barrels [8.6 billion m³]. This was comprised of 29 major oil sand accumulations in Alabama, Alaska, California, Kentucky, New Mexico, Oklahoma, Texas, Utah, and Wyoming (Table 2-2). These estimates of total oil sand resources provide only limited guidance for the potential commercially-viable, environmentally

¹This estimate is one of pessimistic estimates compared to different sources

responsible development of these resources. The resources in each of the states have distinct characteristics that influence current and/or future exploitation (Bata et al., 2019; Schenk et al., 2006).

The distribution of heavy oil around North America shown in Figure 2-1:



Figure 2-1: Location of the heavy-oil/bitumen deposits in America: (A) Main deposits(black dots), including Alberta, Alaska, California, and Utah; (B) Secondary deposits(white dots), including Pine Point and Melville Island, NWT, Canada; Albert Mines, NB; Gays River, Jubilee, Lake Ainslie, NS; Bay St. George, Port-au- Port, NF, Maritimes Basin, eastern Canada; SW Texas and Mid-Continent U.S.A.(Hein, 2006)

Table 2-2: Data of heavy oil resources in the United States

state	no. deposits	API range	measured MMB	measured+speculative MMB
Utah	10	-2.9 to 10.4	11,850	18,680
Alaska	1	7.1 to 11.5	15,000	15,000
Alabama	2	NA	1,760	6,360
Texas	3	-2.0 to 7.0	3,870	4,880
California	6	0.0 to 17.0	1,910	4,470
Kentucky	4	10	1,720	3,410
New Mexico	1	12	130	350
Wyoming	2	NA	120	145

California has exploited heavy oil reserves that amount to greater than 100 million barrels [15.9 million m³]. They are located in the central and southern parts of the state that have the ability to provide a lot of energy for the future of United States energy independence. As of the end of 2017, California's proven reserves were 2,204 million barrels [350.4 million m³] (Bata et al., 2019; U. S. Energy Information Administration, 2016).

Several heavy oil fields are operating in the United States and particularly in California. Except for Poso Creek, all of the principal oil fields in the San Joaquin basin experienced oil production declines in the three years 2015-2017 on the order of 2.4% (Cymric) to 35.1% (Placerita). The three largest fields experienced declines of 7.6% (South Belridge), 14.6% (Kern River), and 21.6% (Midway-Sunset). The Cymric and Coalinga

fields, which earlier in the decade saw respectable increases in production, had the smallest three-year declines of 2.4% and 3.0%, respectively. Even the relatively young (1952) San Ardo field, which had been expanding, saw a 7.2% decline in 2015-2017 (Harris, 2017; Hein, 2006). As the production rate declines in heavy oil fields, the need for new and more efficient methods to increase production rates and improve recovery factors is necessary.

2.2 Enhanced Oil Recovery

Oil recovery processes have been defined as primary, secondary, and tertiary. (EOR) that follow a natural progression of oil production from the start to a point where it is no longer economical to produce. Recovery, especially EOR, is closely associated with the oil price and overall economics (Kokal and Al-Kaabi, 2010).

Primary processes produce oil by natural production into a producing well. Secondary recovery consists of providing energy through injected water or natural gas (Simon, 1981). When secondary recovery is no longer economic, additional supplemental energy of different kinds allow additional oil recovery. A critical distinction that should be noted is that this energy is in addition to, or instead of, the natural or physical displacement mechanisms of the primary or secondary methods.

Enhanced fluid flow conditions within the reservoir are usually induced by the addition of heat, chemical interaction between the injected fluid and the reservoir oil, mass transfer, and/or changing oil properties to facilitate oil movement through the reservoir. Tertiary recovery processes include thermal, chemical, gas miscible, and

microbial methods. They are also often referred to as enhanced oil recovery (EOR) processes (Stosur et al., 2003). The EOR definitions are summarized in Figure 2-2 (Kokal and Al-Kaabi, 2010; Stosur, 2003; Stosur et al., 2003).

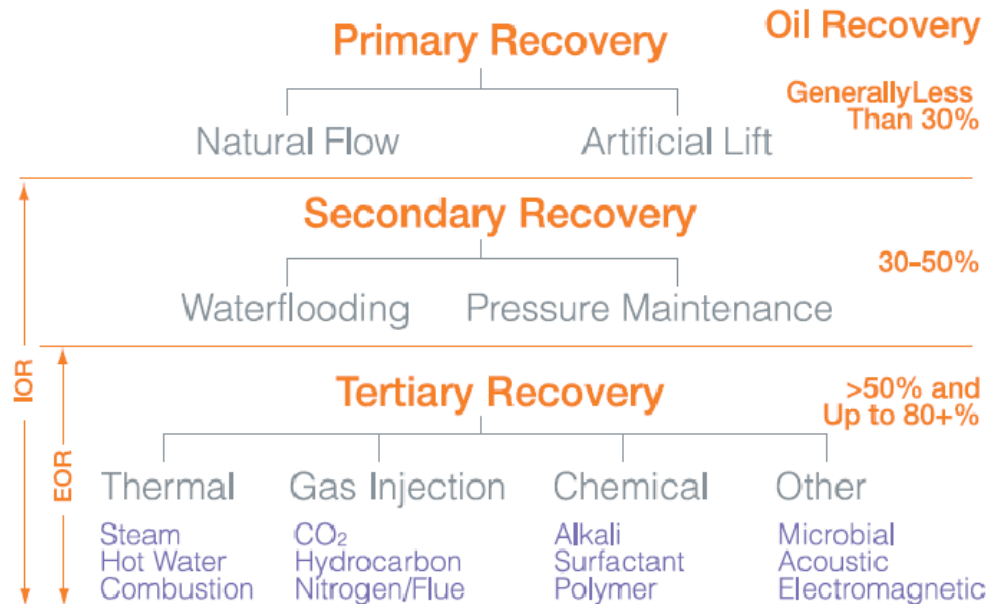


Figure 2-2: EOR/IOR definition

2.3 Heavy Oil Recovery

Compared to the production of conventional oils, heavy oil recovery is problematic due to the fluid properties, high viscosity, high carbon/hydrogen (C/H) ratios, and high heteroatom contents (Guo et al., 2016; Speight, 2013a, 2013b). In the production of heavy oils, primary and secondary recoveries are dominated by cold production and water floods. Similar to Canadian oil sands, Venezuelan heavy oils, and UK Continental

Shelf, these recovery methods are limited to relatively shallow reservoirs or only effective to lighter heavy oils.

To achieve a higher recovery factor, tertiary recovery, or more widely-known as enhanced oil recovery (EOR), is necessary to extract oils left behind by the primary and secondary recoveries (Guo et al., 2016; Shah et al., 2010). Among recovery methods, thermal injection is recognized as a technically effective one with high recovery factors up to 70% of the original oil in place (OOIP). Typical thermal recovery includes steam-assisted gravity drainage, cyclic steam stimulation, and in-situ combustion. These technically successful methods are still challenged economically because of the high cost of heat supply, and environmentally due to excessive carbon dioxide (CO₂) emission and costly post-treatment and maintenance (Zhao et al., 2014; Guo et al., 2016).

For these reasons, there is a need for research on non-thermal, effective methods that can reduce the challenges of thermal methods. Several non-thermal methods have been researched such as polymer flooding, immiscible carbon dioxide flooding, and caustic flooding, with some of them showing favorable results in moderate and high viscosity reservoirs.

2.3.1 Polymer Flooding

Mobility ratio is defined as the mobility of the displacing phase divided by the mobility of the displaced phase. A mobility ratio below 1 generates an improved displacement efficiency, i.e. holding other parameters constant (Fletcher et al., 2012; Guo et al., 2016). When operating a polymer flood, a polymer with high molecular weight is

added to the water phase to increase the viscosity, resulting in a decrease in the mobility of water and thus improve the displacement efficiency. A viscosifier also improves the areal and vertical sweep efficiency of the injected fluid that, when combined with displacement efficiency improves the overall efficiency.

Compared with surfactant flooding, polymer flooding is more sensitive to rock permeability. The fact that the rock tends to act as a filter and retain polymer during the transport process means this technique is only applicable to highly porous rock. While high polymer molecular weight and size can increase the aqueous viscosity, it will also increase the difficulty for polymers to maintain mobility. A similar trade-off is also made with respect to the polymer concentration. The interaction between polymer molecules and the reservoir rock should be considered to minimize polymer retention, which originates from surface adsorption, mechanical entrapment, and polymer degradation. It is also reported that pH value, brine salinity, clay content, and reservoir temperature exhibit a significant impact on the technical and economic success of polymer flooding (Chen et al., 2015; Choi, 2010; Guo et al., 2016; Pu et al., 2015).

2.3.2 Carbon Dioxide Flooding

The mechanisms that contribute to oil recovery by injection of carbon dioxide (miscible) are oil viscosity reduction, oil swelling, interfacial tension reduction, emulsification, and blowdown (Selby et al., 1989). Because of the high solubility of CO₂ in oil, the oil volume increases, and the viscosity decreases when contacted with carbon dioxide under certain temperature and pressure conditions (Holm, 1963; Selby et al., 1989). Carbon dioxide dissolution into oil lowers the oil/brine interfacial tension and

leads to the formation of an acidic emulsion. The solubility of carbon dioxide in crude oil decreases with decreasing pressure, as the pressure of a CO₂-saturated oil is reduced, CO₂ evolves from the oil providing a solution gas drive mechanism (Chung and Burchfield, 1987; Selby et al., 1989). Another mechanism associated with CO₂ flooding is the trapped-gas effect, in which a free gas saturation, formed by CO₂, replaces part of the residual oil in the reservoir, maintaining reservoir pressure (Holm, 1982; Selby et al., 1989).

Since CO₂ viscosity (~0.01 cP) is much smaller than that of heavy oils, CO₂ flooding suffers severe viscous fingering and conformance issues. An early breakthrough occurs from relatively higher permeable layers and consequently, large amounts of recoverable oils remain untouched. In addition, the lower density CO₂ will move upwards within the reservoir, a situation is known as gravity override, which further reduces the recovery efficiency (Huc, 2010; Guo et al., 2016).

To confront the above limitations, CO₂ flooding is selectively applied to reservoirs with depths over 800 m, where the higher reservoir pressures will ensure that the CO₂ will remain in a supercritical state upon injection and the oil density will be typically lower (Guo et al., 2016; Speight, 2013c). In addition, the idea of synergistically combining chemical and gas recovery can be realized by adding surfactants to generate CO₂ foams, so that the viscosity of the injected fluid (foam) significantly increased. Foam-assisted CO₂ flooding has been a focused research area for many years, with both laboratory and field-scale pilot tests being extensively conducted. It has been shown that CO₂ foam can significantly reduce the mobility of CO₂ in high permeability layers which can lead to

improving swept volume in the low permeability zones of the formation (Andrianov et al., 2012; Guo et al., 2016; Jian et al., 2019; Nguyen et al., 2014; Worthen et al., 2012).

2.3.3 Caustic Flooding

Caustic flooding involves the injection of alkaline materials, which reacts with the crude oil, resulting in lowering the oil/water interfacial tension and forming an emulsion. The most common alkaline material used is sodium hydroxide, other alkaline agents include sodium silicate, sodium carbonate, sodium phosphate, ammonium hydroxide, and ammonium carbonate. Three types of reactions are known to occur during caustic injection: alkali-oil reactions, alkali-water reactions, and alkali-rock reactions (Gogarty, 1983; Mayer et al., 1983; Selby et al., 1989).

In alkali-oil reactions, alkaline fluid reacts with organic acids that commonly exist in heavy oils, resulting in the formation of natural surfactants. The natural surfactant reduces the IFT between oil and water and, improves oil recovery (Doorwar and Mohanty, 2011; Guo et al., 2016). Alkali-water reactions serve to reduce the activity of multivalent cations present in the reservoir brine by forming precipitates. The reduction of cations in the brine leads to increased surfactant activity and lowers the interfacial tension. The precipitate formed can lead to improving oil recovery by blocking the more permeable flow channels. Alkali-rock reactions can be detrimental to alkaline flooding because they often constitute the main cause of caustic consumption. Caustic consumption rates are high for clays and low for quartz, calcite, and dolomite. Alkali-rock reactions also can result in the altered wettability of the medium. The wettability can be reversed either

from water-wet to oil-wet or vice-versa, depending on the flooding process involved (Selby et al., 1989).

Caustic flooding may improve oil recovery by four different mechanisms: emulsification and entrainment, wettability reversal, and emulsification and entrapment. Each mechanism occurs due to the different initial conditions with respect to reservoir oil, rock, and injection water properties. Each process is designed to improve oil recovery depending on reservoir conditions (Johnson Jr, 1976).

2.3.3.1 Emulsification and Entrainment

Reisberg and Doscher, working with a Ventura crude oil, placed primary importance on lowering interfacial tension, resultant oil-in-water emulsion formation, and production of the oil as an emulsion in the produced caustic solution. They also felt that the ability of caustic to prevent adherence of oil to sand surfaces and to suppress semi-solid film formation at the oil/water interface played a role (Johnson Jr, 1976). As a result, they concluded that caustic flooding, even with added surfactants, was not a practical EOR process. This was attributed to adsorption effects, reaction with rock, and displacement of connate water would cause the alkali to lag behind the oil-water displacement front. They believed that this would preclude any increase in oil recovery before water breakthrough and would delay production of extra oil until after several pore volumes of caustic had been injected, an economically unfavorable situation. Nevertheless, Doscher and Reisberg did obtain a Canadian patent on the injection of sodium hydroxide into tar sands as a caustic-drive oil recovery process (Johnson Jr, 1976).

2.3.3.2 Wettability Reversal (Oil-Wet to Water-Wet)

Wagner and Leach (1959) presented laboratory tests showing improved oil recovery through the injection of water solutions that reverse rock wettability from oil-wet to water-wet. This was accomplished by adding chemicals that changed injection-water pH including acids, bases, and some salts (Johnson Jr, 1976; Wagner and Leach, 1959).

Mungan published additional laboratory work on wettability effects and caustic flooding, he found the process to be temperature-dependent, working well at 160°F but not at all at 70°F for the particular crude oil used. He also demonstrated that water relative permeability was lower after caustic-wettability reversal from oil-wet to water-wet, giving a more favorable water-oil mobility ratio even though water saturation reached higher values (Johnson Jr, 1976; Mungan, 1966).

2.3.3.3 Wettability Reversal (Water-Wet to Oil-Wet)

Cooke et al. reported a third mechanism by which caustic sodium hydroxide could improve waterflood oil recovery (Cooke Jr et al., 1974). They observed that under proper conditions of pH, salinity, and temperature, some crude oils, and porous media are converted from water-wet to oil-wet. If the composition of the crude oil is favorable, wettability can be reversed, and oil-water interfacial tension can be simultaneously lowered to very low values by the right combination of caustic and salt. Low interfacial tension is achieved by the reaction of alkali with organic acids in the crude oil to form soap.

The mechanics of the process involve first the conversion of water-wet rock to oil-wet. A discontinuous, nonwetting residual oil is converted to a continuous wetting phase, providing a flow path for what otherwise would be trapped oil. At the same time, low interfacial tension induces the formation of an oil-external emulsion of water droplets in the continuous, wetting oil phase. These emulsion droplets tend to block flow and induce a high-pressure gradient in the region where they form. The high-pressure gradient, in turn, is said to overcome the capillary forces, already decreased by lowered interfacial tension, thus reducing residual oil saturation further. Drainage of oil from the volume between emulsified alkaline water drops leaves behind a high water-content emulsion in which residual oil saturation may be as low as 5 percent PV (Cooke Jr et al., 1974; Johnson Jr, 1976).

2.3.3.4 Emulsification and Entrapment

Jennings et al.(Jennings Jr et al., 1974) proposed a fourth mechanism by which caustic injection can improve oil recovery. Their laboratory experiments showed that if interfacial tension were low enough, residual oil in a preferentially water-wet core could be emulsified in situ, could move downstream with the flowing caustic. The oil would be entrapped again by pore throats that too small for the oil emulsion droplets to penetrate. This mechanism of emulsification and entrapment results in reduced water mobility that improves both vertical and areal sweep efficiency. This is especially important in waterflooding viscous oils where waterflood sweep efficiency is notoriously poor. Because the emulsified oil is quickly entrapped again, it is not recovered and, on average, no significant reduction in the capillary-retained residual oil saturation is anticipated.

The reason that the emulsified oil does not get produced is that the interfacial tension is not low enough to let the emulsion droplets penetrate the smaller pore-throats. The pressure drop also not uniform, it increases near the wellbore so the regions with high pressure drop are not volumetrically large (Jennings Jr et al., 1974; Johnson Jr, 1976).

2.3.3.5 Important Factor Affecting Caustic Flooding

The wealth of literature on caustic flooding indicates that the composition of the crude oil is crucial to the caustic flooding process. The nature of the polar compounds in the crude oil determines whether the mechanism involves a wetting change or emulsification, and what ion concentrations will be effective. The literature also points to the importance of the water composition; significant concentrations of multi-valent cations, such as calcium in the water used for the caustic slug should be avoided. Sodium chloride, being monovalent, can help alter the effect of caustic on rock wettability, as well as in lowering the caustic concentration required to achieve minimum interfacial tension (Johnson Jr, 1976).

