EMIRATES INTERNATIONAL UNIVERSITY

COLLEGE OF ENGINEERING AND
INFORMATION TECHNOLOGY

OIL AND GAS ENGINEERING

APPLICATION OF NANOPARTICLES IN ENHANCED OIL RECOVERY

A PROJECT SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIRMENTS FOR THE DEGREE

OF BACHELOR OF SCIENCE

IN OIL AND GSA ENGINEERING

BY

Mahmoud Mane' Abdullah Al-Habl

Fahmy Ahmed Mohammed Al-Kqihal

Aymen Masood Ghilan Al-Alawi

Taha Ahmed Ghaleb Sharaf

Mohammed khaled Abdualrub Al shamiri

Bassam Abdullah Al-Mousaly

Najm Al-Din Abd Al-Hamali

SUPERVISOR

Dr. Yassin Alsalehi

SANA'A

7/2022

الجامعة الإمارتية الدولية
كلية الهندسة وتكنولوجيا المعلومات
هندسة نفط و غاز

استخدام جسيمات النانو في الاستخلاص المعزز للنفط

بحث تكميلي مقدم للإيفاء بمطلوبات نيل

درجه البكالوريوس في

هندسة النفط والغاز

اعداد

محمود مانع عبدالله الهبل

فهمي احمد محمد الخلقي

ايمن مسعود غيلان العلوي

طه احمد غالب شرف

محمد خالد عبدالرب الشميري

بسام عبدالله الموسلي

نجم الدين الحملي

اشراف

الدكتور/ ياسين الصالحي

صنعاء

٢٠٢٢/٧

SUPERVISOR CERTIFICATION

I certify that the preparation of this project entitled:

…………………………………………………………………………………………
…..……………………………,

Prepared by Mahmoud Mane' Abdullah Al-Habl

Fahmy Ahmed Mohamed Al-Kqihal

Aymen Masood Ghilan Al-Alawi

Taha Ahmed Ghaleb Sharaf

Mohammed khaled Abdualrub Al shamiri

Bassam Abdullah Al-Mousaly

Najm Al-Din Abd Al-Hamali

Was made under my supervision at oil and gas engineering department, College of Engineering and Information Technology, Emirates International University, in partial fulfillment of the Requirements for the degree of Bachelor of Engineering in Oil and Gas Engineering.

Signature:

Name: (Supervisor)

Date:

ACKNOWLEDGMENTS

First and foremost, we would like to thank Allah Almighty for giving us strength, patience and ability to complete this project.

We would like to extend our sincere thanks to the supervisor of our project, Dr. Yasin Abdo for his help, suggestions, corrections, long-term guidance in support, the tremendous supervision and warm encouragement throughout our project.

We would like to express our appreciation to our colleagues, friends, lecturers, academic and general staff of the Faculty of Engineering and Information Technology, Emirates University. And we wish to extend our grateful appreciation to all those who had contributed directly and indirectly to the preparation of this project.

We would like to thank our beloved families for all support, patience, understanding, and being helpful throughout our study. Especially, we give our deepest gratitude and sincerest love to our parents for their love, support, encouragement, patience, and assistance through our entire life. We are forever indebted to our parents, who always keep us in their prayers, encourage us to pursue higher goals and cheer us up in the difficult moments.

DECLARATION

We hereby declare that the work in this project is our own except for quotations and summaries which have been duly acknowledged.

Date:

Name	Registartion number	Signature
1- Mahmoud Mane’ Abdullah Al-Habl		
2- Fahmy Ahmed Mohammed Al-Kqihal		
3- Aymen Masood Ghilan Al-Alawi		
4- Taha Ahmed Ghaleb Sharaf		
5- Mohammed khaled Abdualrub Al shamiri		
6- Bassam Abdullah Al-Mousaly		
7- Najm Al-Din Abd Al-Hamali		

ABSTRACT

Nanotechnology has been envisioned to transform every sector of industries, particularly in the petroleum industry. Numerous researches, especially on nano-EOR, have been done in the past few years and shown promising results for improving oil recovery. Injected nanoparticles (NPs) are believed to be able to form adsorption layers on the top of grain surface. The adsorptions layers then alter the wettability of the rock and reduce the interfacial tension. Due to the importance of the adsorption, numerous theoretical studies were performed to simulate the transport behavior of NPs in the porous media.

The purpose of this thesis is to review the state-of-the-art progress of nanoparticles application in the petroleum industry especially in EOR, and simulate the transport and adsorption of nanoparticles in the porous media.

Literatures show that various types of nanoparticles can improve oil recovery through several mechanisms such as wettability alteration, interfacial tension reduction, disjoining pressure and mobility control. Parameters such as salinity, temperature, size, and concentration are substantial for nano-EOR. Several experiments indicate that NPs can improve the oil recovery significantly up to 20% after the primary recovery period.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CNT	Carbon Nanotubes
CEOR	Chemical enhanced oil recovery
EOR	Enhanced oil recovery
HLPN	Hydrophobic and lipophilic polysilicon nanoparticles
PSNP	Polysilicon NPs
Soi	Initial oil saturation
Swi	Initial water saturation
IFT	Interfacial tension
LPG	Liquid petroleum gas
LSW	Low-salinity water
MWNT	Multiwall Carbon Nanotubes
NPs	Nanoparticles
OOIP	Original oil in place
PAM	Polyacrylamide Polyacrylamide
PES	Polyether-sulfone
PNP	Polymer Nanoparticles
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscope
SDS	Sodium dodecyl sulfate
WAG	Water alternating gas

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Nanotechnology has appeared around the forties and is considered a relatively new technology that has been developed since the nineties and aims to revolutionize every sector of industries and the formation of human civilization significantly and has already been achieved in areas such as antibiotics, plastics, computer and silicon transistor industry although nanotechnology is A relatively recent development in scientific research, however, the development of its central concepts occurred over a longer period of time. The emergence of nanotechnology in the 1980s arose due to the convergence of experimental developments such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the clarification and generalization of a conceptual framework for the goals of nanotechnology starting with the 1986 edition of the Engines of Creation. It was proposed by Richard Feynman in 1959. However, the first term "nanotechnology" was introduced by Norio Taniguchi in 1974, then nanotechnology became more popular after Dr. Heinrich Rohrer (Nobel Prize winner and founding father of nanotechnology) scanning tunneling microscope (STM) in 1981 who later presented the promising opportunities for nanotechnology in 1996. Nanoparticles and nanostructured materials are one of the new materials classes that have attracted great interest within the scientific community due to their unique physical and chemical properties. These properties and potential applications are determined by their composition, size (distribution), and shapes.

Naturally including organic (e.g., proteins, sugars, viruses) as well as inorganic (e.g., iron ox hydroxides, alumina silicate, metals) that are produced by Weathering, volcanic eruptions, wildfires and microbe processes . Nanoparticle research is currently an area of intense scientific research, due to its wide range of potential applications in the biomedical, optical, and electronic fields. Nanoparticles are of great scientific interest because they effectively represent a bridge between bulk materials and atomic structures. Or molecular Humans used nanoparticles and structures in the fourth century AD, by the Romans, which showed one of the most interesting examples of nanotechnology in the ancient world. The Italians also used nanoparticles in Renaissance pottery during the sixteenth century and in 1857, Michael Faraday studied the preparation and properties of colloidal suspensions of "sapphire" gold. Its unique optical and electronic properties make it one of the most interesting nanoparticles. Faraday demonstrated how gold nanoparticles produce solutions of different colors under certain lighting conditions.

1.2 OIL PRODUCTION PROCESS

During the life of a producing oil field, several production stages are encountered. Initially, when a field is brought into production, oil flows naturally to the surface due to current reservoir pressure in the primary stage. As reservoir pressure drops, water is typically injected to boost the pressure to displace the oil in the secondary stage. Lastly, the remaining oil can be recovered by a variety of methods such as CO2 injection, natural gas miscible injection, and steam recovery in a tertiary or enhanced oil recovery (EOR) phase.

1.2.1 Primary Recovery

Glover (2001) explained all recovery methods, including primary recovery mechanism as it is the stage when the natural energy of the reservoir is used to transport hydrocarbons towards and out of the production wells. The earliest possible determination of the drive mechanism is a primary goal in the early life of the reservoir, as its knowledge can greatly improve the management and recovery of reserves from the reservoir in its middle and later life. There are five important drive mechanisms: (A) Solution gas drive; (B) Gas cap drive; (C) Water drive; (D) Gravity drainage; (E) Combination or mixed drive. These drives can maintain the reservoir pressure, though water drive maintains much higher than the gas drives (Fig. 1.1).

1.2.2 Solution Gas Drive

In solution gas drive, the expansion of the dissolved gases in the oil and water provides most of the reservoirs drive energy. Solution Gas Drive is associated to two types of

Reservoirs that are related to pressure; under saturated reservoirs (no free gases in oil), drive energy is provided only by the bulk expansion of the reservoir rock and liquids; saturated reservoirs, where the pressure is less than the bubble point pressure. A decline in reservoir pressure causes bubbles of gas to expand. Thus, gas expansion is the primary reservoir drive for reservoirs below the bubble point. Oil recovery from this type is typically between 20% and 30% of original oil in place (Fig. 1.1).

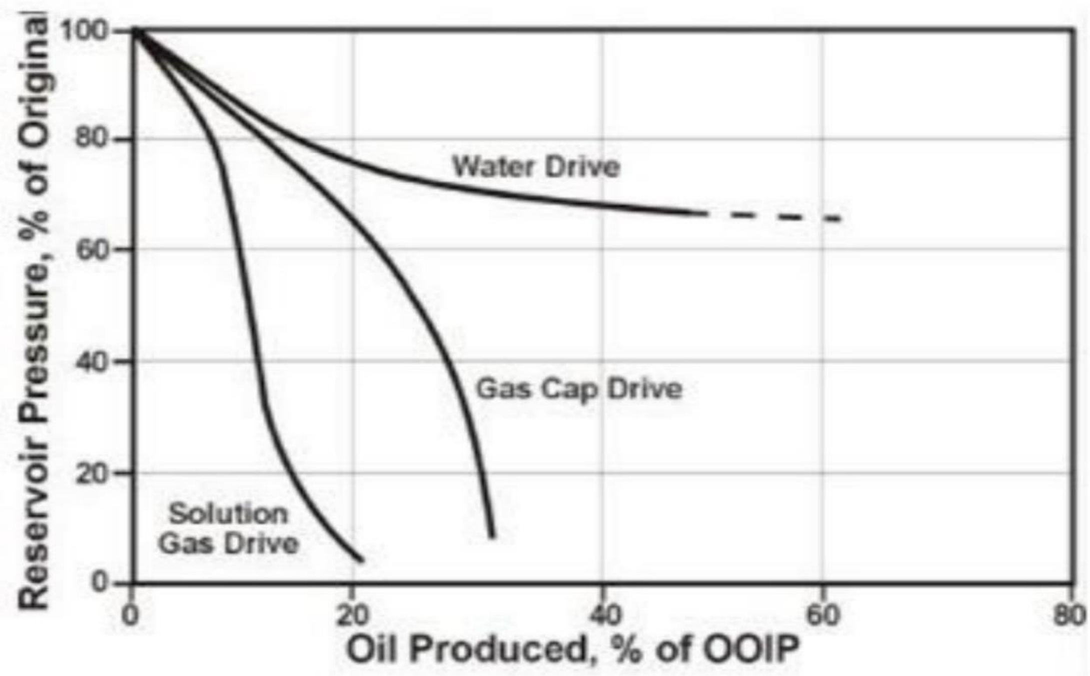

Figure 1.1 Reservoir pressure trends by drive mechanism .