Rock properties are also a factor in caustic flooding, although the quantitative nature of rock effects on the recovery process is less clear. Caustic reaction with rock may be responsible for inducing a favorable wettability. Reaction with rock also consumes caustic, and this can render the caustic process inoperable. Mechanisms like emulsification and entrainment or wettability reversal (water-wet to oil-wet), which require caustic to traverse the reservoir before oil recovery increases can be realized. They will be more vulnerable to high rock reactivity than mechanisms like wettability reversal (oil-wet to water-wet) or emulsification and entrapment. Mobility ratio

improvements behind the flood front can cause substantial increases in oil recovery before caustic or even water breakthrough (Johnson Jr, 1976).

2.4 Nano Particles

The application of nanoparticles for EOR purposes is a new tool that is still under development. The types of nanoparticles that can be used for EOR and some basic information about nanoparticles will be discussed below. The increased interest in nanotechnology-related research and development is reflected in the funds invested in nanotechnology research and development. The NNI (National Nanotechnology Initiative) alone has received almost \$27 billion including their proposed budget for 2019. \$350 million was invested by the Massachusetts Institute of Technology (MIT) for a state-of-the-art nanoscale research center named "MIT.nano". "NanoMech", which is a leading company in nanomanufacturing, received a \$10 million investment from Saudi Aramco Energy Ventures (Alsaba et al., 2020).

Nanotechnology is described as the design, production, and use of substances at the nanometer (nm) level. Generally, the substances with dimensions on the order of 1-100 nm are called nanoparticles. The emphasis is on controlling, manipulating, and engineering of nanoparticles (Kapusta et al., 2012). In general, there are two main approaches to nanoparticle production commonly referred to as "top-down" and "bottom-up". Top-down nanoparticles are generated from the size reduction of bulk materials. They generally rely on physical, the combination of physical and chemical, electrical, or thermal processes for their production. Such methods include high-energy

milling, mechano-chemical processing, electro-explosion, laser ablation, sputtering, and vapor condensation (Casey, 2006; Christian et al., 2008).

The more convenient method for producing nanoparticles on a commercial scale is to use a bottom-up approach where a nanoparticle is “grown” from molecules. The size of the nanoparticle may be controlled in several ways such as limiting the concentration, functionalizing the surface of the particle, or using a micelle to template the growth (Figure 2-3) (Casey, 2006; Christian et al., 2008).

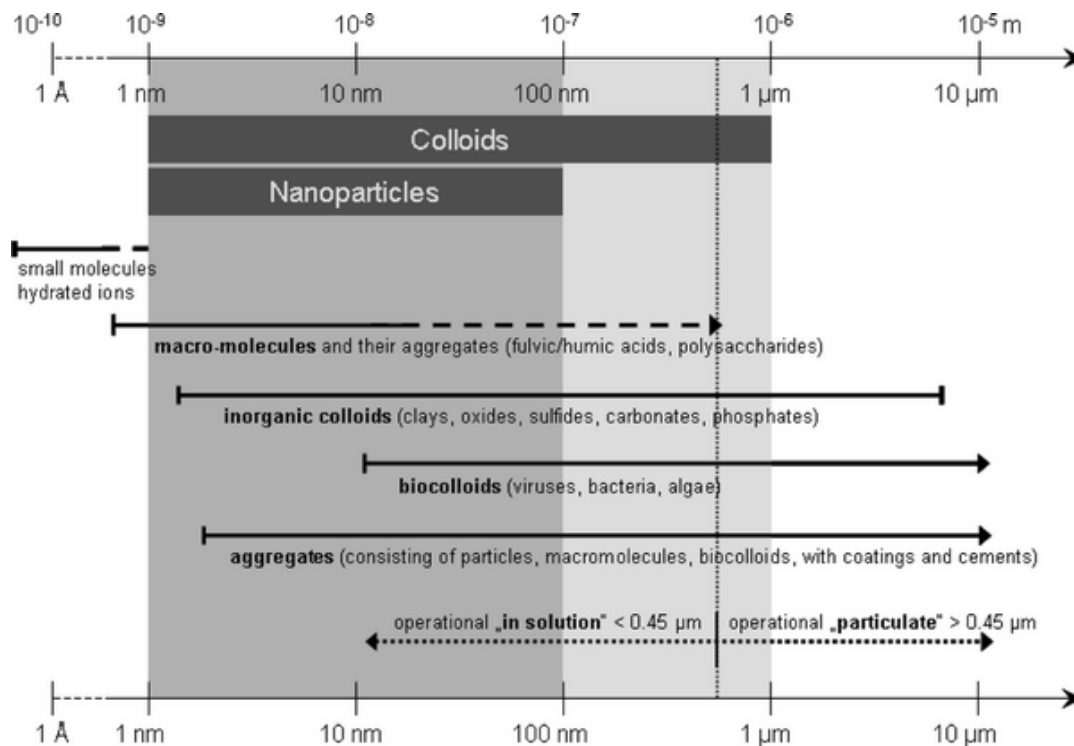


Figure 2-3: Size domains and typical representatives of natural colloids and nanoparticles. The operationally defined cut-off is given for filtration at 0.45 μm (Christian et al., 2008).

Examples of different kinds of nanoparticles include fullerenes, graphene, carbon nanotubes, quantum dots, and a variety of polymeric, metallic, and metal oxides. At these

dimensions, surface and quantum mechanical phenomena become significant, and the behavior of nanoparticles becomes quite different from that of their bulk counterparts. Gold nanoparticles can adopt a range of colors depending on their size, graphene and other carbon structures show an unusual combination of mechanical, electrical, and thermal properties, and nano-structured surfaces can become superhydrophobic, essentially non-wetted by water (Kapusta et al., 2012).

2.5 Nanofluids Preparation and Stability

Nanofluids are a new class of fluids engineered by dispersing nanometer-sized materials (nanoparticles, nanofibers, nanotubes, nanowires, nanorods, nanosheets, or droplets) in base fluids. Nanofluids are nanoscale colloidal suspensions containing condensed nanomaterials. They are two-phase systems with one phase (solid phase) dispersed in another (liquid phase) (Yu and Xie, 2012).

There are many challenges during the fabrication of nanofluids from nanoparticles to stabilize them as a homogenous, single-phase fluid. Since nanoparticles tend to aggregate that resulting in larger particles, it becomes a critical issue to create a stable nanofluid. Stable conditions are achieved when the repulsive forces are relatively high. When the force profile is strongly repulsive, the particles will repel each other, and form a stable suspension. When the force profile is attractive, the particles will approach and contact one another, and aggregate. Initially, particle dimers and trimers will form; as the aggregation proceeds, the particles form larger and larger flocs (or clusters, aggregates). Under some conditions, unstable suspensions can be reversed this process is known as peptization (Trefalt and Borkovec, 2014).

Untreated nanoparticles (both silica and metal oxides), tend to create an aggregate form larger size (in hundreds nano or even micron size) from primary particle size in the range 17-40 nm. This phenomenon will affect the flooding process since the aggregates will be filtered and accumulate in the near-wellbore region rather than be transported through the reservoir (Hendraningrat and Torsaeter, 2014).

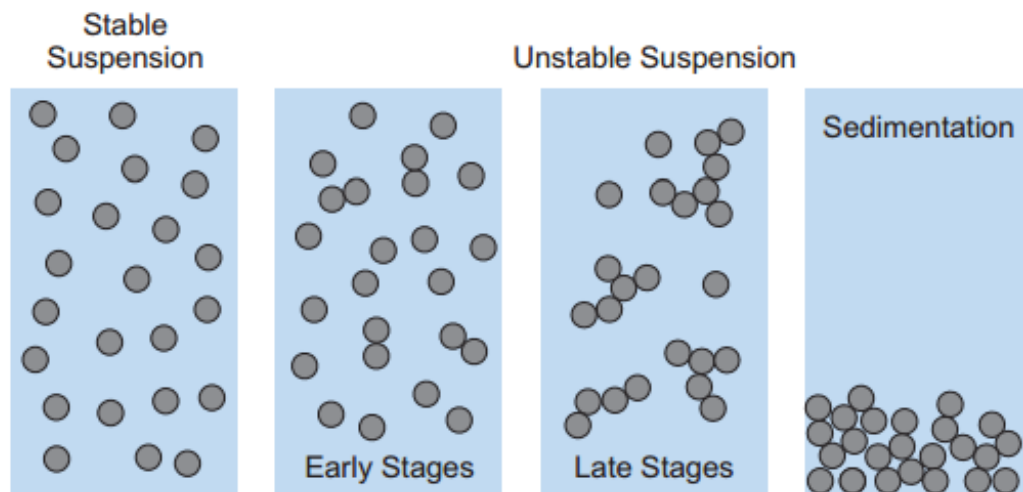


Figure 2-4: Sedimentation stages of a nanofluid (Trefalt and Borkovec, 2014)

2.6 Nanofluids Usage in the Oil and Gas Industry

Concerns are often raised when proposing a new application of nanotechnology in the oil and gas industry. They center on two questions:

- 1) What is the benefit of nanoparticles?
- 2) What makes nanoparticles better than conventional solutions?

Nanoparticles have some distinctive properties such as their size and their relatively large surface-to-area ratio when compared to the same volume that is made from larger particles. This can result in higher reactivity or interaction with adjacent surfaces, enhancing the properties of the carrier fluid with a lower amount of the same material. The small size of nanoparticles and the ability to manipulate them, allows them to be used for changing wetting properties or fluid surface tension, their small size aids in terms of transport through the small pores of the formation allowing them to be delivered to remote parts of the reservoir. Where they have the potential to release surfactants, emulsion breakers, and other chemicals downhole at a precise location (Alsaba et al., 2020; Kapusta et al., 2012).

Micro and nanotechnologies have the potential to introduce revolutionary changes in several areas of the oil and gas industry, such as exploration, drilling, production, enhanced oil recovery, refining, and distribution. Nanosensors might provide more detailed and accurate information about reservoirs. Nanoparticles can be used for scale inhibition. Structural nanomaterials could enable the development of petroleum industry equipment that is much lighter and more reliable and long-lasting. Nanomembranes could enhance the gas separation and removal of impurities from oil and gas streams. Other emerging applications of micro and nanotechnologies in the petroleum industry are new types of “smart fluids” for enhanced oil recovery (EOR) and drilling operations (Kong and Ohadi, 2010).

The research on nanotechnology applications in the petroleum industry is growing and maturing, from initial studies to more sophisticated research. Several kinds of

nanoparticles have been used for oil and gas industry applications In Table 2-2, a brief description of a nanotechnology application is presented for several areas of the upstream industry (Agista et al., 2018).

Table 2-3: different nanoparticles application in the petroleum field of studies (Agista et al., 2018).

Area	Nanoparticle type	Usage
Exploration	Hyperpolarized silicone NPs	Imaging sensors of oil in a hydrocarbon reserve
	Nano-optical fiber	Detecting oil-microbe, which able to estimate reservoir pressure and temperature
	Nano-robots	Well logging and borehole measurement (patent)
	Coated carbon-nano structure	Real-time oil reservoir evaluation with two-dimensional detection technology
	Polyvinyl alcohol functionalized oxidized carbon black	Synthesizing engineered NPs for hydrocarbon detection in the reservoir

Table 2-2: Continue

	Magnetic NP	Detect flood front, fluid contact, hydrocarbon bypass and fracture
	Superparamagnetic NP	Croswell magnetic sensor for tracking flood front
Drilling and completion	Silica NPs	Reduce or stop water invasion to shale by plugging shale pore
	Nano diamond	Improve drilling process in a harsh and demanding environment
	Silica & Alumina NPs	Cement accelerator
	MgO and ZnO NPs	Improving the thermal stability of drilling fluid
	Nano clay	Reduce permeability and porosity of cement and enhanced compressive strength
	Carbon Nanotubes (CNT)	Improve compressive strength in HPHT
	Cellulose nanofibers (CNF) & graphene nano-platelets (GNP)	Increased yield stresses, degree of hydration (DOH), flexural and compressive strengths
Stimulation and production	Pyroelectric NP	Additive for fracturing + viscoelastic surfactant to increase efficiency in fracturing
	Ni-Fe NPs	Hydrate mitigation in the well
	ZnO NPs	Increase low shear rate viscosity on Threadlike micelle (TLM) fluids and more stable

	Table 2-2: Continue	
	Silica NPs	Rheological studies on surfactant based and polymeric fluids
	Metal oxides based	Improves fracturing fluids stability and viscosity in height temperature (300 F).
	Cu and Ni NPs	Thermal recovery by metallic NPs
	Non-ferrous NPS	Combine with surfactant for IFT reduction
Refinery	Nano-supported HDS	Patent on nano-supported hydrodesulfurization (HDS) catalyst
	Nanomembranes	Gas stream separation
	MoS ₂ nano-catalyst	Observing atomic-scale edge structures of MoS ₂
	TiO ₂ NPs	Improving water treatment by reducing the fouling effect
	TiO ₂ , ZrO ₂ , and SiO ₂ NPs	Additive for stabilizing asphaltene in oil under acidic condition
	Magnetic NPs	Accelerate oil removal in water-oil emulsion
	Nickel oxides and alumina NPs	Patent on Nanocatalyst for hydrocracking

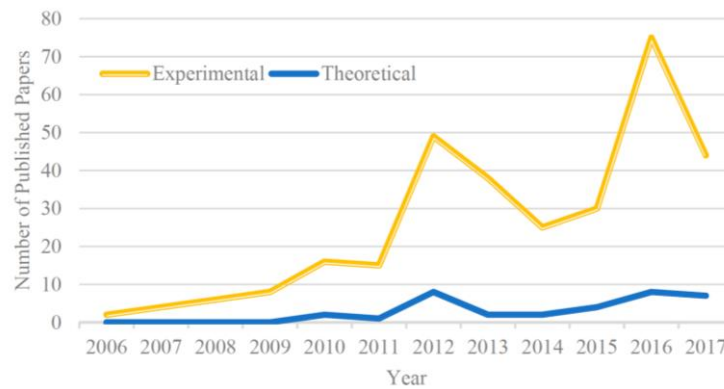


Figure 2-5: Number of published researches in the field of nanotechnology application in the petroleum industry (Agista et al., 2018).

In particular, nanoparticles for use in EOR have several advantages such as a low degree of separation during flow that is dominant over gravitational body forces. Nanoparticle properties depend on the size and shape which may be modified during the manufacturing process; chemical properties of nanoparticles correlate to the surface coating, which may be tailored from hydrophilic to hydrophobic; 99.8% of silica nanoparticles are silicon dioxide which is a dominant substance in sandstone and making it environmentally friendly; low cost of material, as the price is lower than chemicals used for EORs (Agista et al., 2018; Miranda et al., 2012). As can be noted in Figure 2-5, the level of research interest has grown significantly in the area of nanomaterial since 2006, as reflected in the number of publications (Agista et al., 2018).

Despite the points mentioned above, nanoparticle applications for large-scale oil and gas projects face a challenge due to the higher production (making nanoparticles from bulk materials) cost of some kinds of nanoparticles than conventional materials. In

view of the extensive advances made in other industries, the near-term applications will likely be the adaptation of what has already been developed by other industries, i.e., harvesting the “low-hanging” fruits (Ko and Huh, 2019).

2.6.1 Nanoparticle Use for EOR

The effects of nanoparticles (or in combination with surfactants) on reducing the surface forces have been recently investigated (Nazari Moghaddam et al., 2015). Ju et al. (2006) studied and categorized polysilicon nanomaterials based on their wettability behavior into three types: lipophobic and hydrophilic polysilicon (LHP); hydrophobic and lipophilic polysilicon (HLP); and neutral-wet polysilicon (NWP). They also reported that polysilicon nanoparticles could change the wettability of a porous surface by adsorbing on its surface. In addition, silica nanoparticles have good thermal stability when heated up to 650°C, as observed using infrared spectrum, X-ray diffraction, and SEM analysis, suitable for high-temperature reservoirs (Agista et al., 2018; Ju et al., 2006; Wang et al., 1999).

Ogolo et al. (2012) conducted experiments that include sand, crude oil, nanofluids, brine, and sand packs. A laboratory prepared brine of 30 g/L concentration was used and the sand packs used were about 80 cm³ in volume. Nine types of nanoparticles were used: aluminum oxide (Al₂O₃), nickel oxide (Ni₂O₃), magnesium oxide (MgO), iron oxide (Fe₂O₃), zinc oxide (ZnO), zirconium oxide (ZrO₂), Tin Oxide (SnO), silicon oxide treated with silane (SiO₂ (S)) and hydrophobic silicon oxide (SiO₂ (S)) (Ogolo et al., 2012). They selected these different nanoparticles for the EOR experiments because of the potential that they have for being used to address petroleum engineering problems. They

concluded that the choice of dispersant fluid can significantly affect the results of the experiments and the efficiency of nanomaterial. They also stated that aluminum oxide and silicon oxide tended to increase the final oil recovery.

We studied the effect of sodium nanoparticles on the recovery of heavy oil and oil sand because of the properties of the nanosized material mentioned in the literature and the special reactions that sodium generates. Reactions that lower the viscosity by heat generation, create gas inside pores, and creating surfactants to reduce IFT between oil and brine. We designed core flood and static tests to investigate the efficiency of this novel nanomaterial on oil recovery and extraction.

Chapter 3

Equipment and Materials

In this section, a brief description of the equipment and materials used in the flow experiments is described.

3.1 Equipment

3.1.1 Gas Chromatograph and Mass Spectrometer (GC-MS)

A GC-MS system by Agilent Technologies® was used to analyze the remaining oil in the sand pack after the final toluene flood. The specifications are reported in Table 3.1. The chromatography was performed using a flame ionization detector (FID). The MSD has an electron ionization (EI) source with an ion source temperature range from 150°C – 350°C and quadrupole temperature 106°C – 200°C. Helium was used as the carrier gas. An air/hydrogen mixture served as fuel for the flame in FID.

Table 3-1: Gas chromatography and mass spectrometer model

gas chromatography (GC)	7890B
mass spectrometer	7693A

3.1.2 Auto Titrator System

A Metrohm® 888 Titrando with Tiamo Light was used for the titration measurements. This setup was used for measuring the total acid number (TAN).

3.1.3 Pump

A Teledyne ISCO Syringe Pump: Model 266DX was used for flow injection and Teledyne ISCO® Syringe Pump Model 100DX was used to control the confining pressures. It has the capability to control injection rates between 0.001 mL/min to 175 ml/min.

3.1.4 Fluid Reservoirs

Floating piston accumulators were used to isolate and prevent damage to the pumps. The accumulator was a stainless steel cylinder with a floating piston and a maximum pressure of 10,000 psi. Four 100 psig accumulators (Core Laboratories LP) were used for the glass column experiments. The ISCO pumps inject de-ionized water into the bottom chamber of the accumulator which pushes the floating piston and the injection fluids into the samples.

3.1.5 Pressure Differential Transducers and Data Acquisition

Several differential pressure transducers were used in the experiments. For permeability measurement, we used the PX26 series manufactured by Omega® rated for 5 psi maximum. Four TE Connectivity AST20HA 0.1% accuracy gauge pressure transducers (rated 7,500 psi) with 4-20 mA protocol were used with a Horner APG RCC series compact controller and LabVIEW software to collect and record data.

3.1.6 Tubing

Two different kinds of tubing were used in setups. Stainless steel 1/8-inch OD (HiP®) and 1/8-inch OD perfluoroalcoxy (PFA) tubing rated as per ASTM D3307 type II (Swagelok®) were used in different parts of the experimental setup based on the application purpose. The dimensions and other specifications are listed in Table 3-2.

Table 3-2: tubing specifications

<u>PFA tubing specification</u>	
outer diameter	1/8 inch
wall thickness	0.03 inch
pressure rating	275 psig
temperature rating	400 F
<u>stainless steel tubing specification</u>	
outer diameter	1/8 inch
wall thickness	0.06 inch
pressure rating	10000 psig

3.1.7 Valves and Fittings

Stainless steel – 316 (SS316) and rated to 15,000, suitable for 1/8-inch fitting, rated for 300°F (Parker® Autoclave 10V series needle valves) were used and also some two ways and three ways valves rated for 2500 psig were bought from Swagelok® and used in the setup. Nylon ferrules were used for fittings that are compatible with the tubing and had similar pressure and temperature ratings.

3.1.8 Core Holder

The core holder was a Phoenix Instruments® 10,000 psi-rated Hassler-type core holder with C276 Hastelloy-wetted parts capable of accommodating 1.5-inch diameter cores of up to 12 inch length. For cores less than 10 inches in length, spacers were installed.

3.1.9 Glass Column

For low-pressure oil sand experiments, Kimble Chase Kontes Chromoflex columns were used. The columns are jacketed to maintain a constant temperature during the experiments. These columns are rated for 50°C and 100 psig internal pressure.



Figure 3-1: Glass column used for oil sand tests

3.1.10 Fractional Collector

A Teledyne ISCO 500 fractional retriever was used for outlet sample collection. The collector is capable of moving at variable rates and holds up to 72 centrifuge tubes.

3.1.11 Vacuum Pump

A Welch 1400B-01 vacuum pump capable of 10^{-4} torr, was used to pull the vacuum for bulk water fraction measurements.

3.1.12 Centrifugal and Fractional Tubes

Falcon 15 ml and 50 ml high-clarity polypropylene conical centrifuge tubes were utilized in various lab activities related to surfactant analysis and recovery.

3.1.13 pH and Conductivity Meters

A Mettler Toledo S220 SevenCompact pH/Ion meter was used to measure pH.

3.1.14 Water De-ionizer

A Millipore Sigma Milli-DI wall-mounted water purification system capable of producing Type 2 de-ionized lab water was used to prepare the de-ionized water.

3.1.15 Scales

A Mettler Toledo PE 3600 DeltaRange precision balance capable of 0.1 g/0.01 g readability was used for fluid preparation and characterization. An Ohaus Explorer analytical balance (120 g capacity) was used to weigh chemicals for analytical work.

3.1.16 Benchtop Mixers

VWR International hotplate stirrers were used in the preparation of brine solutions.

3.2 Materials

3.2.1 Oil Sands

Oil sand samples were acquired from Alberta Innovates Technology Futures, Alberta, Canada: “Athabasca oil sands high”. Oil sand samples are characterized as low or high quality based on the fines content; higher fines content correlates with lower quality of sand.

3.2.2 Clean Sand

High purity OK-75 grade sand samples were bought from US Silica to prepare the sand pack. OK-75 is 99.8% silicon dioxide and white in color. The specific gravity of OK-75 is 2.65.

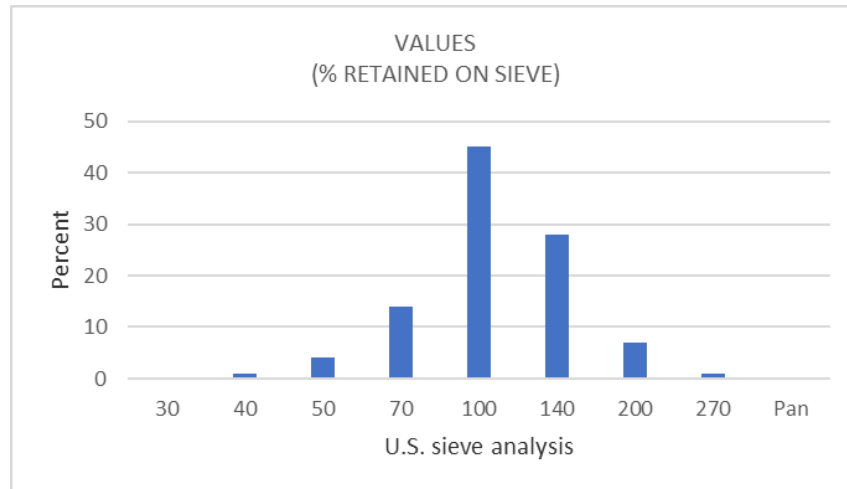


Figure 3-2: U.S. sieve analysis of OK-75 sand

Table 3-3: Chemical analysis of OK-75 sand

typical chemical analysis, %	
SiO ₂ (Silicon Dioxide)	99.8
Fe ₂ O ₃ (Iron Oxide)	0.018
Al ₂ O ₃ (Aluminum Oxide)	0.08
TiO ₂ (Titanium Dioxide)	<0.01
CaO (Calcium Oxide)	<0.01
MgO (Magnesium Oxide)	<0.01
Na ₂ O (Sodium Oxide)	<0.01
K ₂ O (Potassium Oxide)	0.04
LOI (Loss On Ignition)	0.1

3.2.3 Gases

Lab gases nitrogen, argon, helium, hydrogen, and air were purchased from Matheson gas and shipped in 2000 psi industrial cylinders. For the drying operations and pushing the piston down in the accumulators, we used a house pressure line that provided ambient temperature air with pressure ~100 psi.

Table 3-4: Laboratory gases

gas	grade
nitrogen	Ultra-High Purity
helium	High Purity
argon	Ultra-High Purity
hydrogen	Ultra-High Purity
air	Zero Gas

3.2.4 Chemical

Laboratory grade chemicals were purchased from different providers listed in Table 3-5.

Table 3-5: Chemicals and their providers

<u>chemical</u>	<u>vendor</u>
sodium hydroxide	VWR
sodium chloride	Sigma Aldrich
calcium chloride	Sigma Aldrich
toluene	Alfa Aesar
hyamine (0.05M) titrant	Alfa Aesar
anhydrous pentane ≥ 99.0	Sigma Aldrich

Chapter 4

Experimental Procedure

The experimental procedures employed to evaluate the efficiency of sodium nanofluid on the recovery of oil from oil sand and heavy oil reservoirs are discussed in this section.

4.1 The Synthetic Sample Preparation Procedure

The procedure to produce the synthetic sandstone cores required several steps. Care is required to ensure the synthetic sample has homogenous properties through the length and diameter of the sample. The synthetic samples were composed of a standard industrial grain (OK-75 by US Silica©) as reported in Table 3-3. This size range gives a high permeability pack, comprised of 99.8% SiO₂.

4.1.1 Used Tools

4.1.1.1 Kapton Sleeve

Kapton is a polyethylene tube that consists of a thin helically wrapped sleeve. The sleeves are rigid enough to allow simple construction of the sand packs and easily removed after sample freezing.

4.1.1.2 Vibrator

A platform that consists of a small electric motor that shakes due to the eccentric-weighted pulley that is attached to the drive shaft.

4.1.1.3 Distribution Apparatus (Pluviator)

The sand pluviator consists of a column that contains 5 screens that help distribute the sand particles evenly through the sample diameter, so the different sized grains are uniformly distributed through the volume of the sample while raining through the air.

A Kapton® sleeve, 14-inch length, was used for sample preparation. A separatory funnel was used to ensure the sand pours at a consistent rate. The separatory funnel, distribution apparatus, and Kapton® sleeve were aligned vertically and the distribution apparatus and Kapton® sleeve were attached to the vibrator.

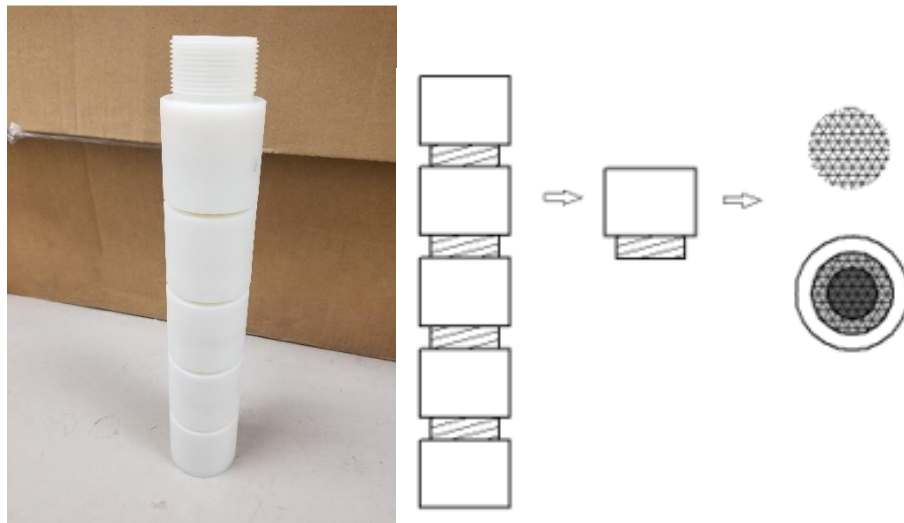


Figure 4-1: Apparatus for sand distribution during synthetic core fabrication (pluviator).

The separatory funnel was filled with the OK-75 sand and the vibrating platform turned on that causes smooth shaking of the Kapton® sleeve and distribution apparatus. After opening the separatory funnel valve, the grains flow uniformly into the Kapton® sleeve after passing through the pluviator. The sand filled Kapton® sleeve is then immersed in an Erlenmeyer flask filled with de-ionized water. The sand column is allowed

to fully imbibe water. After making sure that the whole sample was saturated with water, we allowed the sample to drain so that only a small amount of interstitial water remains.

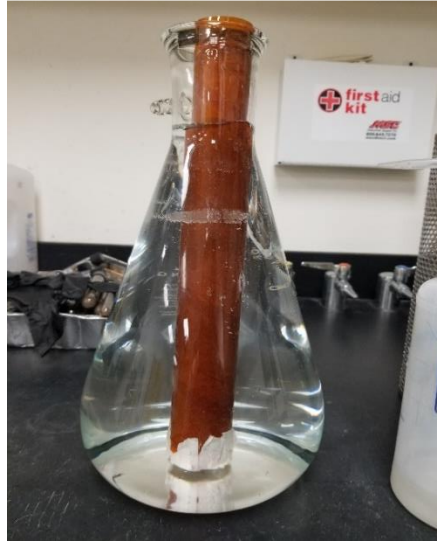


Figure 4-2: 2000 cc Erlenmeyer used with the prepared sand pack in Kapton sleeve

Draining is necessary because water expands during freezing and if the pores are filled during freezing, it will damage the sample. The Kapton® sleeve is lowered into a liquid nitrogen-filled flask at a slow rate to allow sample handling and slow freezing. The Kapton® sleeve, which may be unwrapped helically without damaging the sample, is removed while the sample is frozen and the solid core can be trimmed to a specific length.

The sample is then loaded into the Viton sleeve of the core holder. We used two layers of additional screens between normal core holder end pieces (distributors) and the core to prevent grain migration into the lines. Spacers are added to adjust the core holder for the length of the sample and 500 psi confining pressure is initially applied to the sample.



Figure 4-3: Core holder used for high-pressure experiments

After the sample is loaded, nitrogen gas flow is used to dry the interstitial water while the core holder was heated to 50°C to facilitate drying. After 48 hours, a vacuum pump is used to remove the nitrogen inside the core, this process is continued for 4 hours.

4.2 Brine Fluid Preparation

We chose NaCl salt for the brine and 6 gm of NaCl was mixed with 100 gr of de-ionized water.

4.3 Porosity and Permeability Measurement

We used the following procedures to measure the permeability and porosity of our samples.

4.3.1 Porosity Measurement

To measure the porosity using the saturation process, we measured the amount of brine required to saturate the sample. A graduated cylinder was filled to a recorded line with the prepared brine and with a pre-filled line attached the graduate cylinder to the sample as shown in Figure 4-4. The confining pressure was increased to 700 psi (similar to the flood testing pressure) the valve connecting the graduate cylinder opened, and after stabilization, the level of the brine was recorded giving a measurement of the pore volume after correction for the dead volumes related to the setup. The result of this step was checked with gravimetric analysis, which showed similar results.