1.2.3 Gas Cap Drive

As production continues, the gas cap expands pushing the gas-oil contact (GOC) downwards. Eventually the GOC will reach the production wells and the gas oil ratio (GOR) will increase by large amounts. The recovery of gas cap reservoirs can be (20% to 40% OOIP). Produced gas can be separated and immediately injected back into gas cap.

1.2.4 Water Drive

The drive energy is provided by an aquifer that interfaces with the oil in the reservoir at the oil-water contact (OWC). As production continues, and oil is extracted from the reservoir, the aquifer expands into the reservoir displacing the oil. The recovery from water driven reservoirs is usually good (20-60% OOIP). Oil production from a strongly water driven reservoir remains fairly constant until water breakthrough occurs. When water breakthrough does occur, the well can either be shut-down, or assisted using gas lift.

1.2.5 Gravity Drainage

Gravity Drainage is the fourth drive force that might be considered for drive mechanism where the density differences between oil and gas and water result in their natural segregation in the reservoir. This process can be used as a drive mechanism, but is relatively weak, and in practice is only used in combination with other drive mechanisms.

1.2.6 Combination Drive

In practice a reservoir usually incorporates at least two main drive mechanisms. Therefore, Combination or Mixed Drive can be accounted as the fifth type of Drives.

1.2.7 Oil Lifting by Gas or Pumps

In addition to the previous drive mechanisms, artificial lifting is considered as a primary recovery, which is a process used to increase pressure within the reservoir, when the natural drive energy of the reservoir is not strong enough to push the oil to the surface. The two main categories of artificial lift include pumping systems and gas lift. Gas lift method injects compressed gas into the well to re-establish pressure, making it produce. On the other hand, jack pumps are submersed and used to lift the oil to the surface .

1.3 SECONDARY RECOVERY

After initial discover and production, typical oil reservoirs lose the drive mechanism of gas or water that originally forced the oil to the surface. The second stage of hydrocarbon production in which an external fluid such as water: usually named Water flooding or water injection or gas: referred to as Gas flooding or gas injection, is injected into the reservoir through injection wells located in rock that has fluid communication with production wells.

1.3.1 Water Flooding

Water Flooding is implemented by injecting water into a set of wells while producing from the surrounding wells. Water flooding projects are generally implemented to accomplish reservoir pressure maintenance and/or dispose of brine water (or produced formation water), and/or as a water drive to displace oil from the injector wells to the producer wells.

1.3.2 Gas Flooding

This method is similar to water flooding in principal, and is used to maintain gas cap pressure even if oil displacement is not required. Usually the produced natural gas is re-injected to the reservoir in order to maintain reservoir pressure rather than to displace the hydrocarbon. Later in this paper, gas injection methods are discussed in order to displace oil as well as to maintain the reservoir pressure. These techniques include gases such as Carbon Dioxide or Nitrogen, etc.

Eventually, many oil fields usually produce only 12-15% of the OIIP. By secondary recovery methods, another 15-20% may be produced.

1.4 TERTIARY RECOVERY (ENHANCED OIL RECOVERY)

Primary production and secondary recovery methods on the average produce less than one-third of the original oil in place (OOlP). Tertiary Recovery (Enhanced recovery techniques), EOR, can be used to recover additional hydrocarbons. EOR introduces fluids that reduce viscosity and improve flow. These fluids could consist of gases that are miscible with oil such as carbon dioxide or nitrogen, steam, air or oxygen, polymer solutions, gels, surfactant-polymer formulations, alkaline-surfactant-polymer formulations, or microorganism formulations. However, the diagram of the oil recovery stages is shown in Fig. 1.2.

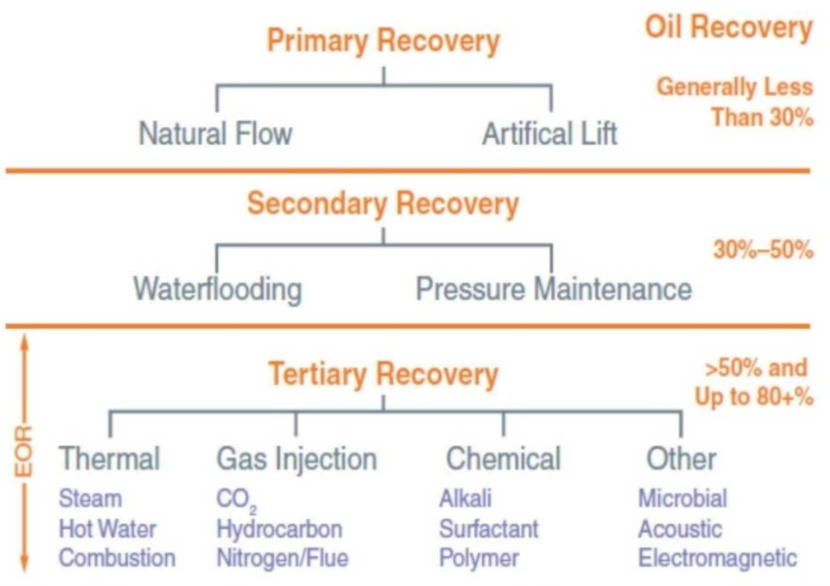

Figure 1.2 The different oil recovery stages and the corresponding oil recovery factor.

1.5 ENHANCED OIL RECOVERY TECHNIQUES

EOR refers to the recovery of oil through the injection of fluids and energy not normally present in the reservoir. The objectives of the injected fluids are to achieve mainly two purposes; First is to boost the natural energy in the reservoir; second is to interact with the reservoir rock/oil system to create conditions favourable for residual oil recovery that leads to reduce the interfacial tension between the displacing fluid and oil, increase the capillary number, reduce capillary forces, increase the drive water viscosity, provide mobility-control, create oil swelling, reduce oil viscosity, alter the wettability of reservoir rock. Enhanced oil recovery can be divided into two thermal and non-thermal recovery. Fig. 1.2 illustrates oil recovery stages by the different EOR techniques.

1.6 THERMAL TECHNIQUES

Thermal methods raise the temperature of the reservoir to heat the crude oil in the formation and therefore reduce its viscosity and/or vaporise part of the oil and thereby decrease the mobility ratio. The increase in heat reduces the surface tension and increases the permeability of the oil and improves the reservoir seepage conditions. The heated oil may also vaporise and then condense to be produced. This operation, however, requires substantial investment in special equipment. Both methods also hardly damage the well bore structure, as well as pose safety risks in the larger production process. Therefore, thermal methods are not generally USED very often.

1.6.1 Steam Injection

Steam is injected into the reservoir either continuously or in cycles. Continuous steam injection involves both injection and production wells, whereas cyclic injection involves one well only which serves as both injection and production well. Steam floods are easier to control than in-situ combustion. For the same pattern size, the response time is 25-50% lower than the response time for additional production by in-situ combustion.

1.6.2 In-Situ Combustion (ISC)

In-situ combustion or fire flooding is a process in which an oxygen containing gas is injected into a reservoir where it reacts with the oil contained within the pore space to create a high temperature self-sustaining combustion front that is propagated through the reservoir. The heat from the combustion thins out the oil around it, causes gas to vaporize from it, and vaporizes the water in the reservoir to steam. Steam, hot water, and gas, all act to drive oil in front of the fire to production wells. In-situ combustion is possible if the crude-oil/rock combination produces enough fuel to sustain the combustion front.

Severe corrosion and increased sand oil production are some of the problems that encountered by implementation of this technique.

1.6.3 Hot Water Flooding

Water-flooding in heavy oils is generally, not an efficient way of production due to high viscosity of heavy oil compared to water. In hot waterflooding, thermal energy will increase oil mobility, and possibly provide a more sweep efficiency. Injecting, regularly hot fresh to saline brines will improve oil recovery by dropping viscosity and decreasing residual oil saturation. If low salinity waters are injected, clay matrix may swell and therefore, clog pore throats. Porosity and permeability can be increased by collapsing some of the interlayer clays, when injecting water with high temperature. According to Seni, Burger and others (1985) emphasized that although the incremental gain in production from injecting hot water is substantial compared with that gained from injecting cold water during typical water flood are less significant than those resulting from injecting steam. Operators seldom employ hot water flooding because heat losses in surface lines, wellbore, and formation are greater than the heat losses in the other thermal processes. The heat losses reduce the processes effectiveness in decreasing oil viscosity.

1.7 NON-THERMAL EOR TECHNIQUES

1.7.1 Chemical Flooding

The best times for using chemical EOR methods were in the 1980's. Polymer flooding was the most important chemical EOR method. However, since 1990's, production from chemical EOR methods has been insignificant around the world except for China. These processes use chemicals added to water in the injected fluid of a water flood to alter the flood efficiency in such a way as to improve oil recovery by: (1) Increasing water viscosity (polymer floods) (2) Decreasing the relative permeability to water (cross-linked polymer floods) (3) Increasing the relative permeability to oil (micellar and alkaline floods).

1.7.2 Chemical EOR Types

a) Polymer Flooding

Polymers improve both vertical and areal sweep efficiency by reducing water-oil ratio. Polymers are injected through water injection wells in order to displace the residual oil. Increasing the displacing fluid's viscosity and lowering its relative permeability through plugging will improve the mobility ratio and this will make an improvement in areal and vertical sweep efficiency.

b) Micellar Polymer Flooding

It is well known that water and oil cannot be mixed until the third component, surfactant or soap, is added to reduce the interfacial tension between oil and water. Since micellar solution makes fluids miscible in the reservoir, almost 100% of oil can be displaced especially in the presence of alkaline (Sodium Carbonate). However, due to reservoir rock non-uniformity in the field, the amount of oil recovered is reduced. The main objective of micellar injection is to reduce interfacial tension to enhance oil recovery. Micellar solutions are mixtures of surfactants, co-surfactants, electrolytes, hydrocarbon, and water. Surfactants are substances known as surface active agents, such as soap. Co-surfactants are used for stability such as alcohols. Electrolytes are salts used to control viscosity and interfacial tension such as sodium chloride or ammonium sulphate.

c) Alkaline-Surfactant-Polymer (ASP) Flooding

During waterflooding residual oil is trapped due to low water viscosity and high water-oil interfacial tension, therefore another way is to inject the three chemicals; Alkaline to minimize surface adsorption; Surfactant to lower interfacial tension and stabilizes the emulsion. On the other hand, Polymer is used to increase viscosity and to improve mobility control and sweep efficiency.

1.7.3 Gas Flooding (Injection)

Gas is generally injected single or intermittently with water and this manner of injection called Water-Alternating Gas (WAG), has become widely practiced over all of world's oil fields. According to miscibility between gas injected and oil displaced, gas injection can be classified into two major types: miscible gas injection and immiscible gas injection. In **miscible gas injection,** the gas is injected at or above minimum miscibility pressure (MMP) which causes the gas to be miscible in the oil. In contrast in **immiscible gas injection,** flooding by the gas is conducted below MMP. This low-pressure injection of gas is used to maintain reservoir pressure to prevent production cut-off and thereby increase the rate of production. In miscible flooding, the incremental oil recovery is obtained by one of the three mechanisms: oil displacement by solvent through the generation of miscibility (i.e. zero interfacial tension between oil and solvent – hence infinite capillary number), oil swelling, and reduction in oil viscosity. Miscible fluids are 100 % soluble in each other. The interfacial tension between miscible fluids is zero. Injection gases include:

a) LPG Injection

Miscible LPG products such as ethane, propane, or butane have first contact miscibility, which means they will be miscible from the first contact with oil. However, LPGs are in such demand as marketable commodity that their use in EOR is limited. In particular, this process uses a slug of propane or other liquefied petroleum gas (2 to 5% PV pore volume) followed by natural gas, inert gas, and/or water. Thus, the solvent will bank oil and water ahead, and fully displace all contacted oil.

b) Enriched Gas Miscible Process

In this process, a slug of methane (C1) enriched with ethane (C2), propane (C3), or butane (C4) (10 to 20% of the PV) and followed by lean gas and/or water is injected from water injection well into the reservoir. When the injected gas contacts virgin reservoir oil, C1-C3 are quenched from the injected gas and absorbed into the oil. The injected HC solvent is usually displaced with cheaper chase leaner or inert gas like Methane or Nitrogen.

At reservoir conditions the most usual problem occurs with the hydrocarbon miscible flood is the gravity over-ride because of its lighter density than the oil and water. So that in any miscible flood the Minimum Miscibility Pressure (MMP) plays the most major role to overcome this problem. As a remedial factor the solvent is to be injected at or above the MMP of the reservoir fluid. Once it becomes miscible then it improves the sweep efficiency and fallouts in optimum recovery.

c) Carbon Dioxide (CO2) Injection

Is one of the most proven of these methods. Almost pure CO2 (>95% of the overall composition) has the property of mixing with the oil to swell it, make it lighter, detach it from the rock surfaces, and causing the oil to flow more freely within the reservoir so that it can be “swept up” in the flow from injector well to producer well. Flooding a reservoir with CO2 can occur either miscibility or immiscibly. Miscible CO2 displacement is only achieved under a specific combination of conditions, which are set by four variables: reservoir temperature, reservoir pressure, injected gas composition, and oil chemical composition. From a fundamental point of view, CO2 EOR works on a very simple principle, namely, that given the right physical conditions, CO2 will mix miscibly with oil, acting much like a thinning agent, the same way that gasoline does with motor oil. After miscible mixing, the fluid is displaced by a chase phase, typically water.

1.7.4 Nitrogen Injection

The nitrogen injection can be used as a substitute for CO_2 in deep light to medium oil reservoirs mainly containing C1 to C7 components. It is applicable in both the Sandstone and Carbonate reservoirs. Nitrogen itself is an inert gas that gets miscible at very high pressure and efficiently reduces the oil viscosity and provides efficient miscible displacement. Based on past studies, nitrogen injection could recover up to 45-90% of initial reserves. Nitrogen was used back to 50's when it played a crucial role in the petroleum industry, such as in well completion and well work over. Nitrogen has long been successfully used as the injection fluid for EOR and widely used in oil field operations for gas cycling, reservoir pressure maintenance, and gas lift. The costs and limitations on the availability of natural gas and CO_2 have made nitrogen an economic alternative for oil recovery by miscible gas displacement.

1.7.5 MICROBIAL EOR METHODS (MEOR)

Microbiological Treatment introduces specific micro-organisms to an oil field which metabolite some of the hydrocarbon, in turn producing byproducts which assist in oil recovery. These bi-products include solvents, acids, alcohols, bio-polymers, bio-surfactants and gasses.

Microbial enhanced oil recovery (MEOR) is a biological technology consisting of manipulating the function or structure, or both, of microbial environments present in oil tanks MEOR is a tertiary oil recovery technique for the additional extraction of trapped oil from the well. In principle, the process of MEOR results in some beneficial effects such as formation of stable oil-water emulsions reduced interfacial tension and clogging the high permeable zones and alteration of wettability by surfactant production and bacterial presence, selective plugging by microorganisms and their metabolites, oil viscosity reduction by gas production or degradation of long-chain saturated hydrocarbons, and production of acids which improves absolute permeability by dissolving minerals in the rock, however, the two first mechanism are believed to have the greatest impact on oil recovery MEOR methods probably is the means by which the substances are introduced into the reservoir. Table1.3 summarizes different microbial consortia, their related metabolites and applications.

Table 1.1 Microorganism, their metabolites and applications in MEOR.

Microbial	product Example microbes	Application in MEOR
Biomass	Biomass Bacillus, Leuconostoc,Xanthomonas	Selective plugging and wettability alteration
Surfactants	Acinetobacter, Arthrobacter, Bacillus, Pseudomonas	Emulsification and de-emulsification through reduction of IFT
Polymers	Bacillus, Brevibacterium, Leuconostoc, Xanthomonas	Injectivity profile and viscosity modification, selective plugging
Solvents	Clostridium, Zymomonas, Klebsiella	Rock dissolution for better permeability, oil viscosity reduction
Acids	Clostridium, Enterobacter, Mixed acidogens	Permeability increase, emulsification
Gases	Clostridium,Enterobacter Methanobacterium	Increased pressure, oil swelling, IFT and viscosity reduction

a) MEOR advantages

1. The injected bacteria and nutrient are inexpensive and easy to obtain and handle in the field.
2. MEOR processes are economically attractive for marginally producing oil fields and are suitable alternatives before the abandonment of marginal wells.
3. Microbial cell factories need little input of energy to produce the MEOR agents.
4. Compared to other EOR technologies, less modification of the existing field characteristics is required to implement the recovery process by MEOR technologies, which are more cost-effective to install and more easily applied.
5. Since the injected fluids are not petrochemicals, their costs are not dependent on the global crude oil price.
6. MEOR processes are particularly suited for carbonate oil reservoirs where some EOR technologies cannot be applied efficiently.
7. The effects of bacterial activity within the reservoir are improved by their growth with time, while in EOR technologies the effects of the additives tend to decrease with time and distance from the injection well.

8. MEOR products are all biodegradable and will not be accumulated in the environment, therefore are environmentally compatible.

9. As the substances used in chemical EOR methods are petrochemicals obtained from petroleum feedstock after downstream processing, MEOR methods in comparison with conventional chemical EOR methods, in which finished commercial products are utilized for the recovery of raw materials, are more economically attractive.

b) MEOR disadvantages

1. The oxygen deployed in aerobic MEOR can act as corrosive agent on non-resistant topside equipment and down-hole piping.

2. Anaerobic MEOR requires large amounts of sugar limiting its applicability in offshore platforms due to logistical problems.

3. Exogenous microbes require facilities for their cultivation.

4. Indigenous microbes need a standardized framework for evaluating microbial activity, e.g. specialized coring and sampling techniques.

5. Microbial growth is favored when: layer permeability is greater than 50 md; reservoir temperature is inferior to 80 0C, salinity is below 150 g/L and reservoir depth is less than 2400m.

1.7.6 NANOPARTICLE TECHNOLOGY

a) Nanoparticle Nanotechnology Definition

The word Nano means very small, and the size of a nanometer is 1 nanometer = (10^9) m, which is about 100,000 smaller than a human hair. Making new things on such an incredibly small scale is called nanotechnology and it is one of the most exciting and fast-moving technologies in today's world. Some secondary substances occurred naturally which we can find everywhere, for example in the ash of volcanoes, in the oceans, in dust, etc. Some naturally occurring nanostructures are also found in plants and animals. During the past years, scientists have achieved significant success in the nanoscience and nanotechnology. Nanotechnology is a field of applied sciences which is focused on design, production, detection, and employing the Nano-size materials, pieces, and equipment. Advances in nanotechnology lead to improvement of tools and equipment as well as their application in everyday life. In the chemistry this size involves the range of colloids, micelles, polymer molecules, and structures such as very large molecules or dense accumulation of the molecules. In physics of electrical engineering, the nanoscience is strongly related to quantum behavior or electrons behavior in structures with Nano sizes. Also, in biology and biochemistry, there are interesting cellular components and molecular structures.is one of the methods which attracts great attention nowadays in enhancing oil recovery because it is cost-effective and environmentally friendly. The size of nanoparticles for oil recovery is in a range of 1 to 100 nm. Enhanced oil recovery methods are utilized to increase the oil recovery by improving the mobility ratio, altering the wettability, and/or lowering the interfacial tension between water and oil. Nanoparticles have attracted the attention due to their unique properties. A large number of nanoparticles have been investigated for enhanced oil recovery applications either alone or in combination with surfactants and/or polymers. **<u>It is Classification</u>**

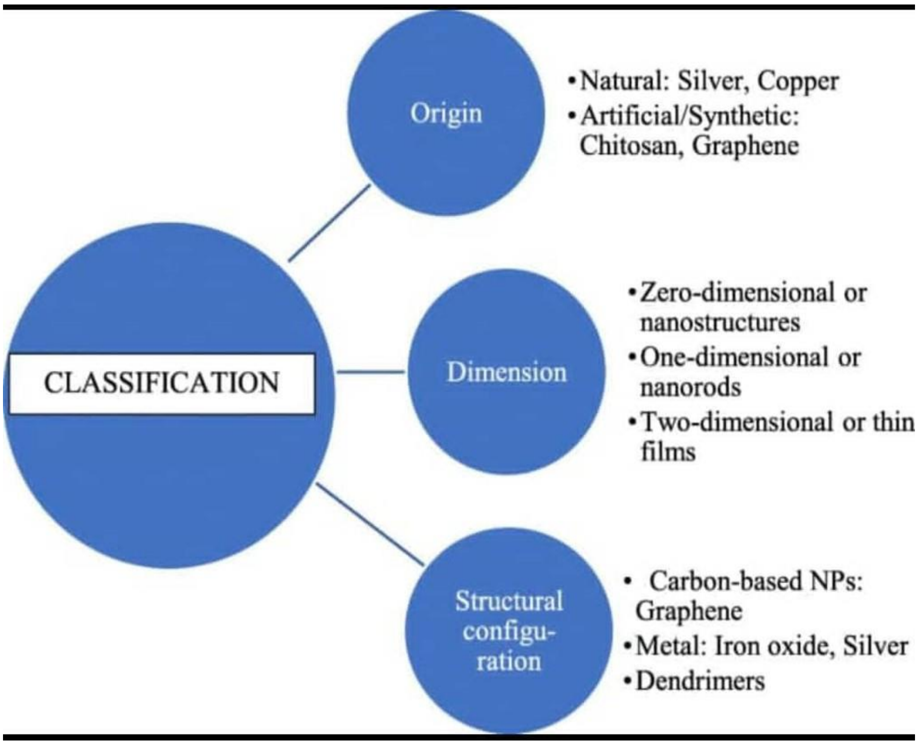

Figure 1.3 Classification of nanoparticles

Now today's scientists can also create secondary structures themselves by rearranging the body's atoms. These organisms can make new nanomaterials with new properties. These characteristics also change according to science and that is the charm of Hyderabad, Mittal Enterprises Nanotechnology. Some of the nanoparticle manufacturers in India are etc., Nano Span Private Limited in Hyderabad, Nano Orbital Private Limited.