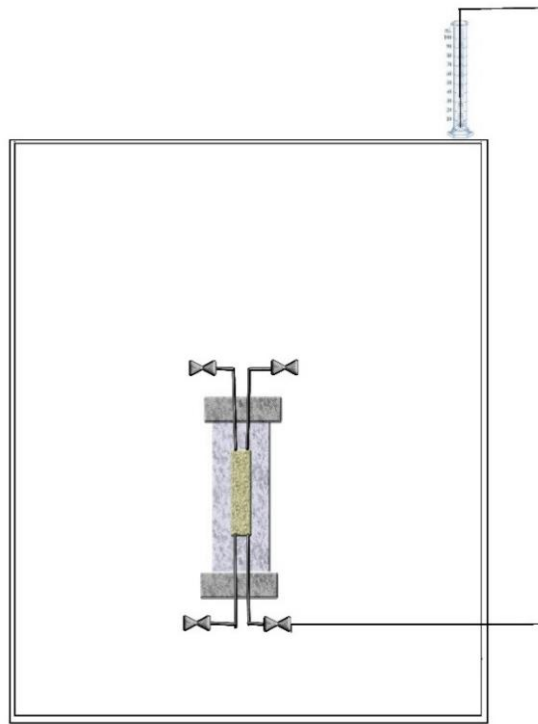


Figure 4-4: porosity measurement setup

4.3.2 Permeability Measurement

The permeability calculated using the Darcy equation, $k = \frac{\mu L}{4.08 * m A}$

where:

$m = \frac{\Delta p}{q}$ - slope of pressure/flow rate data, psi-min/cc

k - permeability, Darcy

μ - viscosity of brine, cp

L - length of the sample, cm

A - sample cross area, cm^2

Δp - pressure difference between flow inlet and outlet, psi

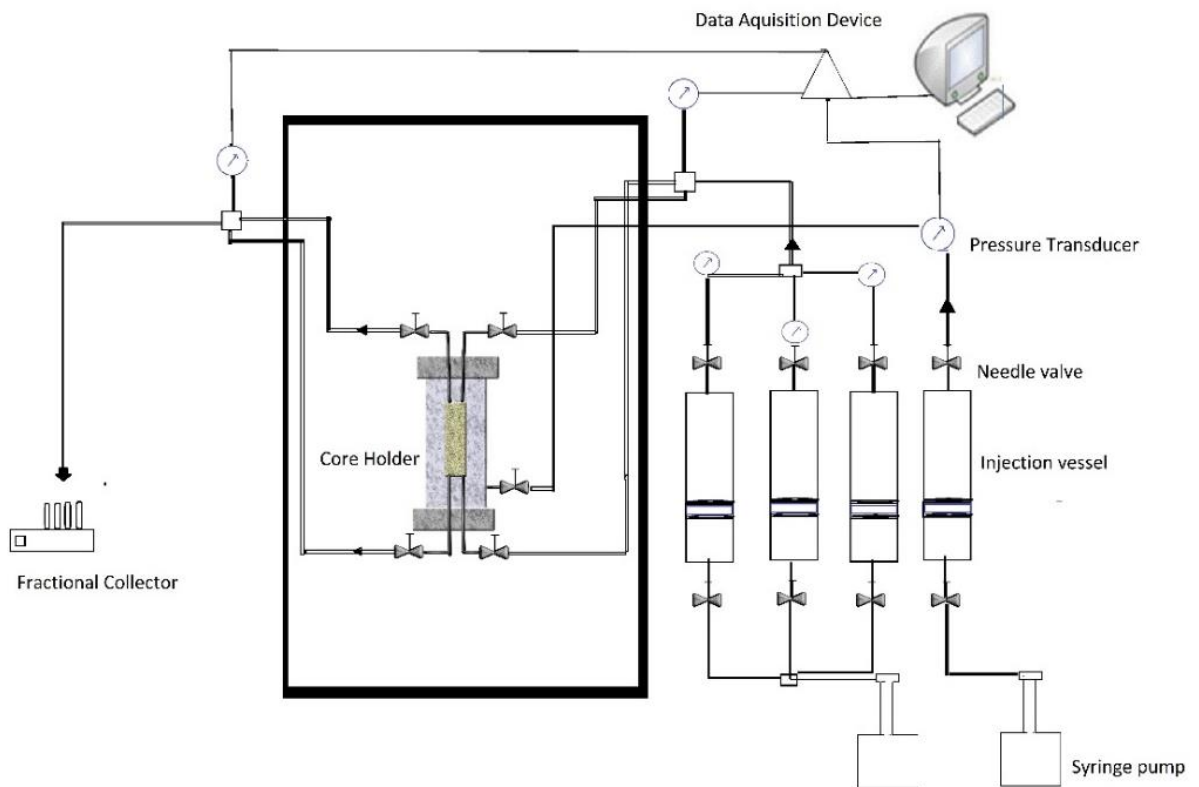


Figure 4-5: Permeability measurement and flood setup used for the heavy oil experiments

Since the height of the sample is small and the permeability is calculated from the slope of a straight line fit to the pressure/flow rate data, the constant elevation difference does not have a significant effect on calculated permeability. Before starting permeability measurements, we did flood the sample in an upward direction to ensure there are no leaks. The upstream and downstream side of the sample was attached to the Omega® differential pressure transducer and then injection started at 2 cc/min rate for one pore volume and then we stopped the injection until the pressure stabilized and recorded the pressure difference at 0 cc/min flow rate. The operation of changing the rate and waiting for pressure to stabilize continued until enough data was gathered. The slope of the resulting data was used to calculate the permeability of the sample. We used the viscosity of the brine at the condition according to previous studies (Kestin et al., 1981; Ozbek et al., 1977) was 0.98 cP.

4.4 Heavy Oil Experiments

4.4.1 Test 1-Silicone Based Nanofluid Into Sand Pack

4.4.1.1 Saturation of Sample with Heavy Oil (Test 1)

For the heavy oil experiments, we used the following procedure to measure the remaining oil in the sample after the sand pack was saturated with heavy oil.

In the setup shown in Figure 4-5, we filled the lines with brine up to the valve next to the core holder this line was then connected to the core holder's input valve to reduce the dead volume measurements and increase the accuracy of calculations. A downward injection of heavy oil from the accumulator performed while tracking the amount of

injected oil and the amount of collected effluent fluids. The effluent was collected by using the automatic fraction collector.



Figure 4-6: Accumulators used for flood tests

4.4.1.2 Brine Injection

After saturation with heavy oil up to the residual water saturation, brine is injected at the same rate to produce the oil until the final residual saturation was reached. The brine was injected upward (from the bottom) at a rate of ~ 1 ft/day.

Table 4-1: Brine flooding properties

flow rate (cc/min)	confining pressure (psi)	flow direction
0.077	700	upward

The effluent was collected using centrifugal tubes using an automatic fraction collector. We continued the injection of the brine until no additional amount of oil was produced.

4.4.1.3 Nanofluid Injection

Sodium nanofluid was then injected into the sample to see how much incremental oil can be produced.

Table 4-2: Properties of silicone-oil based nanofluid

concentration (mg/cc)	dispersant part	active element
33	silicone oil	sodium

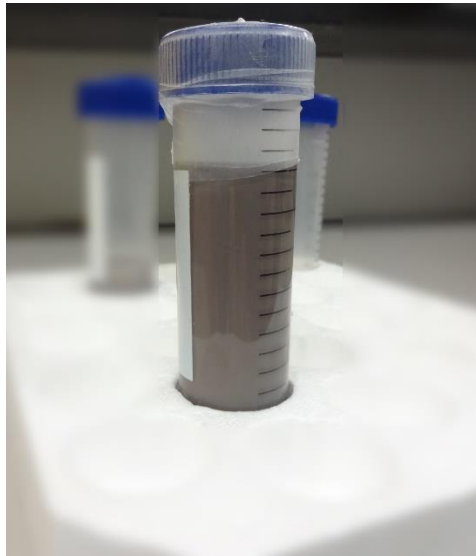


Figure 4-7: Prepared nanofluid before injection

The nanofluid specific gravity was lower than that of brine, so we injected it downward (from the top) to maintain a gravity stable flood. A low rate of injection (0.03 cc/min) (0.4 ft/day) and a volume of 0.65 PV were injected into the sample.

Table 4-3: Nanofluid injection step properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03 (0.4 ft/day)	700	downward	30

4.4.1.4 Brine Injection

After allowing a 30-minute soak after ending nanoparticle injection, brine injection was started in the same flow direction and at the same rate to produce the remaining oil that mobilized due to nanofluid exposure.

Table 4-4: Test 1 first brine injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03 (0.4 ft/day)	700	downward	174

4.4.1.5 Nanofluid Injection

Another set of nanofluid injection experiments was designed to see if increased oil production occurs with a second injection step. An additional 13 cc (0.3 PV) of nanofluid was injected into the sample at the same rate as the previous steps (0.03 cc/min). The effluent fluid was collected with a fractional sampler.

Table 4-5: Test 1 second nanofluid injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03 (0.4 ft/day)	700	downward	13

4.4.1.6 Brine Injection

Similar to the previous steps, brine was injected following nanoparticle injection to determine any potential incremental recovery. The expelled fluids were again collected with centrifugal tubes and the fractional collector.

Table 4-6: Test 1 second brine injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03 (0.4 ft/day)	700	downward	95

4.4.1.7 pH Measurement

The pH of the aqueous portion of fluid collected in each tube was measured to track the alkalinity of the expelled fluid with the understanding that pH change was caused by the generation of sodium hydroxide within the sand pack.

4.4.1.8 Washing with Toluene

Toluene was injected to remove any oil remaining in the sand pack as the last step, which would verify the amount of oil recovered. Toluene injection continued until the color of effluent toluene was unchanged. GC-MS measurements were made to determine the concentration of oil dissolved in the toluene. The oil remaining in the synthetic sand pack after all cycles of nanofluid and brine injections was determined using this method.

4.4.2 Test 2 – Silicone Oil Into Sand Pack

A base test was designed to measure the effects of the nanofluid dispersant on incremental recovery.

4.4.2.1 Saturation Of Sample With Heavy Oil

The same procedure as Test 1 was employed for this test except for reducing the amount of heavy oil used for the initial oil flood to connate water saturation. We injected 23 cc of oil into the sample. The effluent was again collected by using the automatic fraction collector.

4.4.2.2 Brine Injection

After the heavy oil injection, brine was injected until residual oil saturation was reached. The brine was injected upward (from the bottom) at a rate of 1 ft/day. Similar to Test 1, the effluent was collected using centrifugal tubes. The brine injection continued until no additional amount of oil was produced.

Table 4-7: Test 2 first brine injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction
0.077	700	upward

4.4.2.3 Silicone Oil Injection

Pure silicone oil was injected into the sample in an operation similar to previous nanofluid injection to assess its effect on incremental oil recovery.

Table 4-8: Properties of silicone oil

specific gravity (-)	viscosity (cP)
0.963	45-55

Because the specific gravity silicone oil is less than brine, a downward injection (from the top) is employed for a gravity-stable displacement with a low rate of injection (0.03 cc/min, 0.4 ft/day) for a total volume of 0.65 PV.

Table 4-9: Test 2 silicone oil injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03	700	downward	33

4.4.2.4 Brine Injection

After allowing the silicone oil to soak for 30 minutes, brine was injected in the same direction and at the same rate to investigate the impact of the silicone oil alone on oil recovery. A total of 104 cc of brine injected was injected in a downward direction.

Table 4-10: Test 2 brine Injection properties

flow rate (cc/min)	confining pressure (psi)	flow direction	total injected fluid (cc)
0.03	700	downward	104

4.5 Oil Sand Experiments

Floods were performed in a glass column that was packed with field-obtained oil sand to determine whether the nanofluid can be used to extract oil.

4.5.1 Porosity and Permeability Measurement for The Samples

We used the same procedures as in previous experiments to measure the porosity and permeability of the column. The glass column used in these experiments does not have the ability to apply confining pressure.

4.5.2 Test 3 - Silicone-Based Nanofluid Recovery from Oil Sand

4.5.2.1 Nanofluid Injection

After permeability measurement, about 0.6 PV of nanofluid was injected into the sand pack.

Table 4-11: Test 3 nanofluid injection properties

injected nanofluid (cc)	injected rate cc/min	flow direction
13 (0.6 PV)	0.089 (3 ft/day)	downward

Because of hydrogen gas generation due to the nanofluid injection, the residual fluid saturations were very low. This was true for both the brine and the silicone oil used as the dispersant for the sodium nanoparticles. The automatic fraction collector was used but due to hydrogen generation, the first tube quickly filled and it became necessary to manually advance the initial tubes of collected fluids.

4.5.2.2 Brine Injection

Brine was injected into the sand pack following nanofluid injection according to Table 4-12.

Table 4-12: Test 3 brine injection properties

rate of injection (cc/min)	total brine injection (cc)	flow direction
0.1	50	downward

4.5.3 Test 4 - Silicone-Based Nanofluid Recovery from Oil Sand

4.5.3.1 Nanofluid Injection

After the sand pack was prepared and the properties measured, 0.5 PV of nanofluid was injected. This was followed by 0.5 PV brine to assure that there is sufficient water in the sand pack to initiate the chemical reaction with sodium. The sample was allowed 92 hours of soaking time to allow and alkali fluid generated time to react with the naphthenic acids present in the oil. The injection rate was increased due to previous clogging issues.

Table 4-13: Nanofluid injection properties

nanofluid volume (cc)	brine volume (cc)	flow rate (cc/min)	flow direction	soaking time (hrs)
11	11	10 cc/min	upward	92

4.5.3.2 Brine Flood

After the 92 hours soak mentioned above, brine with properties reported in Table 4-14 was injected into the sand pack.

Table 4-14: Test 4 brine injection properties

injection rate (cc/min)	injection volume (cc)	flow direction
0.085	114 (6 PV)	upward

4.5.4 Test 5 – Silicone-Based Nanofluid Recovery from Oil Sand

Since the incremental oil recovery during Test 4 was lower than expected, Test 4 was repeated with more additional steps aimed at understanding the cause.

4.5.4.1 Nanofluid Injection

The same procedure was repeated as described in the previous experiment with reported properties in Table 4-15.

Table 4-15: Test 5 nanofluid injection properties

nanofluid volume (cc)	brine volume (cc)	flow rate (cc/min)	flow direction	soaking time (hrs)
11	11	10	upward	80

4.5.4.2 Brine Flood

A volume of 100 cc brine was injected upward with no additional oil produced. The glass column then inverted to change the direction of gravity force to see if that can be effective in producing any possible extracted oil and an additional 100 cc of brine was injected downward.

Table 4-16: Test 5 brine flood properties

stage	injection rate (cc/min)	injection volume (cc)	flow direction
before inverting	0.085	100 (5 PV)	upward
after inverting	0.085	100 (5 PV)	downward

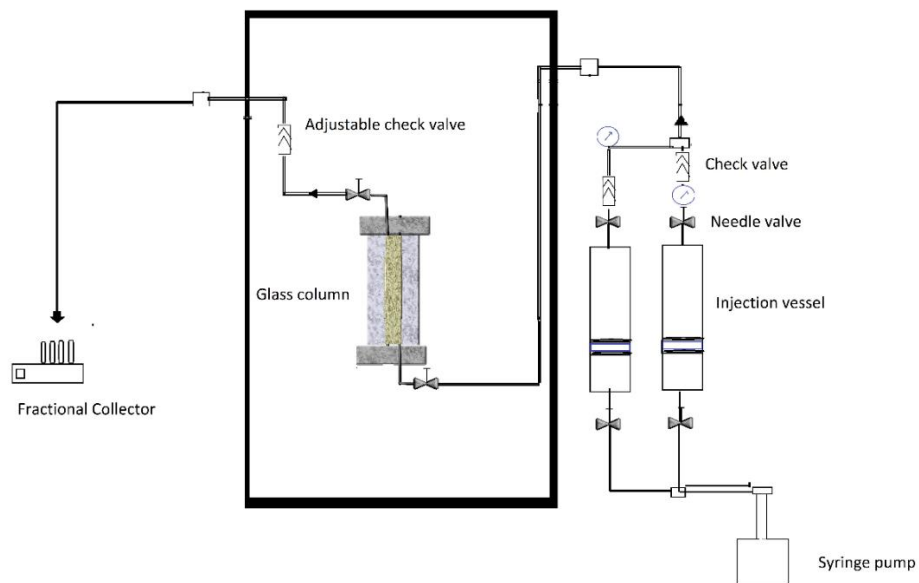


Figure 4-8: Setup used for oil sand tests

4.5.4.3 Static Tests

A static exposure experiment was performed to better understand the underlying cause for low oil recovery from oil sands in Tests 4 and 5 when using nanofluid. These

tests effectively added the effect of turbulent flow to the oil sand post Test 5 flow results. The glass column was opened and 10 gr of sand from three sections of the column was collected and placed in three fractional tubes with 10 cc of brine and agitated.

4.5.5 Test 6 – Pentane-Based Nanofluid Recovery from Oil Sand

Nanomaterial with a concentration of 33 mg/ml was dispersed into pentane instead of silicone oil. The previous procedures (Test 4) were repeated.

4.5.5.1 Nanofluid Injection

Table 4-17: Test 6 nanofluid injection properties

nanofluid volume (cc)	brine volume (cc)	flow rate (cc/min)	flow direction	soaking time (hrs)
11	11	10	upward	76

4.5.5.2 Brine Flood

The previous test results indicated that if the nanomaterial were allowed adequate soak time within the porous media and then resume flooding, the production of oil increased so this was incorporated in subsequent tests.

Table 4-18: Test 6 brine floods properties

brine flood	injection rate (cc/min)	injection volume (cc)	flow direction
(a)	0.085	100 (5 PV)	upward
(b)	0.085	100 (5 PV)	upward
(c)	0.085	20 (1 PV)	upward
(d)	0.085	10 (0.5 PV)	upward

4.5.6 Test 7 – Pentane Recovery from Oil Sand

Pentane, used as a nanoparticle dispersant, is a solvent for hydrocarbons and may therefore result in additional produced oil even without the addition of nanoparticles. To measure the impact of pentane on the final oil recovery, pentane was injected alone and using the same procedures as reported for Test 6 was applied.

4.5.6.1 Nanofluid Injection

Table 4-19: Test 7 nanofluid injection properties

nanofluid volume (cc)	brine volume (cc)	flow rate (cc/min)	flow direction	soaking time (hrs)
11	11	10	upward	74

4.5.6.2 Brine Flood

Table 4-20: Test 7 brine floods properties

brine flood	injection rate (cc/min)	injection volume (cc)	flow direction
(a)	0.085	100 (5 PV)	upward
(b)	0.085	100 (5 PV)	upward
(c)	0.085	20 (1 PV)	upward
(d)	0.085	10 (0.5 PV)	upward

4.5.7 Static Tests

After Test 3, where no oil was produced from oil sand, static tests were designed (samples 1-6) to investigate the cause of the poor result using the nanofluid. Several static tests were performed on the oil sands in the fractional tubes. This allows agitation and

increases the exposure of oil sands to the nanomaterials, and allows visual observation of the materials. The result helped with experiment design and understanding of nanofluid behavior. Various fractions of oil sand, brine, and nanofluid/brine were added to test tubes and gently shaken. They were then allowed to 'age' at varying temperatures to observe the amount of extracted oil.

Static tests were performed on samples 11, 12, and 13 to investigate the effects of varying the fractions of nanofluid and brine on the final extraction results. The steps for these three static tests were as follows:

- 1) Loaded equal mass of oil sand into test tubes.
- 2) Add fluids of varying ratios according to Table 5-11.
- 3) After six days, add brine and examine (photograph).