1.8 PROJECT OBJECTIVES

1. Review of existing researches on the types of nanoparticles used for enhanced oil recovery and its manufacturing methods.
2. Deeply understanding the mechanisms and parameters affecting recovery improvement of Nanoparticles and its importance for enhanced oil recovery.

1.9 PROJECT OUTLINES

This project thesis consists of five chapters. The focus and coverage of each chapter are briefly as follows:

Chapter 1 this chapter discusses the methods of oil production in terms of the natural production of reservoirs, secondary injection methods, and third injection methods in general, including methods of enhancing oil recovery in full, and discusses a brief overview of nanotechnology and some of its advantages and characteristics over the previous methods.

Chapter 2 discusses the fundamental theory of nanomaterial, nanoparticle and nanofluid. Nanomaterial, nanoparticle, and nanofluid will be briefly defined. The fabrication process of nanomaterial and the fabrication process of nanoparticle and the preparation of stable nanofluid will be elaborated with the methods used for enhancing the stability of nanofluids.

Chapter 3 covers the recent application of nanoparticles and nanofluids in the petroleum industry. The chapter will summarize the utilization of nanoparticles for exploration, drilling, production, and refinery briefly.

Chapter 4 investigates the experimental research on nanofluids, which have been done for EOR purpose. In this chapter, the mechanism on how nanoparticle could improve oil recovery is elaborated. Thereafter the parameters, which affect the performance of nanoparticle during EOR process, are illustrated.

Chapter 5 includes the conclusion of literature study. Then, some recommendations in use of nanotechnology for petroleum industry especially for EOR are proposed.

CHAPTER 2

FUNDAMENTALS OF NANOPARTICLES

2.1 INTRODUCTION

This chapter discusses the fundamental concept of nanomaterials, including both nanoparticles and nanofluids. Where the nanomaterials will be defined. Then the methods of preparation of nanomaterials will be discussed. Then the nanoparticles will be defined. Then the structures of nanoparticles will be explaining together with various methods to manufacturing nanoparticle. Then after that, the nanofluids will be explained. Then the preparation of nanofluid will be discussed.

2.2 NANOMATERIALS: DEFINITION AND PREPARATION

2.2.1 Definition of Nanomaterials

Nano materials are micro-chemical materials that are used with high quality in many industrial applications such as communications, electronics and medical fields because they contain many physical and chemical properties, and are prepared in several ways, all of which share their dependence on the atomic scale, that is, an atom in the direction of another atom, to obtain desirable results, The differed the scale of the size of the mass of the substance, the differed the chemical effectiveness, meaning whenever the smaller the scale, the greater the chemical effectiveness of the substance.

2.2.2 Methods for Preparing Nanomaterials

a. Physical methods

Are prepared starting from the vapor state of the material by heating the material or bombarding them with a beam of electrons or thermally dissolving them using laser beams, then the vapor is cooled by striking it with a neutral gas to become more saturated and then placed on a cold surface quickly to avoid crystal building, and then Nanomaterials are prepared using waves, lasers, PVD or Epitaxies.

b. Chemical methods

i. Reactions in the vapor state:

The vapor of the material to be prepared enters the CVD reactor, then the particles of the material mix on a substrate surface at a certain temperature and react with other gases to form a solid tape on the surface of the substrate. This method is used to prepare nanomaterials such as quantal quilt.

ii. Reactions in a liquid medium:

Water or organic liquids are the most widely used, and Nano materials are prepared by changing the conditions of physical chemical equilibrium through double chemical precipitation reactions or water analysis to obtain spherical particles whose dimensions can be controlled, or through the use of sol gel techniques using colloidal solutions at low temperatures.

c. Mechanical methods

i. Mechanical installation:

By crushing a material consisting of micrometric particles from (1 to 30) into several mixtures and mixing them, this technology is characterized by the preparation of homogeneous nanomaterials, as well as the production of huge materials of several tons.

ii. The first monitoring and glazing process

By converting the atomic material into a huge piece through two stages, the stage of mechanical Monitoring, and the stage of dissolving the metals powder to form it after cooling.

iii. Strong distortions techniques

By distortion of a crystal material force as a metal or porcelain with a view to improving the properties of sclerosis and plasticity of materials.

iv. Grinding Method

It is used to produce Nano materials in the form of powder, where the basic material is exposed to very high energy, and then grinded using balls made of steel that move in a vibratory, planetary or vertical manner, and the size of the Nano materials that are manufactured range from 3 to 25 nanometers.

v. Rubbing method

By placing ultra-thin silicon strips in chemicals such as HF, rubbing the silicon strips to get silicon particles on the surface of the strips, placing these strips in a solution such as isopropanol and then in an ultrasound machine to drop the molecules into the solution.

vi. Electrochemical method

By placing a silicon chip at the positive electrode and a polycarbonate sheet at the negative electrode in a chemical solution, and exposing the slides to an electric current.

vii. Laser ablation method

By exposing the material to a very high-energy pulsed laser, so that the laser beam interacts with the target, which leads to the volatilization of the material particles and the formation of plasmas that are deposited on the base and form thin films.

viii. Deflating method

By exposing the material to a very low pressure emptied of air and with a cold base, it is exposed to a magnetic field, which leads to the extraction of the particles of the material and deposited at the base, forming a thin film.

2.3 NANOPARTICLES: DEFINITION AND STRUCTURE AND MANUFACTURING PROCESS

Nanoparticles: Nanoparticles are the simplest form of structures with sizes in the nm range. In principle, any collection of atoms bonded together with a structural radius of $<$ 100 nm can be considered a nanoparticle.

The tiny nature of nanoparticles results in some useful characteristics, such as an increased surface area (Figure 2.1) to which other materials can bond in ways that make for stronger or more lightweight materials. At the nanoscale, size does matter when it comes to how molecules react to and bond with each other.

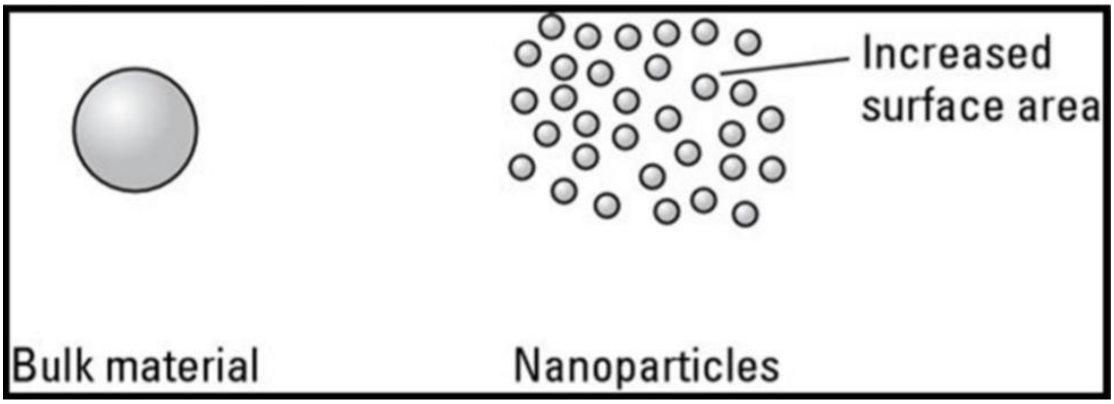

Figure 2.1 Increasing the surface area with nanoparticles.

Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid forming ‘Nanofluid.

Atomic assembly has magic numbers of atoms to form nanoparticles. Silicon nanoparticles, for example, consist of only specific numbers 1, 1.67, 2.15 and 2.9 nanometers. When these particles are exposed to ultraviolet rays, they emit light of a visible color whose wavelength is inversely proportional to the square of the particle's diameter, and thus certain visible colors can be seen. When the size of nanoparticles reaches the nanoscale in one dimension, it is called a (quantum well), but when its nanoparticle size is in two dimensions, it is called the (quantum wire), and when these Nano-sized particles are in three dimensions, they are known as (quantum dots dots).

It must be noted here that the change in the nanoscale dimensions in the three aforementioned structures will affect the electronic properties of them, leading to a significant change in the optical properties of the nanostructures. Nanoparticles gain scientific importance as they lie between the large volumetric structure of the material and the atomic and molecular structure, as these particles usually contain 106 atoms or less, while a molecule can contain 100 atoms or less and may reach a radius of more than one nanometer.

2.3.1 Definition of Nanoparticles

And the nanoparticles can also be defined as a microscopic atomic or molecular assembly ranging in number from a few atoms (molecule) to a million atoms, bound together almost spherically with a radius of less than 100 nanometers. A particle of one nanometer radius will contain 25 atoms, most of which are on the surface of the particle, and this differs from a molecule that may include a number of atoms because the dimensions of the nanoparticle are less than critical dimensions necessary for the occurrence of certain physical phenomena, such as: the average free path that electrons travel between two successive collisions with vibrating atoms, and this determines the electrical conductivity.

Generally, any nanostructure materials will have higher surface area to volume ratio due to its smaller size. A good analogy to understand how a smaller particle can yield higher surface area to volume ratio is presented in Figure 2.2. In comparison to micro-particle, the nanoparticle has 1000 times higher surface area to volume ratio. Due to the larger surface area to volume ratio, a nanoparticle has different surface properties compared to its bulk material that increases its potential utilization to a wider range. Moreover, the nanostructure of one material has unique properties which cannot be found in its macro-size analogy.