Chapter 5

Results and Discussion

5.1 Heavy Oil Flood

Two flooding procedures consisting of brine, nanofluid, and heavy oil injection were performed on samples at residual oil saturation to determine the impact of sodium nanofluid on the final recovery.

These flow tests were performed on the sand pack prepared by using OK-75 sand using the methods explained in Chapter 4. The floods were performed at room temperature and a constant flow rate. As reported in Table 5-1 the permeability of the porous medium was measured to be 14.1 Darcy with a porosity of about 30 %.

Table 5-1: Test 1, 2 properties of the sand pack

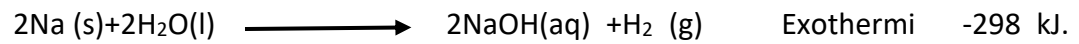
test	length (inches)	diameter (inches)	porosity %	permeability (Darcy)	pore volume (cc)
1	5	1.5	30	14.1	42.25
2	5	1.5	29	13.9	41.75

5.1.1 Test 1 – Silicone-Based Nanofluid Into Sand Pack

The sample was saturated with brine after the permeability measurement, heavy oil was then injected at the rate of 0.077 cc/min (≈ 1 ft/day) until no brine was produced. About 38.5 cc of oil was left in the sample at the end of the saturation process. The flow direction was downward so the flow is gravity stable. In the next step, 293 cc (6 PV) of brine were injected into the sample in an upward direction (gravity stable) at the same

rate (Table 5-3) to produce oil until irreducible oil saturation was reached. 15 cc of oil was produced from the sand pack, 39% of the total oil (38.5 cc) that remained in the sample from the previous step.

Sodium nanofluid (Table 4-2) was prepared and shaken well before injection into the sample. The rate was reduced to 0.03 ft/day (0.4 ft /day) to increase the contact time of nanofluid with the heavy oil. Sodium reacts with water as follows:



(Lakshmanan, 2012)

The molar weight of Na is 22.99 gr/mol and H₂O molar weight is 18.01 gr/mol. If we consider injection of 10 cc of nanofluid with a concentration of 33 mg/cc sodium nanoparticles we have:

$$33 \text{ mg/cc} * 10 \text{ cc} = 0.33 \text{ gr Na per 10 cc of fluid}$$

$$0.33 \text{ gr} / 22.99 \text{ (gr/mol)} = 0.0144 \text{ mol Na per 10 cc of nanofluid}$$

Every mole of Na produces 1 mol of NaOH and molar weight of sodium hydroxide is 39.99 gr /mole :

$$0.0144 * 39.99 \text{ gr/mole NaOH} = 0.5759 \text{ gr NaOH}$$

Every mole of Na produces 0.5 mole of H₂ so $7.2 * 10^{-3}$ moles of H₂ is produced

The volume of every mol of H₂ in standard conditions is about 22.4-liter:

$$7.2 * 10^{-3} * 22.4 \text{ liter/mole} = 0.1612 \text{ liter (volume of H}_2\text{ / 10 cc of sodium nanofluid)}$$

This volume of gas is produced by the injection of 10 cc nanofluid into a porous media.

This energy is available to expel heavy oil and mobilize fluids.

Table 5-2: The result of heavy oil injection into synthetic sand pack

Injection rate (cc/min)	confining pressure (psi)	total injected oil (cc)	produced brine (cc)	produced oil (cc)	residual oil in the sample (cc)
0.077	700	61.7	38.5	23.2	38.5



Figure 5-1: Test 1 effluent collected in fraction tubes during the heavy oil injection step

Table 5-3: Test 1 result of initial brine injection

total injected brine (cc)	produced oil (cc)	remained oil in the sample (cc)
293	15	23.5

After the nanofluid flood was started, oil was produced at a high initial rate. Bubbles were also present in the effluent fluid. Both gas production and heat generation are believed to have contributed to this increased oil production.

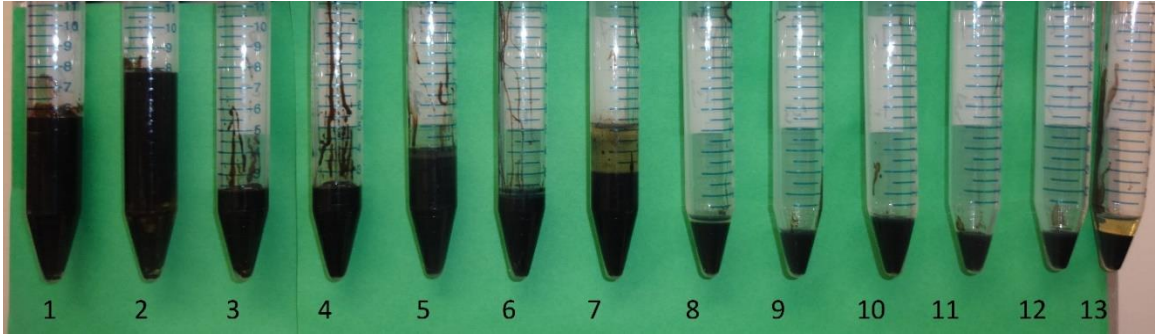


Figure 5-2: Test 1 effluent from the injection of nanofluid into the sand pack

Silicone oil is colorless, but a color change occurs (yellow color) after silicone-oil based nanofluid exposure to heavy oil. To establish the origin of the yellow color in the silicone oil, some static tests were performed by mixing:

1. silicone oil, synthetic sand, and brine
2. nanofluid, synthetic sand, and brine
3. nanofluid, synthetic sand, brine, and heavy oil

Only case three caused a color change, indicating that an interaction between silicone oil and heavy oil occurred.

After the conclusion of the nanofluid flood and allowing 30 minutes of soaking, we started to inject brine with the same rate as nanofluid (0.03 cc/ min, 0.4 ft/day). As seen in Figure 5-3 additional oil production occurred. The amount was significantly less than what was produced during the nanofluid injection step, indicating that the hydrogen gas propellant and heat generation had a significant role in the incremental recovery.

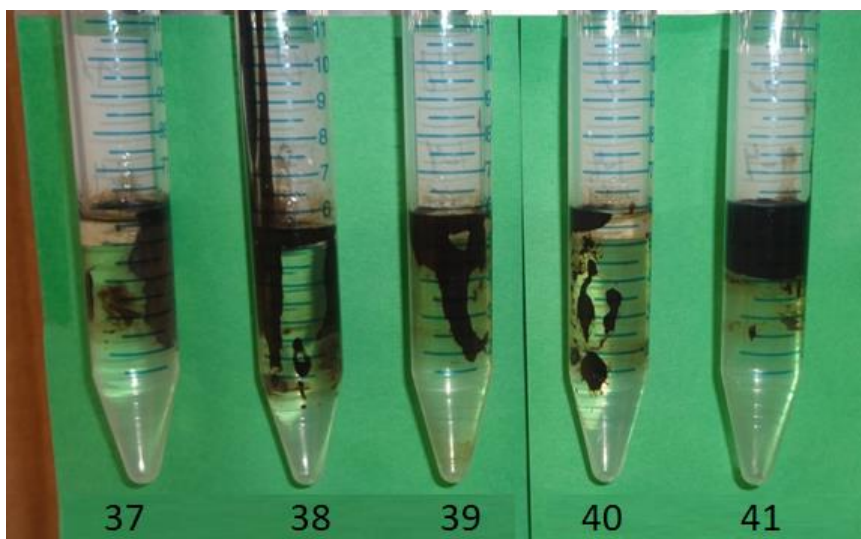
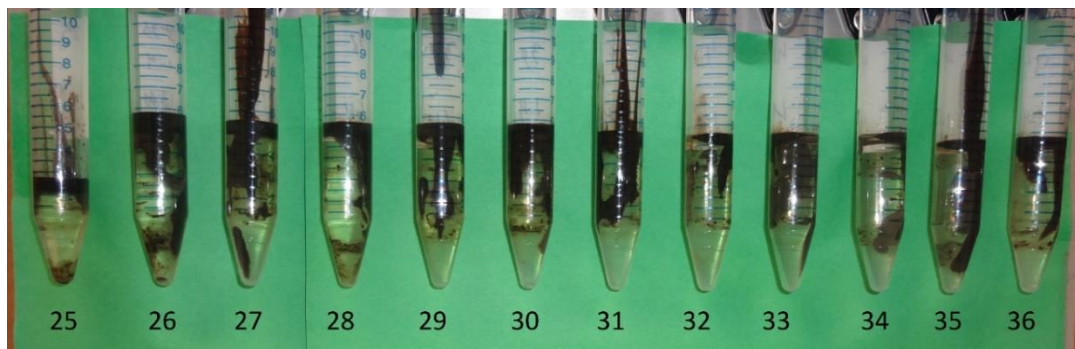
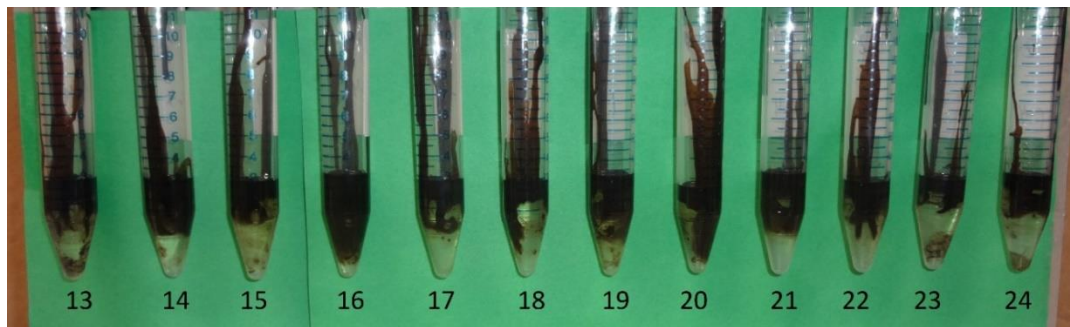
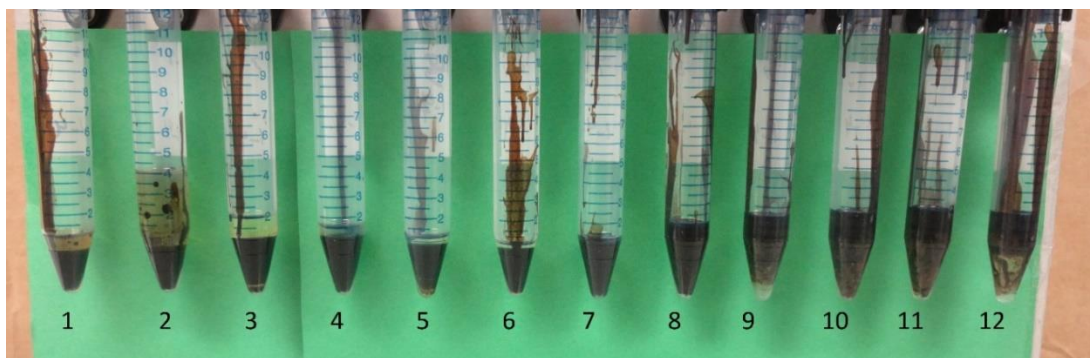


Figure 5-3: Test1 effluent fluids of the first brine flood after exposure to nanomaterial

Another second set of nanofluid injection flood was performed to determine if injecting more sodium nanoparticles into the sample increases incremental recovery. As seen in Figure 5-4 the amount of oil produced by the second round of injection was not significant. The optimum amount of nanofluid injection is expected to depend on the individual field cases.

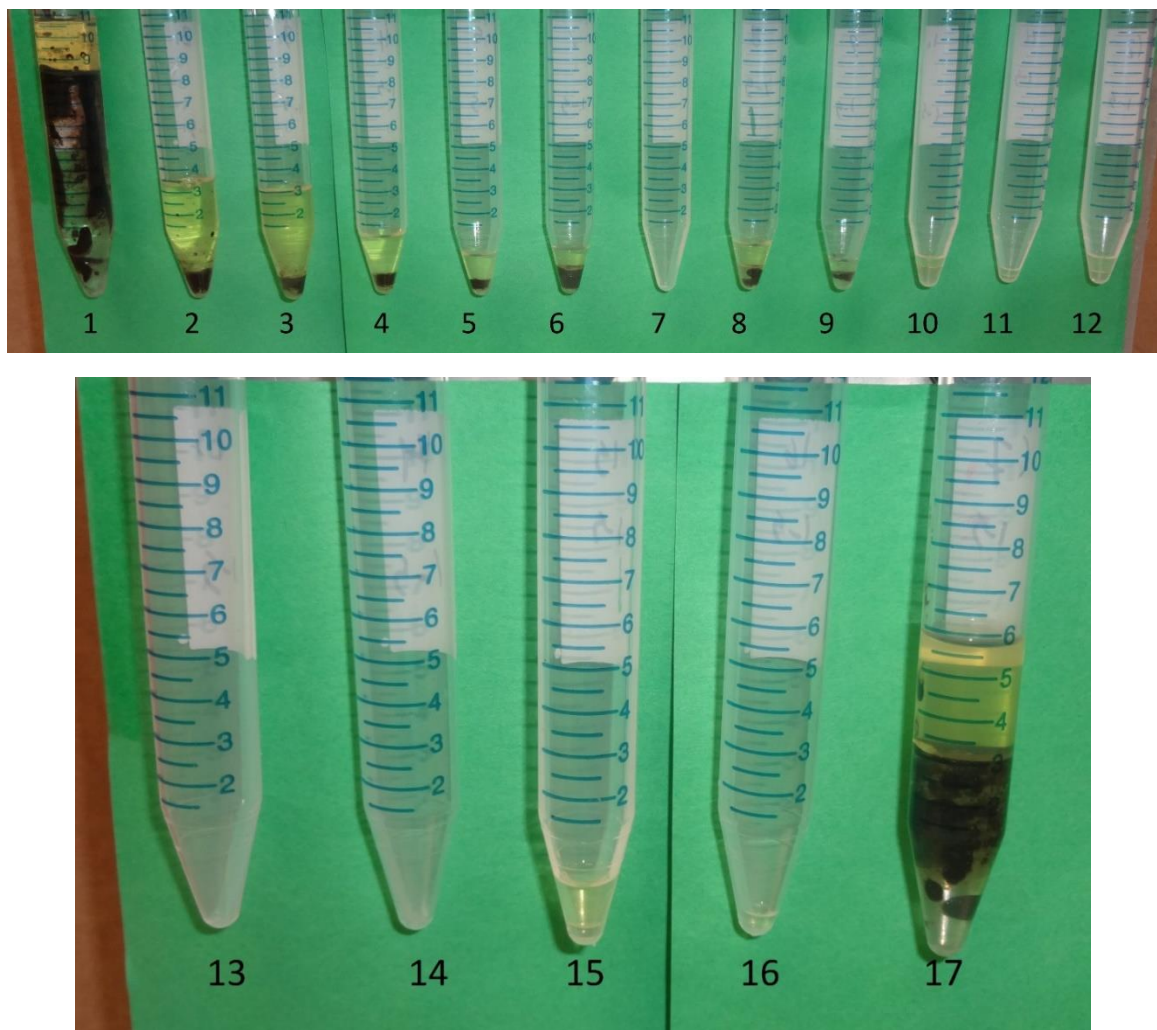


Figure 5-4: Test 5 effluent fluids during second nanofluid flood

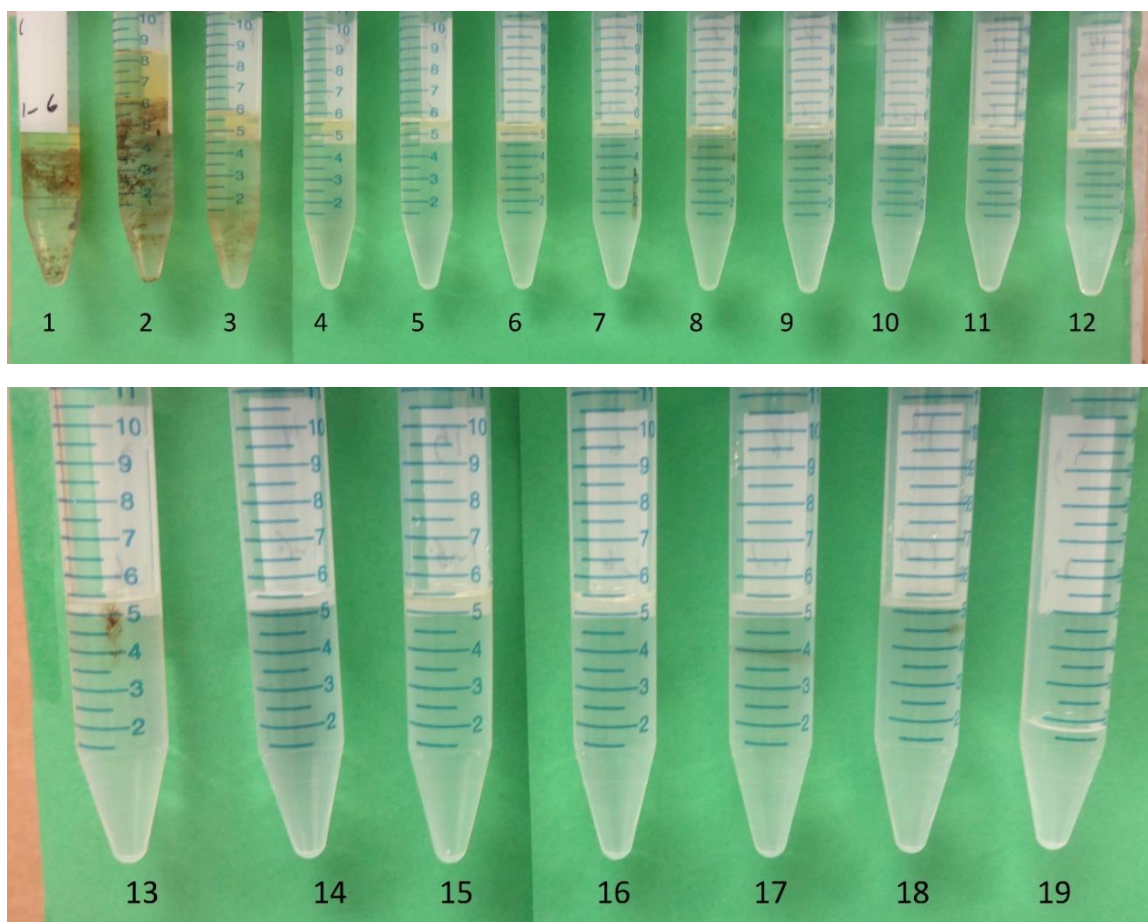


Figure 5-5: Test 1 effluent fluid after the final brine flood. Most of the oil came during the first step nanofluid/brine injection and during this second nanofluid/brine injection no significant amount of oil was got produced.