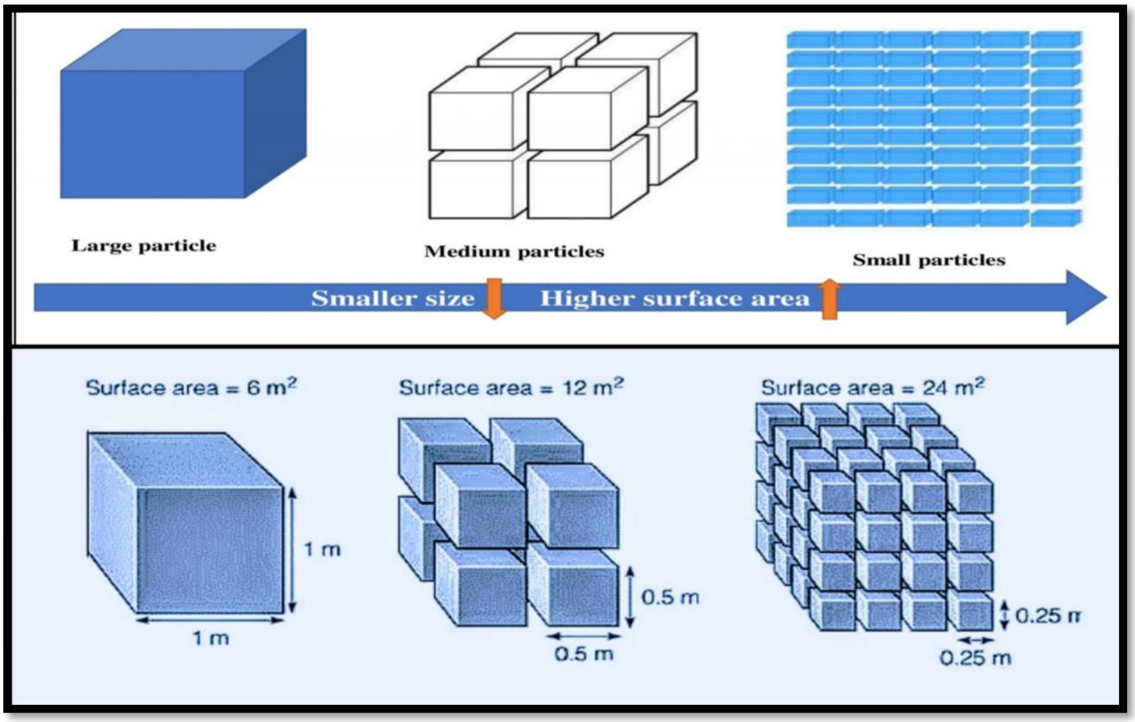

Figure 2.2 Surface area to volume ratio of particle with different dimension.

2.3.2 Nanoparticles Structure

In general, nanoparticle consists of several layers, the core, a surface and an additional shell (see Figure 2.3). The core of a nanoparticle is located at the center of its structure, and it is used to identify the type of NPs. Generally, the properties of NPs are associated with the composition of the core which is mostly made of inorganic material. The surface of the nanoparticle is an outer layer of the core which is functionalized by using metal ion, a surfactant or a polymer. The shell is an outer layer of structures with chemically different materials. It is constructed from oxide, nitride or an organic material (surfactant or polymer). In some inorganic NPs (e.g. silica NPs), the extension layer of a core can be considered as a shell. Moreover, the molecular shell consists of three different groups which are, the tail group, the hydrocarbon chain and the active head group.

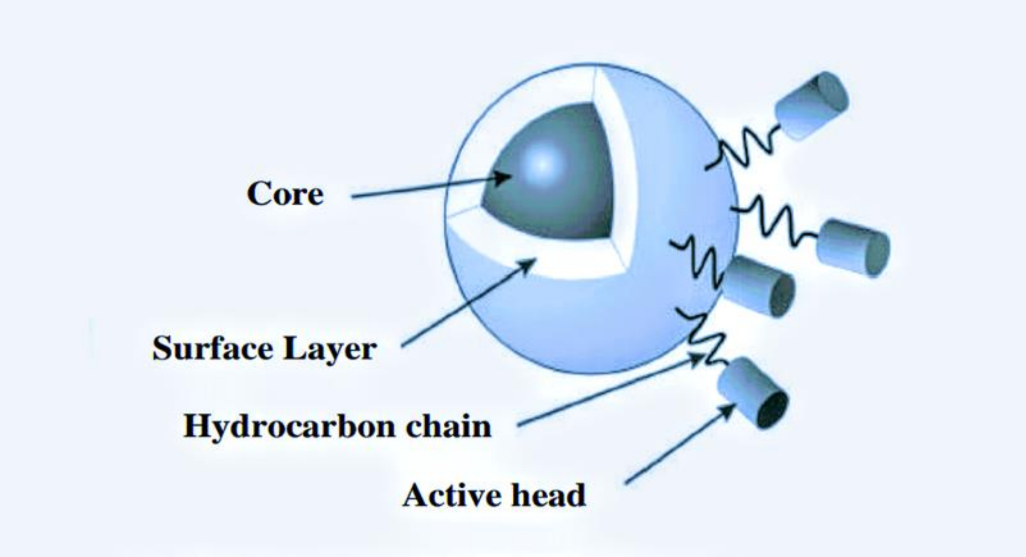

Figure 2.3 A nanoparticle structure (modified from).

2.3.3 Nanoparticles Manufacturing Process

In general, there are two methods in manufacturing NPs which are the top-down and bottom-up process. In the top-down process, external forces are implemented to breakdown the original solid material into the smaller particle. On the other hand, bottom-up process form NP by the coalition of atoms based on molecular condensation or atomic transformation. Figure 2.4 shows the typical methods used in the top-down process and bottom-up process.

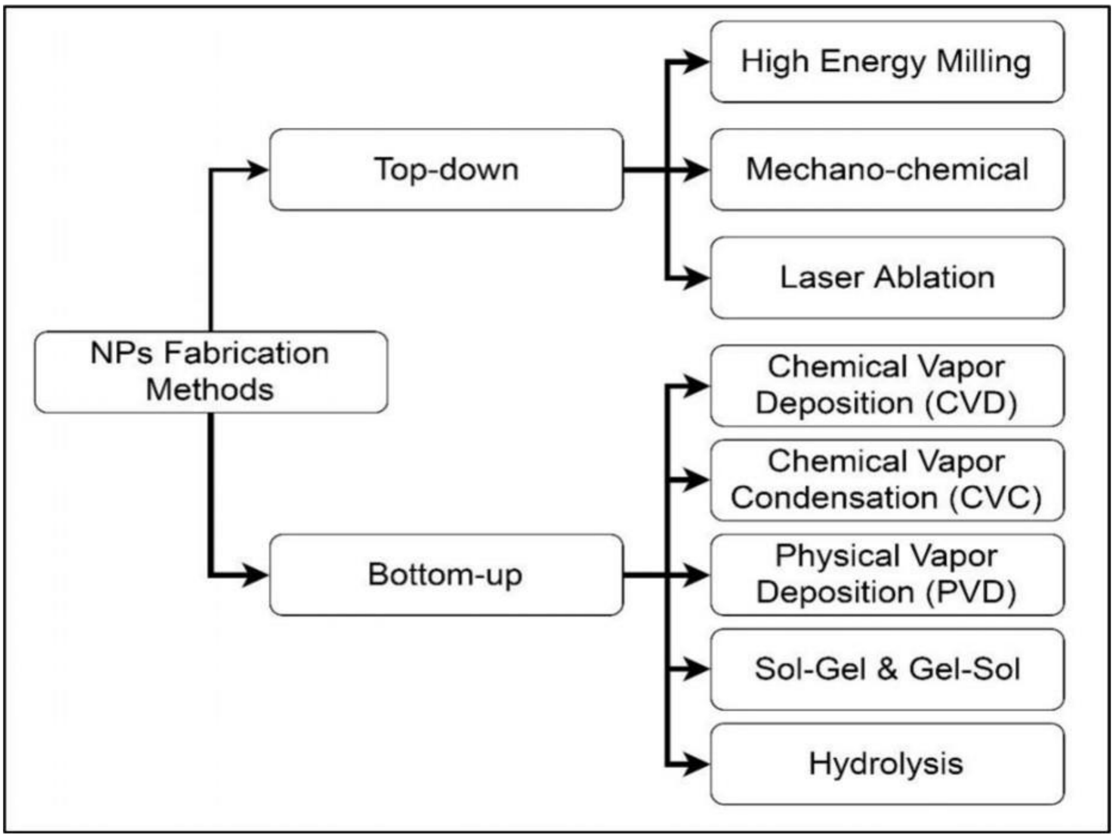

Figure 2.4 Nanoparticle fabrication methods (Modified from).

a. Top-down method

This process produces NPs by removing building blocks from the substrate to form smaller size particles. It simply means reducing the bulk particle size to produce smaller size (nanoscale) particles. The advantages of this process are the simplicity of the process, lower production cost, and scalability. The top-down method can be divided into three broad categories such as physical process (high energy milling), physical-chemical process (chemical-mechanical milling) and mechanical alloying.

i. High energy milling

In 1970, Benjamin et al. synthesized powder material for the first time by using the high energy milling principle. The high energy milling process involves applying physical forces to bulk solid material in order to break the material into smaller size. The forces employed in this process mostly are the combination of impact and shear. The breakdown of solid material can occur by different mechanisms such as attrition, abrasion, fragmentation or chipping. Mechanical milling has the ability to induce defects and activate the frozen state of NP which resulted in stable composition. There are several types of mills that are commonly used such as vibratory mills and planetary mills.

Grinding process is affected by the size and frequency of the force, material properties (size and strength), the amount of energy applied in the system, and efficiency of the process. Temperature also affects the grinding process due to the diffusivity and the concentration of defects in the powder that further influence phase transformation. Increasing temperature will lead to the formation of intermetallic compounds. On the other hand, a lower temperature will result in amorphous phases when energy is sufficient.

ii. Chemical-mechanical milling

Basically, the concept of chemical-mechanical milling is combined the physical and chemical forces in order to improve the overall process. During the milling process, chemical reactions occur at the Nano-sized particle interface and continuously happens during the milling. The chemical reactions can occur at low temperature without external heating process needed. Lu et al. synthesized nanocomposite of Mg, Al, and Ti, by using mechanochemical process, and the resulting nanocomposite showed higher yield strength and ductility. Ding et al. fabricated ultrafine Co and Ni NPs using mechanochemical principal. They succeeded in producing uniform sized NPs (10-20 nm) by chemical reduction of Co and NiCl2 by grinding with Na. Sheibani et al. reduced Cu2O with graphite to produce Nano-crystalline copper with an average size of 27 nm in high energy planetary ball mill. They found out that increasing milling time will increase the amount of fine Cu powder to an optimum point, after which agglomeration of the particle will dominate. By milling for about 30 hours, they could get Cu NPs with an average size of 27 nm.

b. Bottom-up method

During the bottom-up process, NPs are synthesized by adding the building blocks into the substrate. It means that by this approach NPs are synthesized by reacting each atom in the solution to form larger structures. During the process, the size of NP is controlled by regulating concentration, functionalizing the surface, and applying micelle for setting the growth. It has various advantages compared to the top-down process such as better quality of the product (fewer defects NPs), higher homogenous chemical composition, and better stability. There are numerous processes involving the bottom-up principle.

i. Chemical vapor deposition

Chemical vapor deposition (CVD) is one of the bottom-up processes where a solid is deposited due to the reaction from the vapor phase. There are several variations in the CVD process such as thermal, plasma and photo-laser. In thermal CVD, the reaction occurs at high temperatures above 900 °C. In plasma CVD, the reaction is activated by plasma at temperatures around 300 to 700 °C. While in photo-laser CVD, the reaction is initiated by ultraviolet radiation to break the chemical bond between the molecules and the deposition will occur at room temperature.

ii. Chemical vapor condensation

Chemical vapor condensation (CVC) process was developed in Germany in 1994. This method involves pyrolysis of metal-organic-precursors' vapors in a reduced pressure . The metal-organic-precursor vapors are led into the reactor by using mass flow controllers. The process can achieve above 20 gr/hour and can be improved by adjusting the reactor and mass flow of the input. This process has a limitation in size, morphology and phase control for the NPs product. However, CVC is widely used for fabricating silica NP from silicon tetrachloride.

iii. Sol-gel

The sol-gel process is the well-known method to fabricate metal oxides NPs. Compared to the chemical and physical deposition, the sol-gel technique is very cost-efficient. Sol is defined as a colloidal or a molecular suspension of solid particles in a solvent. While the gel is a semi-rigid mass of continuous network of particles and ions, taking shape when the solvent began to evaporate. This process involves a combination of metal precursors in solution and the deposition of the precursors. The deposition will occur on suitable substrate and heat condition, leading to the oxidation and sintering to the final product. Wang et al. had successfully fabricated TiO2 based NP with sol-gel technique. The sol-gel method is one versatile fabrication process that can be scaled up with further advances in the synthesizing technology.

2.4 NANOFLUIDS: DEFINITION AND PREPARATION AND STABILITY

Nanofluids are engineered fluids that disperse the nano-scale materials in the specific fluid. The fluid can be polar (water or alcohol) and non-polar (oil or toluene). It means that a nanofluid is made of solid and liquids, in which NPs as solid are dispersed in the liquid called base fluid. As NPs are dispersed into the base fluid, the characteristic of the nanofluids will not be similar to its pure base fluid. Nanofluids were proven to have higher thermal conductivity, diffusivity, viscosity and heat transfer than its pure base fluids that enable a wide range of application in many areas.

Due to the specific characteristics that can be engineered, nanofluid has wide potential applications such as mass and heat transfer , friction reduction, magnetic enhancement, and many other uses. It is also proposed for the petroleum industries application as drilling fluid enhancement, exploration and reservoir characterization, refinery and EOR. Several nanofluids are proposed as the successor of the existing chemical EOR as nanofluids are relatively cheaper and possess tremendous potential for the future applications.

2.4.1 Simplified Definition of Nanofluids

A nanofluid is simply defined as a base fluid with NPs that have an average size of less than 100 nm in colloidal suspension. The base fluid can be any liquid such as oil, water or gas. Generally, nanofluids formed by adding various NPs in water or brine are used to improve water flooding recovery. The EOR mechanisms of nanofluids have already been investigated in literatures, which mainly includes disjoining pressure, pore channels plugging, viscosity increase of injection fluids, IFT reduction, wettability alteration and preventing asphaltene precipitation. The schematic of the EOR mechanisms of nanofluids is shown in Figure 2.5.

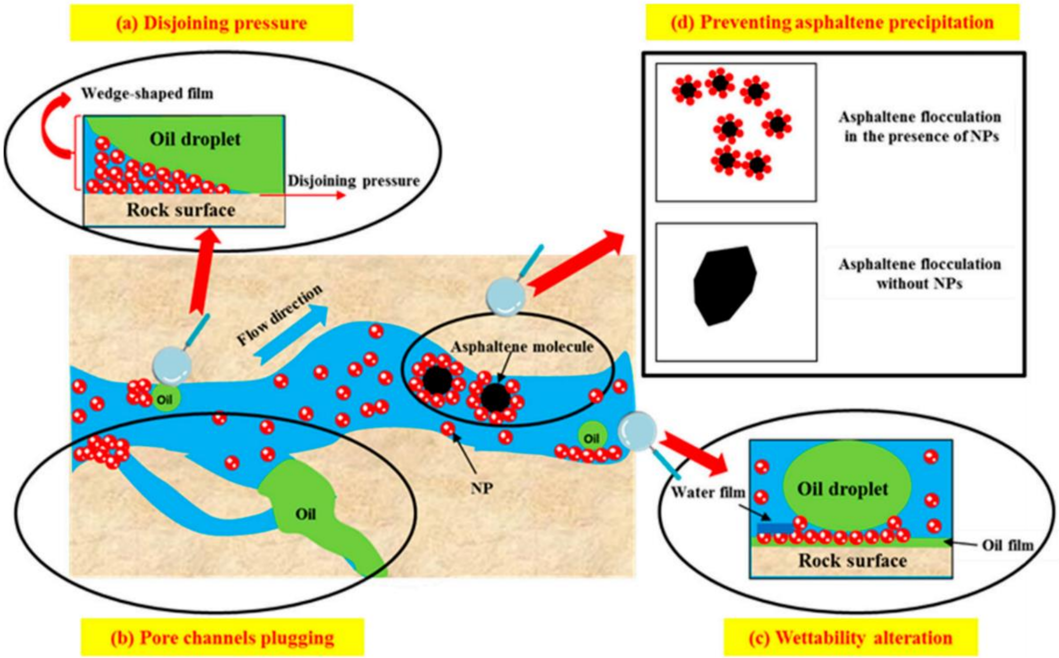

Figure 2.5 The schematic of the EOR mechanisms of nanofluids.

2.4.2 Preparation of Stable Nanofluids

Since NPs tend to aggregate to make bigger particle, preparing stable nanofluid is a challenging task. When NPs are dispersed in a liquid, high surface energy of each nanoparticle tends to be stabilized by forming bigger particles (agglomerates). As seen in Figure 2.6, stable condition is achieved when the repulsion forces are relatively high. However, once the attraction force starts to overcome the repulsion, the particles will stick to each other. Particles dimers and trimers will form at the beginning, then as the aggregation and agglomeration occur continuously, sedimentation will likely follow. At some condition, unstable suspension or dispersion can be reversed and the process is known as peptization. In general, nanofluid can be prepared by using two different methods, one-step and two-steps.

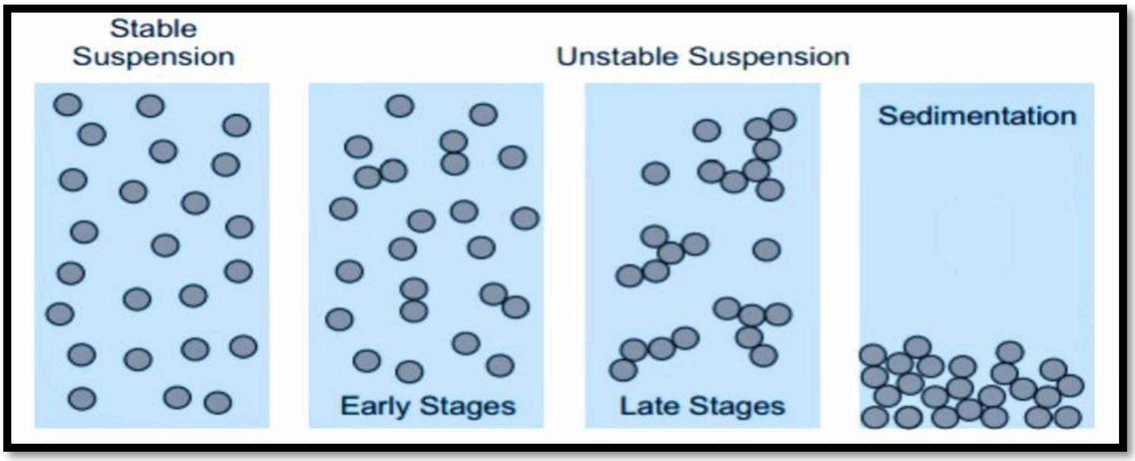

Figure 2.6 Stable and unstable suspension.

The two-step method is the most common process that has been used to prepare nanofluids. In this process, dry NP powders produced from mechanical or chemical synthesis are dispersed in a base fluid. However, due to the high surface energy of NPs, agglomeration of some particles cannot be avoided which then reduce the homogeneity of the nanofluids. Due to the quick agglomeration, several attempts can be done such as adding a surfactant to improve the dispersion could be carried out.

The stability could thus be improved, but limited to the high-temperature application. One of the advantages of this process is the economic feasibility for a larger scale production since the production of NP powders has been already induced in industrial scale.

One-step method is a process that simultaneously synthesizes nanoparticle and nanofluid. The base fluid is formed at the same time as the NP synthesis. The processes such as drying, storing and transporting process associated with nano-powder fabrication are removed, minimizing the agglomeration and improving the fluid stability. By using one-step process, the uniformity of the dispersed particle and the stability became higher. However, this process has several disadvantages and limitations, e.g., limited to the small-scale production, only applies to low vapor pressure host fluids, and produces the remaining residuals due to incomplete reaction or stabilization.

2.4.3 Methods Used for Enhancing the Stability of Nanofluids

Preparation of nanofluids is the first step in nanofluid flooding. The delicate preparation of a nanofluid is important because nanofluids need special requirements such as an even suspension, stable suspension, low agglomeration of particles, and no chemical change of the fluid. Coagulation/agglomeration is a main problem during preparation of nanofluids. Unstability of nanofluids will lose their potential benefits when they are injected into reservoirs. Stability of nanofluids depends on the preparation methods, NP characteristics, type of base fluids, surfactants, pH, ultrasonication, etc.

a. There are several methods used for enhancing the stability of nanofluids

1. Changing the pH value: Isoelectric point (IEP) is the value of pH at which a particular molecule carries no net electric charge, or hydration forces are negligible. When the pH of nanofluids is equal or close to the IEP, nanofluids become unstable. Zeta potential is zero at the isoelectric point, repulsive forces between NPs suspended in base fluid are zero and there is a tendency of coagulation. Hydration forces between NPs must be high in order to enhance the stability of nanofluids. A stable nanofluid must have pH around 7 because very high or low pH values may damage the heat transfer surface due to corrosion especially at high temperature.
2. Using surfactants: Surfactants can act as a bridge between NPs and base fluids which creates continuity between NPs and base fluids . Hydrophilic NPs such as oxides NPs will be easily dispersible into the polar base fluids like water. However, when there is a need to disperse hydrophobic NPs into polar base fluids and hydrophilic into non-polar base fluids, then addition of surfactants is required to stabilize the nanofluids. It should be mentioned that the addition of surfactant which affect the thermophysical properties of nanofluids.
3. Using ultrasonic vibration: Ultrasonication is an accepted physical technique to disperse agglomerated NPs into the base fluid. To disperse the aggregates of NPs, ultrasonication bath- or probe-based ultrasonic devices are most commonly used. The probe based ultrasonic devices operates at very high frequency. So, there may be the probability of contamination of nanofluids due to the detachment of very minute metal particles from the surface of metal probe. This may affect the stability of nanofluids adversely.