The total oil recovered was analyzed by performing GC/MS measurement for oil content in toluene that was used to wash the remaining oil from the sand pack.

Table 5-4: Final recovery result of Test 1

initial	oil produced by	brine flood	oil in effluent	incremental oil produced	total recovery
oil (cc)	brine flood (cc)	recovery %	toluene (cc)	by nanofluid (cc)	%
38.5	15	39	10	13.5	74

We measured the pH of the aqueous phase of selected fraction tubes. As reported in Table 5-5, the produced brine was basic even after injection of 200 cc. This shows the

potential to generate “soap” by reacting with naphthenic acid compounds in the oil. The minimum pH that “soap” can be generated in the sample is about 9.5 (Sheng, 2015) which is consistent with the pH measurements of the effluent fluids.

Table 5-5: Test 1 result of pH measurement for different steps

sample	pH
(2) first nanofluid inj.	7.4
(36) brine flood after first nano inj.	12.65
(48) brine flood after first nano inj.	10.84
(17) second nanofluid inj.	12.67
(1) brine flood after second nano inj.	13.86
(3) brine flood after second nano inj.	13.42
(18) brine flood after second nano inj.	11.3

5.1.2 Test 2 - Silicone Oil Into Sand Pack

We performed a base test to determine the effect of silicone nanofluid on the final recovery. The amount of heavy oil used to saturate the sand pack was 22.5 cc, enough to saturate the sand pack to an amount close to the measured residual oil saturation after brine flood in Test 1. A total of 128 cc of brine was injected afterward to move the oil out from the sand pack, and no significant amount of oil was collected during this brine flood. During the subsequent silicone oil flood, 2.5 cc of oil was produced. Compared to Test 1

where 13.5 cc of oil was produced by injection of silicone oil-based nanofluid demonstrates that the main mechanism of incremental oil production in Test 1 was due to the nanoparticles added to the silicone oil.

Table 5-6: Test 2 results of heavy oil injection into the sand pack

rate (cc/min)	confining pressure (psi)	total injected oil (cc)	produced brine (cc)	produced oil (cc)	residual oil in sand pack (cc)
0.077	700	22.5	22	0	22.5

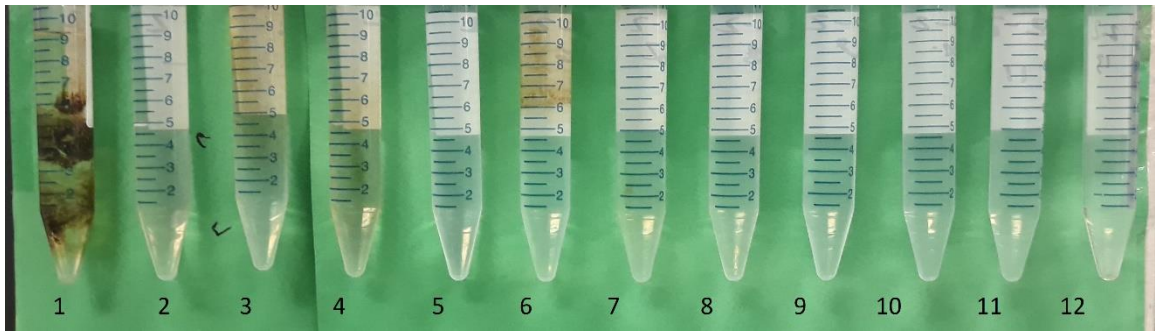


Figure 5-6: Test 2 result of brine injection before silicon oil injection

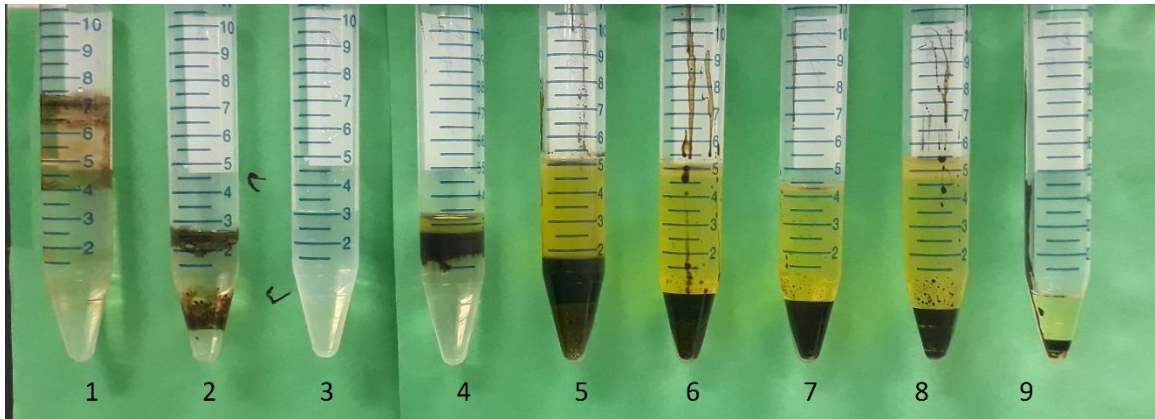


Figure 5-7: Test 2 result of silicone injection into the sample

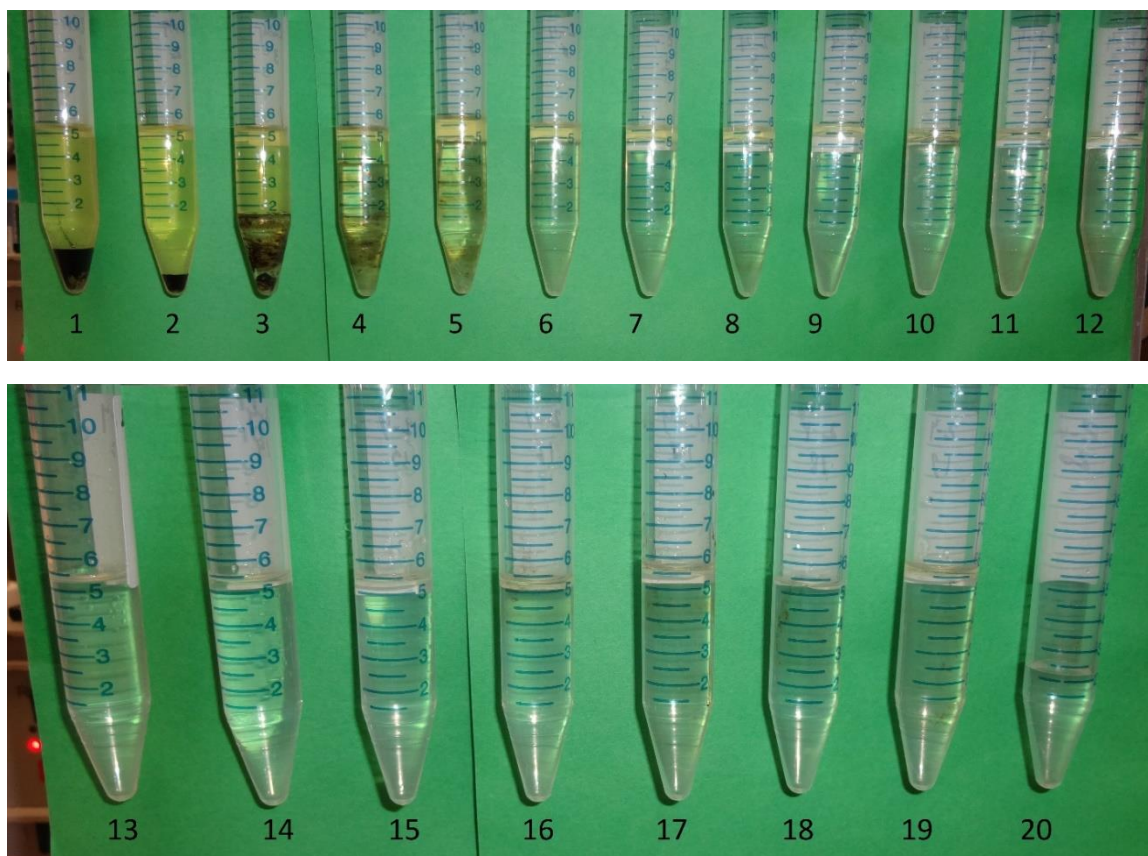


Figure 5-8: Test 2 result of final brine injection

5.2 Oil Sand Experiments

Table 5-7: Measured properties of sand packs that been used for tests 3-7

test	sand grams	diameter, cm	length, cm	porosity	permeability Darcy
3	126	2.5	15	0.24 (17.66 cc)	15
4	133.5	2.5	15	0.26 (19.13 cc)	14
5	126.8	2.5	15	0.27 (19.87 cc)	15
6	129	2.5	15	0.27 (19.83 cc)	14.5
7	130	2.5	15	0.26 (19.20 cc)	13.8

5.2.1 Bitumen Characterization

A previous Ph.D student (Dr. Pushpesh Sharma) measured the properties of the same oil sand that was used in this research, including the extracted bitumen. We refer

to his research with Dr. Konstantinos Kostarelos and Mohamad Salman. The average bitumen content for high-grade sand was 12.8 wt.% (Sharma, 2019). The API gravity of bitumen was measured to be 6.8 °API. Results of SARA (saturates, aromatics, resins, and asphaltenes) analysis of bitumen are listed in Table 5-8. SARA and API gravity analysis was conducted at the Center for Petroleum Geochemistry at the University of Houston (Sharma, 2019).

Total Acid Number (TAN) for bitumen was measured to be 2.94 mg of KOH per g of oil using ASTM – D664 – 18e2 (Sharma, 2019). The measured viscosity of the bitumen sample decreases drastically with temperature as reported in Table 5-9 (Sharma, 2019).

Table 5-8: SARA results for bitumen

saturates (%)	aromatics (%)	resins (%)	asphaltenes (%)
23.85	28.21	15.13	32.81

Table 5-9: Bitumen viscosity variations with temperature at shear rate = 10 s^{-1} (Sharma, 2019)

<u>temperature</u>	<u>viscosity</u>
[°C]	[mPa·s]
10	17248
15	10001
20	6039
25	3777
30	2440
35	1631
40	1120
45	792
50	572

5.2.2 Test 3 - Silicone-Based Nanofluid Recovery from Oil Sand

Nanofluid floods using the same procedure as were used on the heavy oil sand pack samples resulted in no additional oil being produced. In order to produce oil (bitumen) additional residence time, or “soaking time”, was needed to generate “soap” (surfactants) due to reactions with the heavy oil.

5.2.3 Static Test

The static tests determined that nanomaterial dispersed in silicone oil will extract oil if sufficient time is allowed for the chemical reactions to take place and enough exposure happens between the material and the oil sand. Figure 5-9 for sample 1 and Figure 5-10 for sample 2, demonstrate that the nanofluid extracts oil at room temperature and oven temperature but requires a long residence time for the process to complete at room temperature. The extraction process is even more successful at higher temperatures according to this comparison. The difference between the static test on sample 2 (Figure 5-10) and the glass column flood experiment was the agitation of fractional tubes which triggers the complete exposure of the sand particle’s surface with sodium hydroxide and better extraction of oil.

Sample 3, 4, 5, and 6 were performed with no nanomaterial in the dispersant. The results of these tests are shown in Figures 5-11, 5-12, 5-13, and 5-14. No significant color change occurred except for sample 6 (Figure 5-14). Comparing sample 4, which contains silicone oil, to sample 6 (Figure 5-14), which contains only brine, demonstrates that sample 6 had appeared to have slightly more dissolved hydrocarbons. This observation

together, with the results of Tests 4 and 5 lead us to replace silicone oil as the dispersant with pentane for the subsequent Tests 6 and 7.

Table 5-10: Static test tubes properties

sample	sand (gr)	nanofluid (gr)	brine (gr)	silicon oil (gr)	temperature (°C)
1	8	2.6	10.5	-	50
2	8.1	2.6	10.5	-	22 (RT)
3	8	-	12.6	-	22 (RT)
4	8	-	10.4	2.6	50
5	8	-	10.5	2.6	22 (RT)
6	8	-	12.6		50

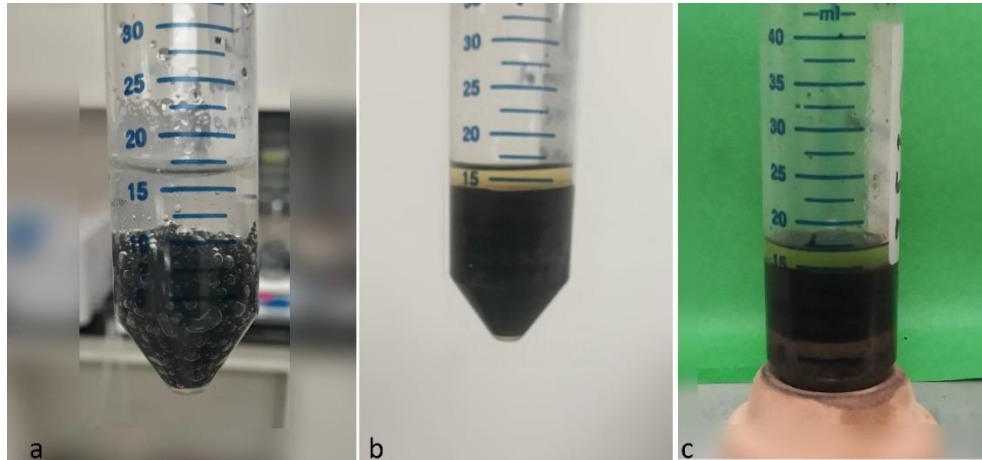


Figure 5-9: Static test sample 1 fractional tubes (a) sample at the moment of mixing (b) sample after 72 hours (c) sample after 144 hours. Increased oil is evident after longer soak times

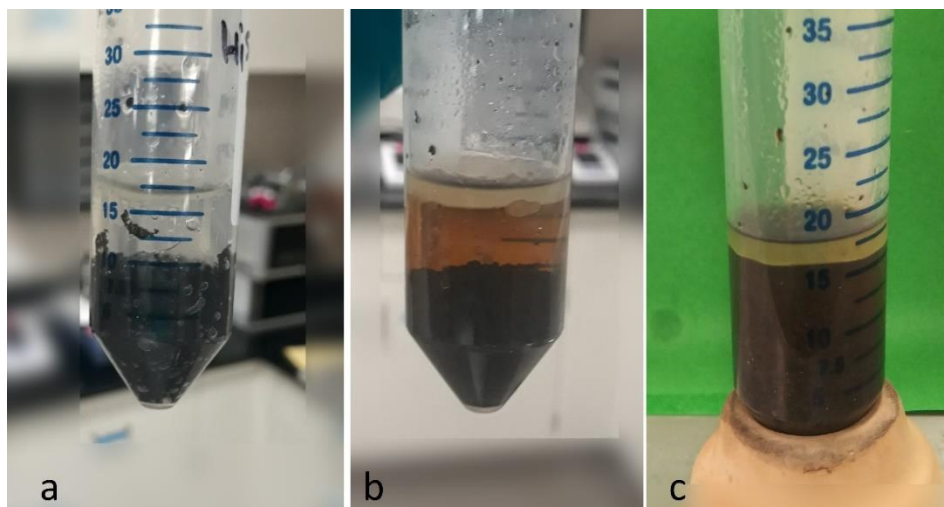


Figure 5-10: Static test sample 2 fractional tubes (a) sample at the moment of mixing (b) sample after 72 hours (c) sample after 144 hours. Again, increased oil is evident after longer soak times.