The use of these techniques depends on the required application of the nanofluid. Selection of suitable surfactants depends mainly upon the properties of the solutions and particles. Stability of NP dispersion in base fluid is indicated by zeta potential value, high zeta potential value indicates good stability.

CHAPTER 3

NANOPARTICLE APPLICATION IN PETROLEUM INDUSTRY

Nanoparticle could potentially revolutionize the petroleum industry for both upstream and downstream, including exploration, drilling, production, and EOR as well as refinery processes. It provides a wide range of alternatives for technologies and material to be utilized in petroleum engineering. Nanoscale materials in various forms such as solid composite, complex fluids, and functional NP-fluid combinations are the key to the new technological advances. Studies on nanotechnology related to petroleum industry have been growing rapidly in the past few years. Figure 3.1 presents the number of scientific journals published in this field, displaying high research activities even during the down time of petroleum industry.

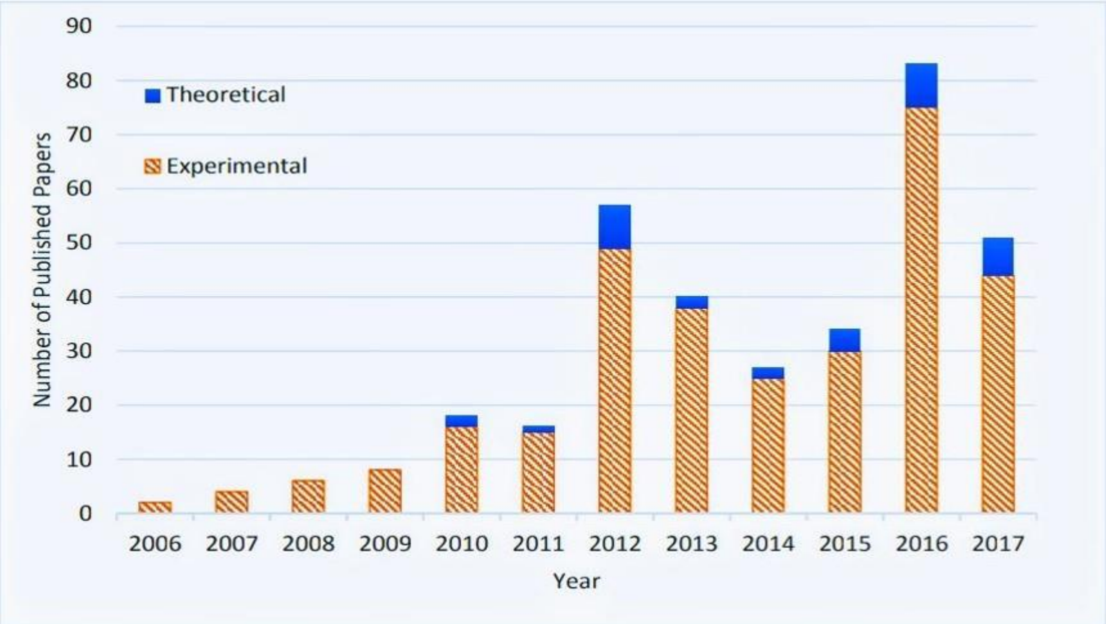

Figure 3.1 Nanotechnology in petroleum industry research (Taken until March 2017 and modified from]).

Engineered nanoparticles have been studied in many potential applications in the petroleum industry, especially as nano-sensors in exploration, mud additive in drilling, emulsion stabilizer and wettability alteration in enhanced oil recovery (EOR) and nano-catalyst in refinery process. The summary of important studies related to the utilization of nanotechnology is presented in Table 3.1. The detailed summary of each area is elaborated in the next sub-section.

Table 3.1 Summary of the literature studies.

Area	Nano Type	Purpose	References
Production & Stimulation	Pyroelectric NP. Ni-Fe NPs. ZnO NPs. Silica NPs. Metal oxides based. Cu and Ni NPs. Non-ferrous NPS.	Additive for fracturing + viscoelastic surfactant to increase efficiency in fracturing. Hydrate mitigation in the well. Increase low shear rate viscosity on Threadlike micelle (TLM) fluids and more stable. Rheological studies on surfactant based and polymeric Fluids. Improves fracturing fluids stability and viscosity in height temperature (300 F). Thermal recovery by metallic NPs. Combine with surfactant for IFT reduction.	Crews et al. (2008) Bhatia & Chacko (2009) Crews and Gomaa (2012) Fakoya and Shah (2013) Li et al. (2016) Hamedi et al. (2010,2011) Suleimanov et al. (2011)
Refinery	Nano-supported HDS. Nano membranes. MoS2 nano-catalyst. TiO2 NPs. TiO2, ZrO2, and SiO2 NPs. Magnetic NPs. Nickel oxides and alumina NPs.	Patent on nano-supported hydrodesulphurization (HDS) catalyst. Gas stream separation. Observing atomic-scale edge structures of MoS2. Improving water treatment by reducing fouling effect. Additive for stabilizing asphaltene in oil under acidic Condition. Accelerate oil removal in water-oil emulsion. Patent on Nanocatalyst for hydrocracking.	Mohajeri et al. (2009) Kong & Ohadi (2010) Hansen et al. (2011) Sotto et al. (2011) Mohammadi et al. (2011) Ko et al. (2014) Patiño and Cortés (2016)
Exploration	Hyperpolarized silicon NPs. Nano-optical fiber. Nano-robots. Coated carbon-nano structure. Polyvinyl alcohol functionalized oxidized carbon black. Magnetic NP. Superparamagnetic NP.	Imaging sensors of oil in a hydrocarbon reserve. Detecting oil-microbe, which able to estimate reservoir pressure and temperature. Well logging and borehole measurement (patent). Real-time oil reservoir evaluation with two-dimensional detection Technology. Synthesizing engineered NPs for hydrocarbon detection in reservoir. Detect flood front, fluid contact, hydrocarbon bypass and fracture. Crosswell magnetic sensor for tracking flood front.	Song and Marcus (2007) Jahagirdar (2008) Pratyush and Sumit (2010) Li and Meyyappan (2011) Berlin et al. (2011) Al-Shehri et al. (2013) Rahmani et al. (2013)
Drilling & Completion	Silica NPs. Nanodiamond. Silica & Alumina NPs. MgO and ZnO NPs. Nanoclay. Carbon Nanotubes (CNT). Cellulose nanofibers (CNF) & graphene nano-platelets (GNP).	Reduce or stop water invasion to shale by plugging shale pore. Improve drilling process in harsh and demanding Environment. Cement accelerator. Improving thermal stability of drilling fluid. Reduce permeability and porosity of cement and enhanced compressive Strength. Improve compressive strength in HPHT. Increased yield stresses, degree of hydration (DOH), flexural andcompressive strengths.	Sharma et al. (2012), Hoelscher et al. (2012), Xu (2012), Cai et al. (2012) Chakraborty et al. (2012) Santra et al. (2012) Gurluk et al. (2013) Murtaza et al. (2016) Khan et al. (2016) Sun et al. (2017)
EOR	Silica NPs. Alumina NPs. Cu and Al based NPs. Silica NPs. ZnO NPs. TiO2 NPs. Al, Ni, Si, and Ti based NPs.	Wettability alteration, improving oil recovery. IFT study of methylbenzene–water with alumina NPs. Emulsion stability effect study. Generate very stable CO2-in-water foam. IFT study on anionic surfactant liq-liq interface. Heavy oil recovery in sandstone core. Recovery factor sensitivity study.	Ju et al. (2006), Maghzi et al. (2013), Hendraningrat et al. (2013) Saien et al. (2013) Mensah et al. (2013) Espinosa et al. (2013) Moghadam and Azizian (2014) Ehtesabi et al. (2014) Alomair et al. (2015)

3.1 EXPLORATION AND RESERVOIR CHARACTERIZATION

Early in the twenty-first century, nanotechnology has been powerful in the oil and gas industry, with many applications that have moved from laboratory and digital simulation studies to successful experimental applications in the field Nanotechnology has the potential to revolutionize the petroleum industry both upstream and downstream, Including exploration, drilling, production and enhanced oil recovery, as well as refinery operations, Presenting recent advances in the applications of nanofluids and nanoparticles in the real environments of the oil and gas industry, these applications cover more than 20 wells in Colombia that have been treated to overcome various damage mechanisms of formation, such as asphaltene deposition/deposition, fines migration, and inorganic scale deposition.

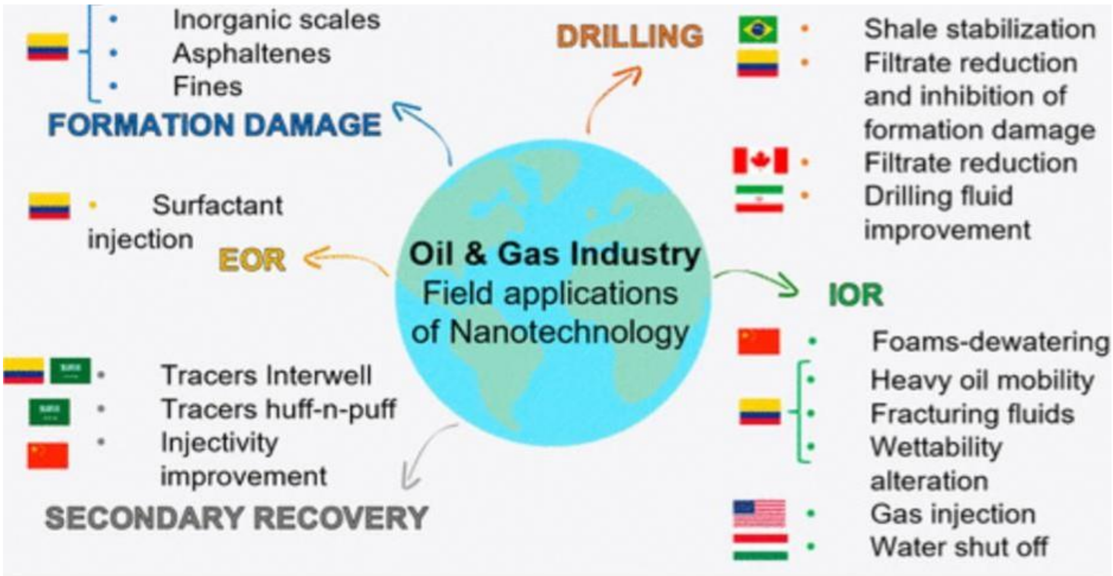

Figure 3.2 Oil and gas industry field applications of nanotechnology.

Also, different methods of enhancing drilling fluids are investigated in Canada, Brazil, Iran and Colombia, in the case of improved oil recovery (IOR), different applications, and (2CO) in the presence of nanoparticles in the Austin Chalk, Buda and Eagle Ford formations in the United States, and the use of Nanoparticle-assisted foams for well dewatering in China. For secondary and tertiary recovery, we explore the design and implementation of quantum dots and carbon as tracers in Saudi Arabia and Colombia, respectively, hydrophobic nanoparticles as drag reducer in injection wells in China, and secondary fluids to enhance chemically enhanced oil recovery processes in southern Colombia.