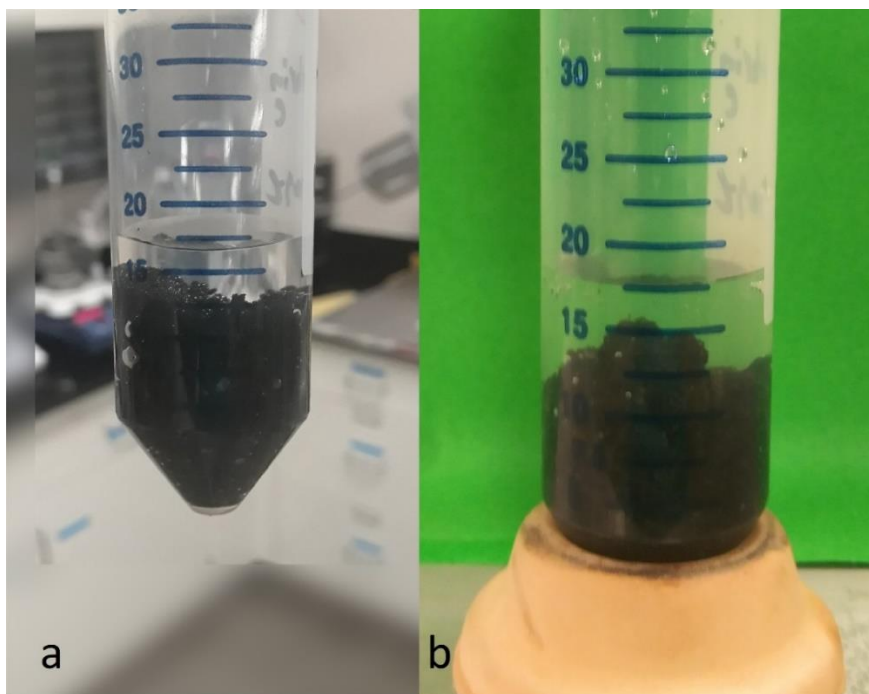


Figure 5-11: Static test sample 3 fractional tubes (a) sample at the moment of mixing (b) sample after 408 hours

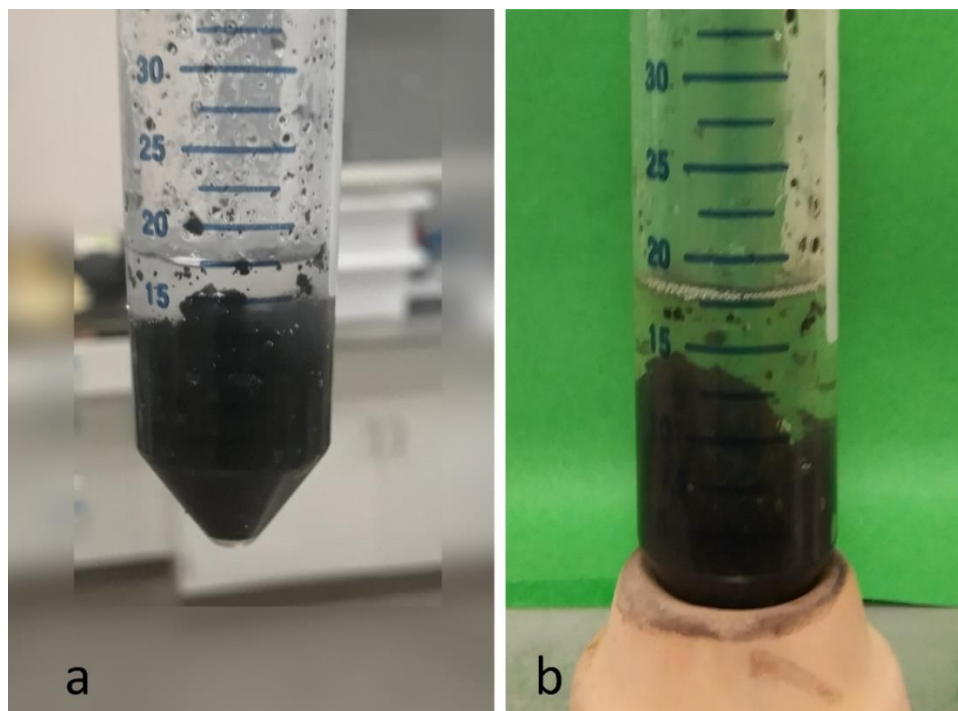


Figure 5-12: Static test sample 4 fractional tubes (a) sample at the moment of mixing (b) sample after 408 hours

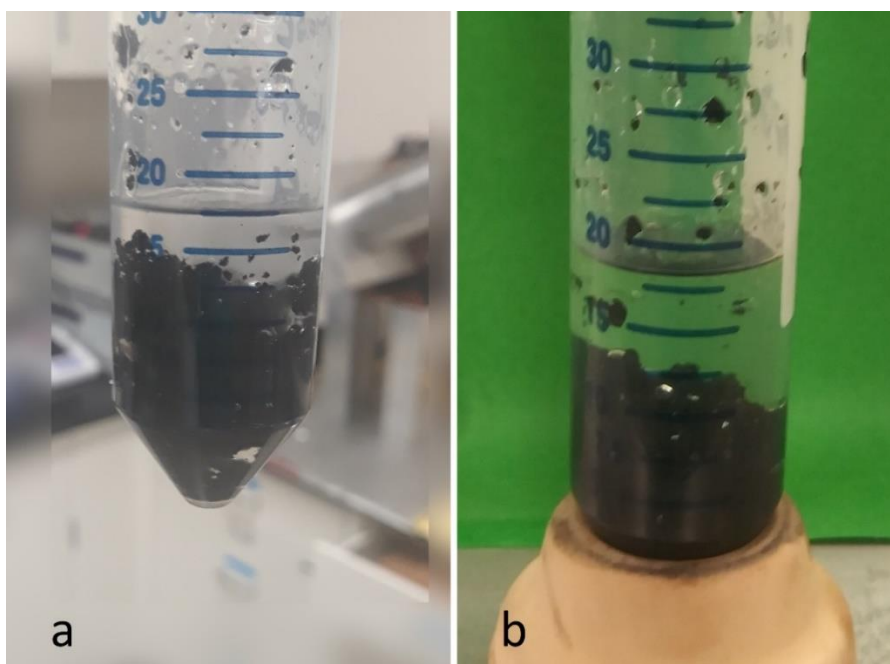


Figure 5-13: Static test sample 5 fractional tubes (a) sample at the moment of mixing (b) sample after 408 hours

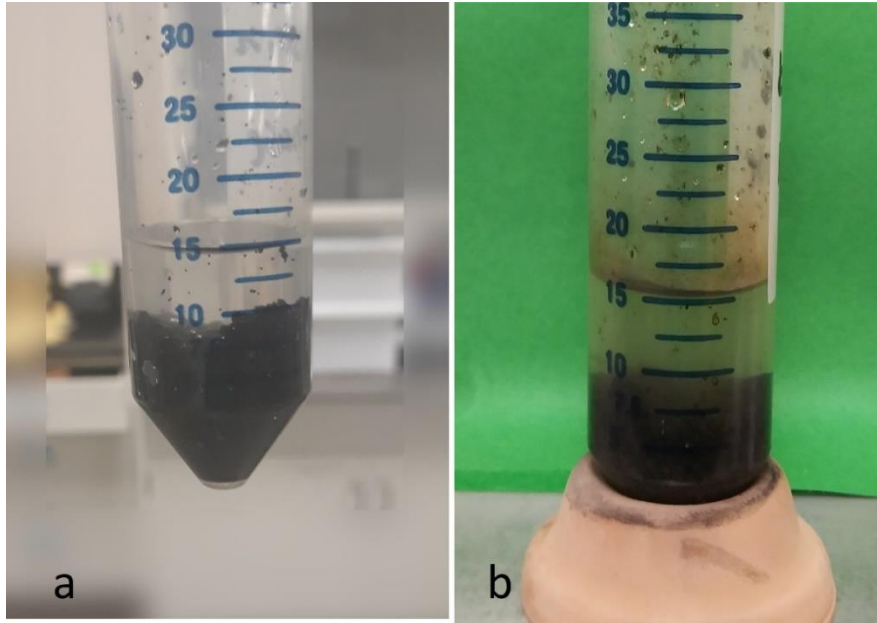


Figure 5-14: Static test sample 6 fractional tubes (a) sample at the moment of mixing (b) sample after 408 hours

The tests on samples 11, 12, and 13 were designed to evaluate the extraction capability by changing the fraction of nanofluid in flood operation. No significant difference between different samples in this examination was observed.

Table 5-11: Static tests 11,12,13 properties

sample	sand (gr)	nanofluid (cc)	brine (cc)	temp (°C)	note
11	10	0.8	0.8	22 (RT)	similar to flood condition
12	10	0.8	7	22 (RT)	high brine portion
13	10	2	0.8	22 (RT)	high nano portion

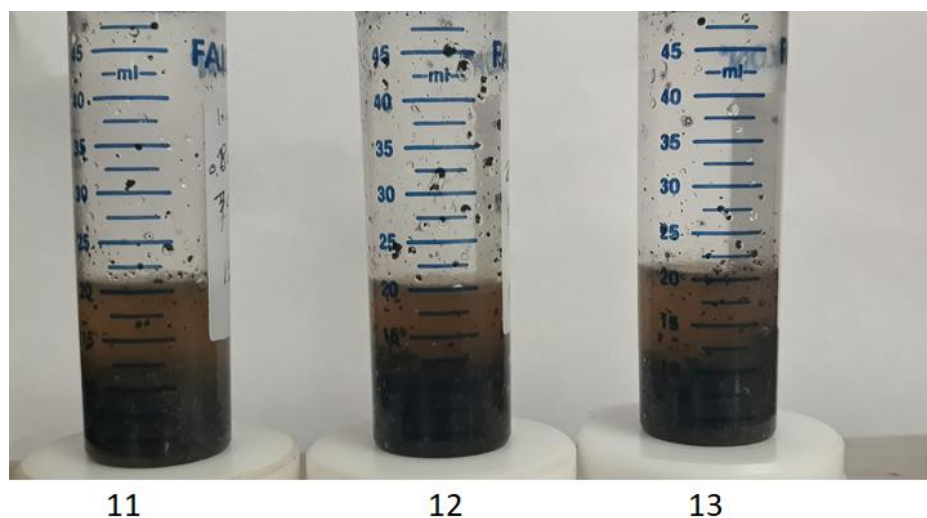


Figure 5-15: Samples 11, 12, and 13 to evaluate the effect of varying fluid ratios.

5.2.4 Test 4 – Silicone-Based Nanofluid Recovery from Oil Sand

Three days of soaking time after the injection of nanofluid were added to the experimental protocol. A one-half pore volume of nanofluid was injected at a rate of 10 cc/min followed by one-half pore volume of brine to ensure enough water to react with the nanofluid. The pH of effluent during nanofluid and brine injection was monitored, with an average value of 11.80 measured.

The results of the brine flood after the soaking process is shown in Figure 5-16 were the same as Test 3 with no additional oil extracted. This was despite the high pH measurements reported in Table 5-12 and hydrogen production. The volume of silicone oil collected in the fractional tube was lower than the amount of nanofluid that injected. We repeated Test 4 (Test 5) but added 3 check valves in the setup (Figure 4-8) to ensure the unidirectional flow of the nanofluid.

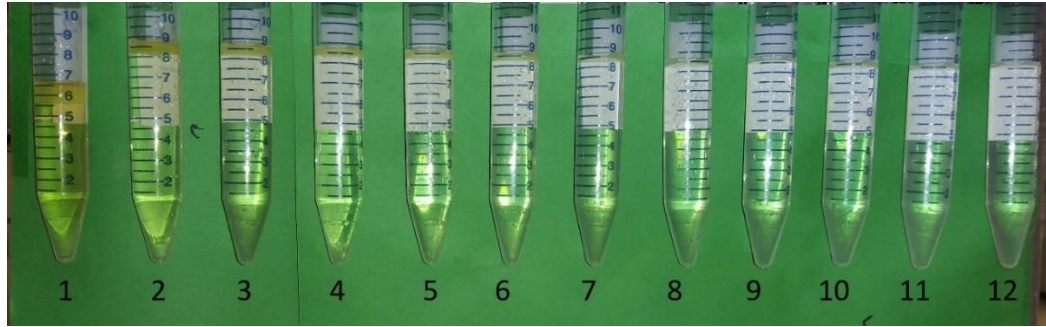


Figure 5-16: Test 4 result of brine flooding after soaking

Table 5-12: Test 4 result of pH measurement for effluent fluids

tube	pH
1	13.27
3	11.98
5	11.64
7	11.39
9	11.23
11	11.08

5.2.5 Test 5 - Silicone-Based Nanofluid Recovery from Oil Sand

No additional oil was extracted from the sample (Figure 5-9). In an effort to understand whether gravity effects were playing a role, the glass column was inverted and brine injected downward (same entrance of glass column) and still no visual change was observed to effluent fluids (Figure 5-17). The same results were observed in Test 5; the amount of silicone oil in the effluent fluid was less than the amount of injected oil. We concluded that the silicone oil dispersant tends to wet the sand surface and prevents oil sand particles from exposure to the alkali brine (Table 5-13) so that soap could not be generated effectively.

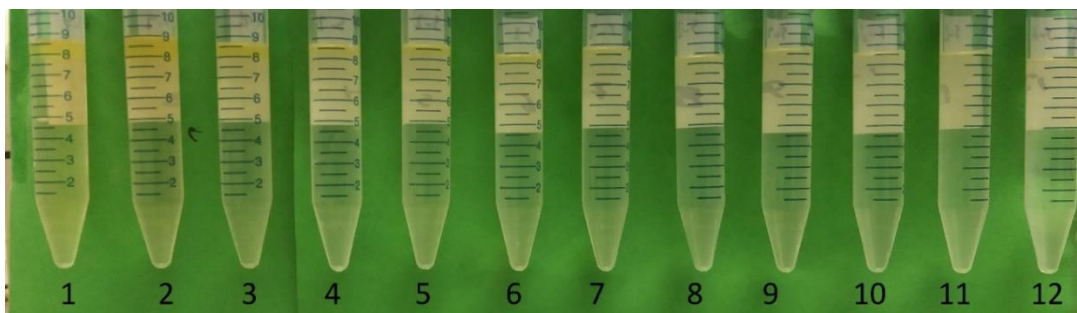


Figure 5-17: Test 5 result of first brine injection

Table 5-13: Test 5 effluent's pH measurement

tube	pH
1	13.10
3	12.28
5	12.03
7	11.69
9	11.34
11	11.36
12	11.27

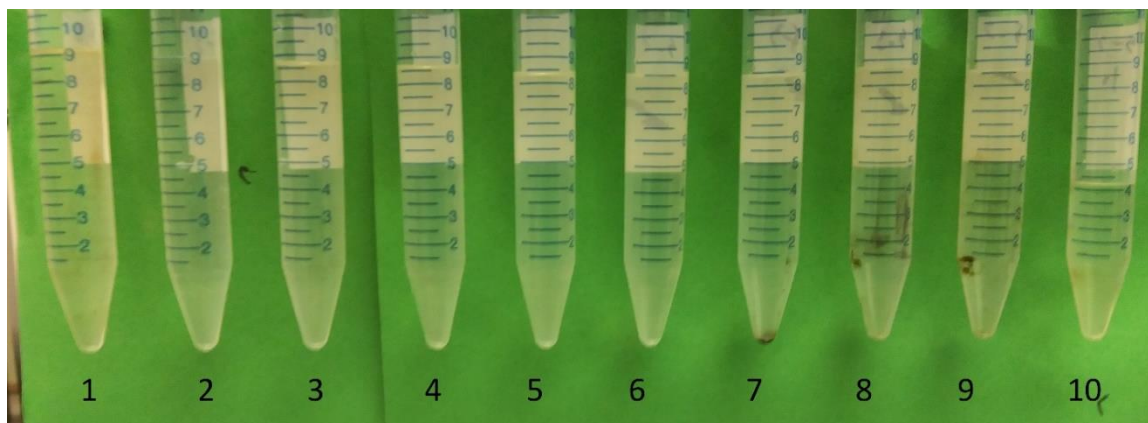


Figure 5-18: Test 5 result of brine flood after flipping the sample

The static test results on the upstream, middle, and downstream sections of the sand pack of test 5 confirm the lack of increase in produced oil as shown in Figure 5-19.

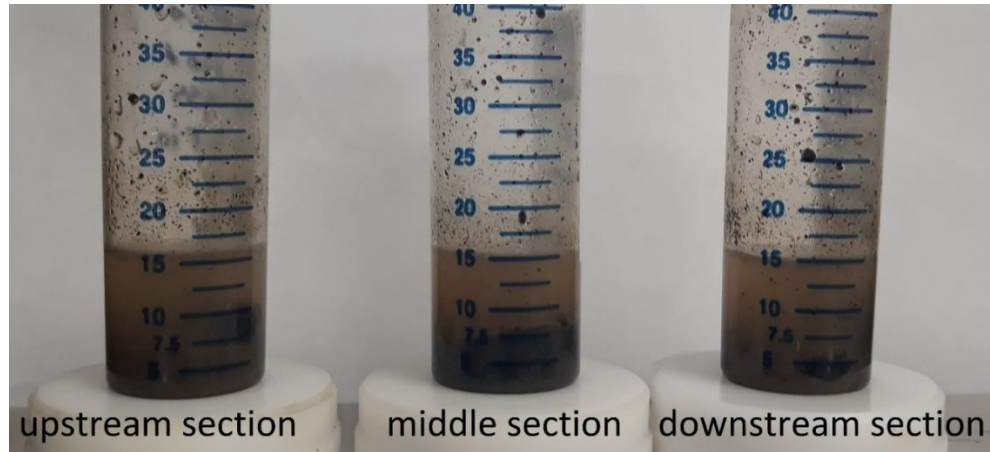


Figure 5-19: Test 5 result of static test

5.2.6 Test 6 – Pentane-Based Nanofluid Recovery from Oil Sand

Additional experiments were designed using pentane as the dispersant instead of silicone oil to prevent preferential wetting of the solids. In this case, additional oil was extracted using a pentane-based nanofluid. Some of the oil extraction was possible due to the solubility of pentane into oil sand hydrocarbons, and this was explored further.

The total amount of oil that could be extracted from 129 gr of oil in the sand was 16.5 gr according to the extraction process used by Sharma (2019). After concluding the initial pentane-based nanofluid flood, the column was exposed to low-velocity air to dry out, and the mass of the column was used to calculate that 5.5 gr of oil was extracted from the column. The total recovery was therefore interpreted to be 35% by injection of pentane-based sodium nanofluid. We realized that an increased soak time during brine flood operation could result in a movable oil bank to form and increased oil production.

Therefore, the floods were performed in 4 steps, each being 24 hours apart. As reported in Table 5-14, the pH was high enough to generate surfactant in the column and extract additional oil.

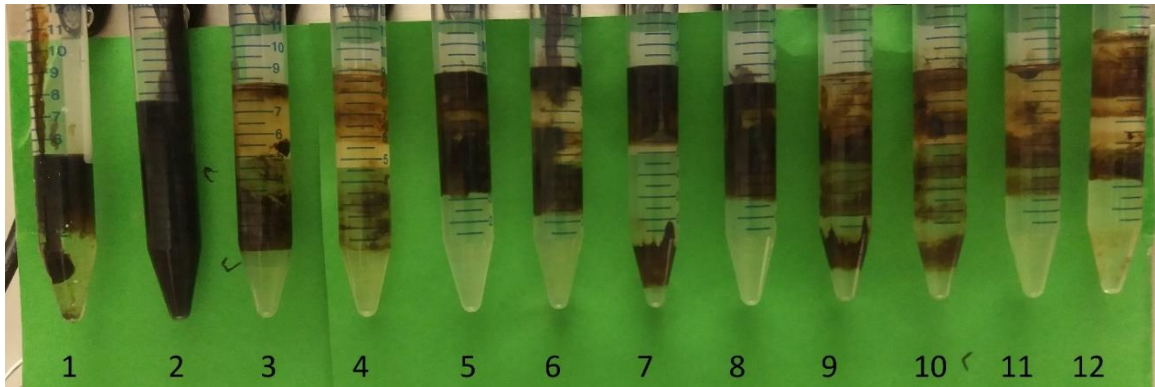


Figure 5-20: Test 6 result of brine flood (a)

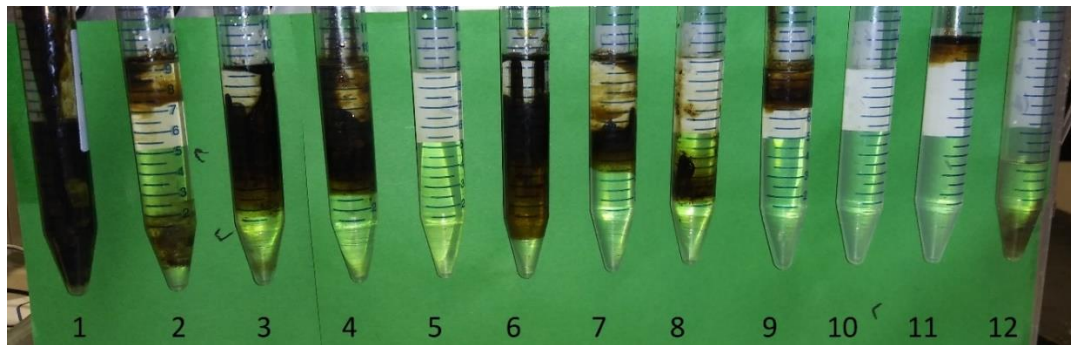


Figure 5-21: Test 6 result of brine flood (b)

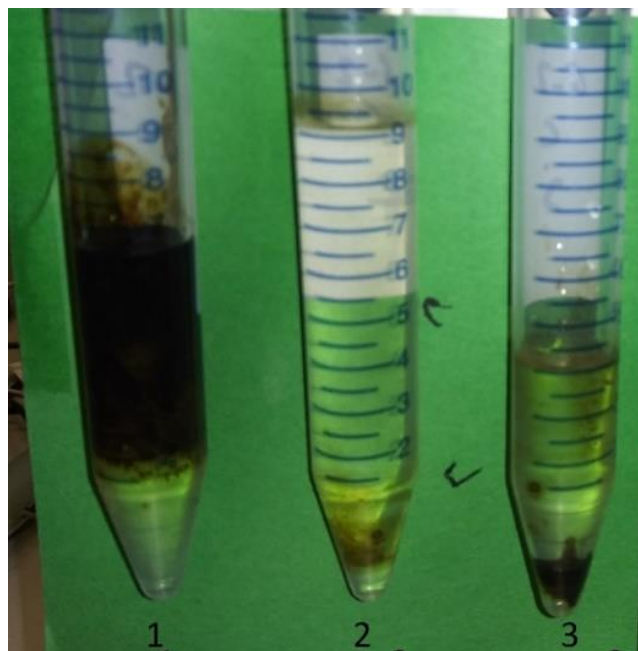


Figure 5-22: Test 6 result of brine flood (c)

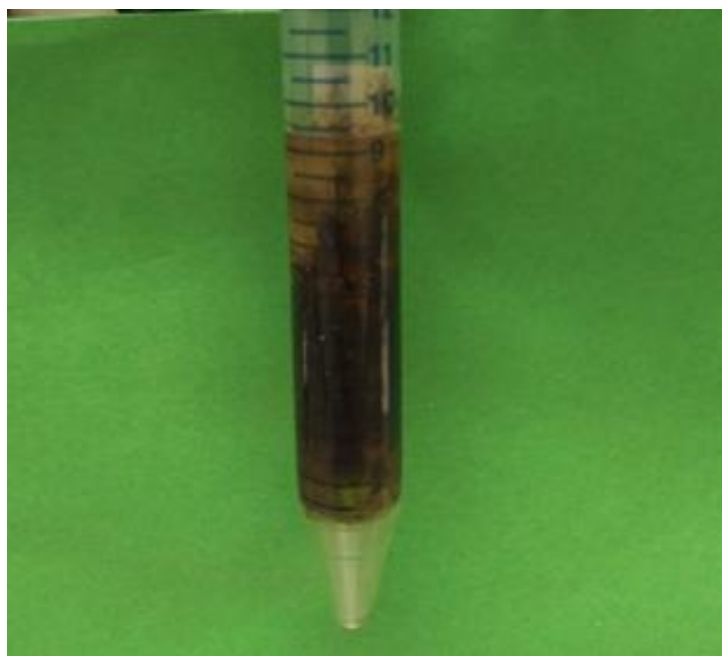


Figure 5-23: Test 6 result of brine flood (d)

Table 5-14: Test 6 effluent pH measurements.

flood	tube	pH
a	3	12.04
	4	11.97
	8	10.97
	10	10.82
	11	11.36
	12	11.51
	13	10.78
b	2	10.86
	6	9.82
	10	9.57
	12	9.34

Table 5-15: Test 6 final oil recovery.

mass of sand in column (gr)	% oil in oil sand	produced oil (gr)	% recovery
130	12.8	5.5	34

5.2.7 Test 7 - Pentane Recovery from Oil Sand

The pentane that was injected into the sand pack did dissolve and extract some oil. The same procedure and timings were applied to evaluate this base case and account for the recovery mechanism(s) more accurately. As can be seen in Figures 5-24 and 5-27, the oil extraction declined more rapidly once pentane injection ceased and brine injection was started because the main factor was the dissolving effect of pentane. In Test 6, the oil production lasted longer which can be interpreted as the effect of surfactant generation and the heat released during the nanofluid flood. The total recovered oil was

less than half of the case where nanoparticles were injected along with the pentane (Test 6).

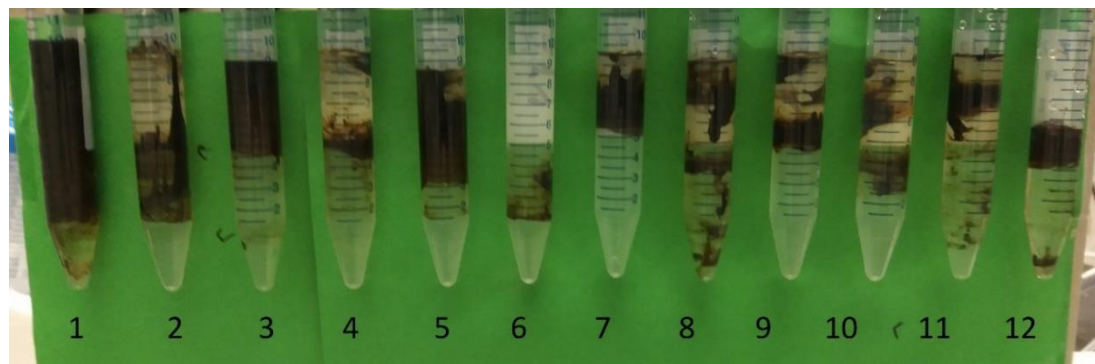


Figure 5-24: Test 7 result of brine flood (a)

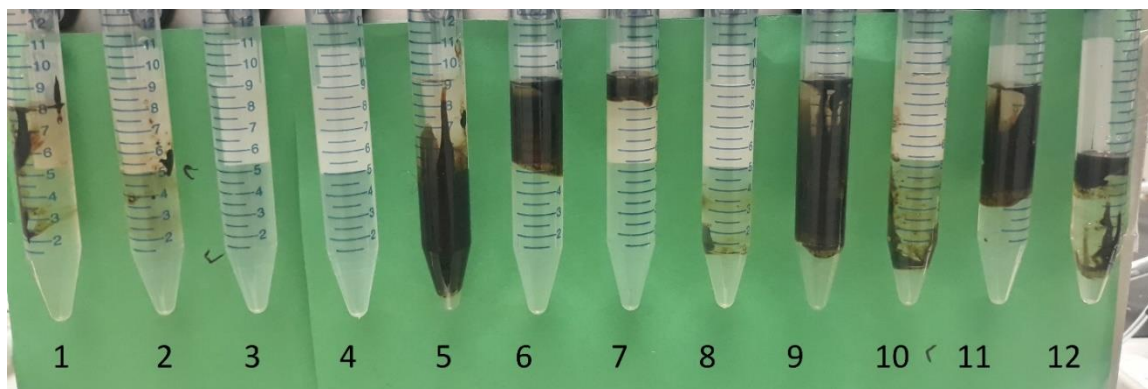


Figure 5-25: Test 7 result of brine flood (b)

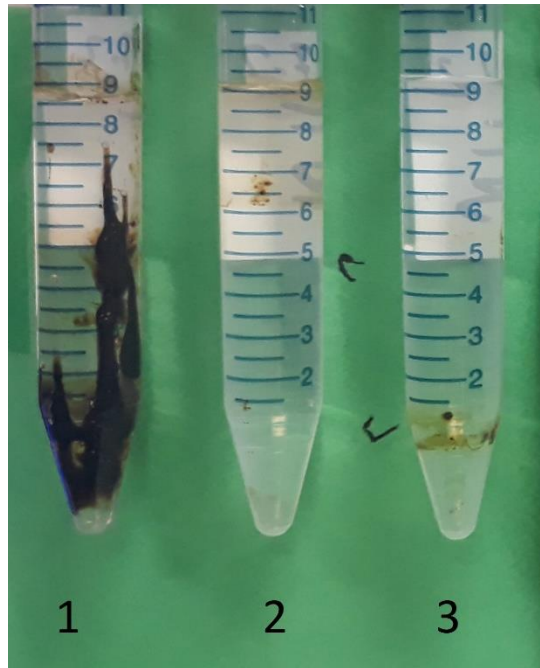


Figure 5-26: Test 7 result of brine flood (c)

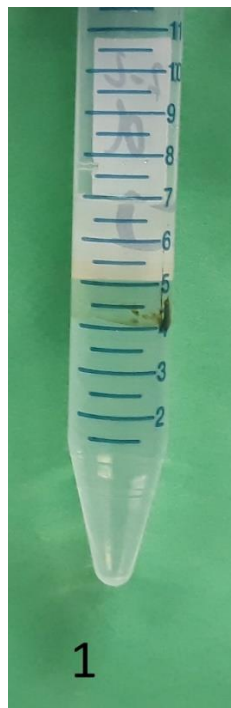


Figure 5-27: Test 7 result of brine flood (d)

Table 5-16: Test 7 final recovery measurement results

mass of sand in column (gr)	% oil in oil sand	produced oil (gr)	% recovery
130	12.8	2.5	14.9

Chapter 6

Conclusions and Recommendations

This research investigated a new method using sodium nanofluid to produce and extract oil from heavy oil and oil sand resources. This is a non-thermal method that consumes less energy and would help meet the world's demand for non-thermal methods for producing such reservoirs. The recovery result for applying sodium nanofluid into the synthetic sand pack filled with heavy oil was highly efficient and showed promise to be improved with further study. The extraction of oil from the oil sand samples was more challenging but the nanofluid and the associated generated alkali brines produced showed that it has the ability to produce a significant amount of incremental oil with longer residence times, even at room temperature.

6.1 Summary

6.1.1 Heavy Oil

Heavy oil was chosen as the first candidate because few methods are available to improve oil production in these reservoirs. The nanofluid triggers reactions that generate heat and gas acting as additional energy sources to mobilize the heavy oil. The sodium hydroxide generation was shown to have a positive effect on the production of oil from heavy oil resources. The results can be summarized as follow:

1. Immediately after injection of nanofluid, increased oil production occurs because the hydrogen gas generated inside porous media creates additional energy to mobilize residual oil.

2. The exothermic nature of the reactions between sodium and water improves the efficiency of oil extraction due to the reduction of regional viscosity.
3. Sodium hydroxide is the product of the reaction between brine and sodium that has a lasting effect by generating surfactants due to reactions with heavy oil's naphthenic acids, leading to higher amounts of recovered oil from the reservoir.
4. Recovery of around 75% was achieved despite the low temperature of the floods (room temperature); higher temperatures should improve efficiency.
5. The pH measurements showed that the increase in fluid alkalinity lasts significantly, even after ceasing nanofluid flood during the brine flood. After injection of 5 PV of brine, the pH of the effluent was still above 9.0.

6.1.2 Oil Sands

Oils sands were investigated as an alternative to the current methods that are known to require both energy and fresh water, and result in waste management issues.

1. The extraction of oil from oil sand was more challenging since the oil is immobile and must be detached from the sand surface. The mechanism that performs this appeared to be the surfactant produced by the reaction of sodium hydroxide with naphthenic acids present in the hydrocarbons.
2. The first test using a silicone-based sodium nanofluid was not successful. It was followed by static tests that showed that nanofluid has the capability of detaching oil from oil sand surface, but wetting of the solids by the dispersant appeared to retard the process. The dispersant for the nanofluid needs to be optimized for the matrix.

3. The static test results also showed that the nanofluid extracted oil at higher temperatures more efficiently.
4. The static tests showed that the exposure time of the sand surface to the sodium hydroxide and the turbulence generated in the porous medium was important.
5. The pentane-based nanofluid demonstrated that the nanoparticle flood can have around 20% percent incremental oil recovery compared to a pentane flood. The total recovery was around 34% for the pentane-based nanofluid flood.

6.2 Conclusion

Sodium nanofluid floods show promise for increasing oil production from the heavy oil and oil sand resources. They have the promise to become a new, efficient method to improve oil production from these resources.

6.3 Recommendations

This study has provided the framework for future studies on sodium nanofluid injection. For the case of production from heavy oil reservoirs, research on oil samples with different viscosity, TAN, and the effect of temperature should be investigated. Since hydrogen is generated, its effects on the efficiency of a single-well injection method (“push-pull”) of oil production should be investigated. Also, hydrogen will combust in presence of oxygen. If air is injected into the reservoir this could be a method that could be combined with the *in-situ* combustion method, which provides heat and energy to lower oil viscosity and increase reservoir pressures.

We conducted a cursory assessment of the cost of the sodium for this method before the start of this research. There is a need for a more elaborate study on the cost of operation and material and the optimum concentration of sodium once additional data from further studies are available.

For oil sand, there is a need to choose an optimum dispersant fluid considering the difficulties encountered with the separation of the oil. The effect of the TAN and the temperature of the oil sand reservoir should also be investigated. To be more quantitative, we recommend that a study involving the use of GC/MS analysis to monitor the production of hydrocarbon during floods.

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