“Nanosensors” have been proposed to characterize, interpret and evaluate seismic formation in geochemical exploration. When NPS is injected into the tank, some of it will pass through the pores while others will be adsorbed onto the surface of the grain. Information about the chemical and physical properties of rocks and the three-dimensional distribution of formation can be obtained from the analysis of adsorbed NPs . The functional structures of nanoparticles and liquids are the key to new technological progress. The application of nanotechnology is also used in exploration and reservoir characterization, drilling and completion, production and stimulation, And the filter. Then, this paper focuses on the application of secondary particles in enhanced oil recovery. The different types of nanomaterials, such as silica, aluminum oxides, iron oxide, nickel oxide, titanium oxide, zinc oxide, zirconium oxide, polymers and carbon nanotubes that have been studied in EOR are [discussed with regard to their properties, performance, advantages and disadvantages.

The idea of hyperpolarized silicon as nanosensors in NPS Hyperpolarized use for the first time in oil and gas exploration, tested Hyperpolarized NPS for the first time with promising results in biomedical engineering as alternative imaging tracking molecules.

MRI (magnetic resonance) Detection of oily microbes in the tank using secondary optical fibers based on the principle of Raman Raman spectroscopy. Since (RRS), microbes only live in certain conditions, this method can be used to measure the characteristics of the tank indirectly such as pressure, temperature and salinity. Some researchers obtained a patent for two-dimensional real-time analysis of oil reservoir evaluation, using engineered carbon magnetic NPs secondary structure and surface sensors studied to detect the flood front and oil-water interfaces, the result showed the time-traveling tomography ability to detect magnetic NPS in different media, Which was a big step in the use of magnetic nanosensors . The most recent progress in the nanotechnology on oil and gas exploration is the utilization of reservoir Nano-robot by Liu et al. They successfully tested as a Nano detection device, which integrates reservoir sensor, micro-dynamic system, and micro-signal transmission. In the same year, a patent on the Nano-robot's system for well logging and measurement was granted to Pratyush and Sumit. For a Nano Robot System for Well Recording and Measurement These studies show that NPs have the potential to be used for reservoir characterization and hydrocarbon exploration, however, the problem that needs to be solved to make secondary sensors feasible is to protect the sensor from deterioration by fouling and at the same time access the sensors to tank fluids.

3.2 DRILLING AND COMPLETION

Nanotechnology for drilling and completion has been widely studied for the past few years, including drilling fluids, cementing additive and drilling tools. In 2010, Amanullah projected that various NPs can be an answer for several drilling operation challenges such as, shallow water, unconsolidated formation, borehole instability, lost circulation, torque and drag, pipe sticking problem, gumbo and bit bailing, gas hydrate zone, acid gas, HPHT, and fracturing fluids.

Utilization of nanomaterials such as silica, graphene and other NPs have been suggested for drilling fluids additive. Nano based mud is defined when at least one additive of mud using nanomaterial with a size range between 1-100 nm. The use of silica-NP in drilling mud were studied by several researchers. By using silica NPs, Sharma et al. observed improvements in the stability of the mud at elevated pressures and temperatures at different rheology by reducing 10-100 times of shale invasion. Hoelscher et al. performed experiments on Marcellus and Mancos shales with 3 wt.% of silica NPs as additives in the water-based mud. The result showed that silica NPs could physically plug the shale and significantly reduce the fluid invasion to shale zone at the lower loading level in the water-based mud. Cai et al. also performed experimental tests with 10 wt.% of 6 types of silica NPs for Atoka shale. They found a drastic reduction in shale permeability impairment and observed that the mud had a higher plastic viscosity, lower yield point, and fluid loss reduction. Potassium silicate function on handling shale formation had also been investigated by McDonald . Srivatsa and Ziaja conducted an experimental study using the combination of biopolymer- surfactant and nanoparticle for mud additives. They concluded that nanoparticle combined with bio-polymer and surfactant could be a solution to solid free fluids in horizontal drilling.

3.2.1 Drilling Fluids

a. Fluid loss control and wellbore stability

There are several researchers working on using nanoparticles as drilling fluid additives to reduce the fluid loss and enhance the wellbore stability. The filter cake developed during the Nanoparticles-based drilling fluid filtration is very thin, which implies high potential for reducing the differential pressure sticking problem and formation damage while drilling.

In shale formations with nano Darcy (ND) permeability, the nanometer-sized pores prevent the formation of the filter cake that is responsible for fluid loss reduction. Nanoparticles can be added to the drilling fluid to minimize shale permeability through physically plugging the nanometer-sized pores and shut off water loss. Hence, Nanoparticles can provide potential solution for environmentally sensitive areas where Oil-based muds used as a solution to shale instability problems (Price et al., 2012).

b. Bit balling

According to (Amanullah and Al-Tahini, 2009), Nanomaterial-based drilling mud with hydrophobic film forming capability on the bit and stabilizer surfaces is expected to eliminate the bit and stabilizer balling totally. Due to high surface area to volume ratio and very low concentration requirement compared to macro and micromaterial-based fluids, nano-based fluid could be the fluid of choice for drilling in shale which is very reactive, highly pliable, and tenacious and thus can stick easily to the bit, stabilizers, tool joints, etc. as it prevents the reduction in ROP and in total operating cost.

c. Torque and drag

Due to fine and very thin film forming capability of nanomaterials, Nano-based fluids can provide a significant reduction of the frictional resistance between the pipe and the borehole wall due to the formation of a continuous and thin lubricating film in the wall-pipe interface.

Moreover, the tiny spherical nanoparticles may create an ultra-thin bed of ball bearing type surface between the pipe and the borehole wall and thus can allow easy sliding of the drill string along the Nano-based ball-bearing surface. This highlights the extraordinary role of Nano-based smart fluid in reducing the torque and drags problems of horizontal, extended reach, multilateral and coiled tubing drilling (Amanullah and Al-Tahini, 2009).

d. Removal of toxic gases

Hydrogen sulfide is a very dangerous, toxic and corrosive gas. It can diffuse into drilling fluid from formations during drilling of gas and oil wells. Hydrogen sulfide should be removed from the mud to reduce the environmental pollution, protect the health of drilling workers and prevent corrosion of pipelines and equipment.

Sayyadnejad et al., 2008, used 14-25 nm zinc oxide particles size and 44-56 m2/g specific surface area to remove hydrogen sulfide from water-based drilling fluid according to the following chemical reaction

$$(ZnO + H_2S \rightarrow ZnS + H_2O) \qquad (3.1)$$

The efficiency of these nanoparticles in the removal of hydrogen sulfide from drilling mud was evaluated and compared with that of bulk zinc oxide. Their results demonstrated that synthesized zinc oxide nanoparticles are completely able to remove hydrogen sulfide from water-based drilling mud in about 15 min., whereas bulk zinc oxide is able to remove 2.5% of hydrogen sulfide in as long as 90 min. under the same operating conditions.

e. Increase down hole tools life

The down hole tools and equipment are always exposed to abrasive forces due to high kinetic energy associated with the particles present naturally in the subsurface formations and the drill solids added to the drilling fluid system for specific functions. These forces cause the wear and the tear for most of the down hole equipment, especially in deviated and horizontal wells where the tools are more exposed to these abrasive forces.

Because of their extremely small size, nanoparticles are preferred to be used in drilling fluid design as their abrasive forces are negligible with less kinetic energy impact. In addition to all advantages of using nanoparticle in mud design, it is safer than conventional mud from the point of environmental view. The nanoparticles are added to mud in small amount, with low concentration about 1%. So, Nano-based drilling fluids could be the fluid of choice in conducting drilling operations in sensitive environments to protect other natural resources (Amanullah et. al., 2011).

3.2.2 Drilling Bits

a. Nanodiamond PDC technology

Carbon nanomaterials are extremely interesting because of their unique combination of mechanical, structural, electrical and thermal properties. In case of challenging drilling operations, harsher conditions are met and the need for effective drilling bits increases.

Nanodiamond particles have been functionalized for polycrystalline diamond applications such as polycrystalline diamond compact (PDC) cutters for drill bits. They give PDC cutters unique surface characteristics that allow them to integrate homogeneously into PDC synthesis.

Chakraborty et al., 2012, studied the functionalization of nano diamond, integration into the PDC matrix and subsequent property enhancement in comparison to the base PDC matrix. The performance of PDC cutters produced, the behaviors and proposed mechanisms are still an area of interest.

3.2.3 Down Hole Tools

High Strength Nanostructured Materials: Flow control and Completion devices such as fracturing balls, discs, and plugs are used for sleeve actuation or stimulation diversion during fracturing. Traditional light weight material for ball or plug applications are prone to early yielding or shape changes. The yield strength of conventional aluminum alloys is usually less than 400 MPa.

Nanotechnology can be effectively employed to enhance the mechanical properties and other desirable properties through engineering the material microstructure (Zhang et al., 2012).

Current polymer material must be milled away, flowed back or otherwise removed before production. Severe deformation of currently used materials that prevent flow back have been reported, leading to potential restrictions in the tubing which requires costly intervention operations to either remove or replace the tools and resulting in higher operational inefficiency.

Using controlled electrolytic metallic (CEM) nanostructured material that is lighter than aluminum and stronger than some mild steels, but disintegrates when it is exposed to the appropriate fluid. The disintegration process works through electrochemical reactions that are controlled by nanoscale coatings within the composite grain structure. The nano matrix of the material is high strength and has unique chemical properties that conventional materials do not. Salinas et al., 2012, explained the chemistry and layering of the nanoscale coating within the grain structure, the unique material properties, and lab testing data of this truly intervention less nanostructured material technology.

3.2.4 Cement

a. Cement spacer

Nano-emulsions are emulsions where the droplet size of the internal phase is in the nanoscale (<500 nm). Due to their small dimensions they have a high surface area and show very different properties. Maserati et al., 2010 proposed that solvent in water Nano-emulsions used as cement spacer formulation could allow optimizing the cleaning of the casing during the cement job with a high improvement of the performances of the spacers currently in use

Maserati et al., 2010, studied the formulation of direct Nano-emulsions (O/W), with a selected solvent as internal phase, in order to improve the casing – open hole cleaning and reverse the surfaces wettability to allow better adhesion of slurry between casing and hole

Using this methodology, based on high efficiency system with reduced chemical dosage, can also result in a considerable optimization of product cost of effective cement operation.

b. Enhancing cement properties

Due to the very high surface area of nanomaterials, they can also be used in oil well cementing to accelerate the cement hydration process, increase compressive strength, help control fluid loss, reduce probability of casing collapse and prevent the gas migration which is one of the cementing problems in gas wells. Moreover, they are often required in small quantities.

c. Santra et al., 2012, managed to investigate several types of nanomaterials to be used in the oil well cementing industry:

1. nanosilica and nanoalumina as potential accelerators.
2. nanomaterials including carbon nanotubes (CNTs) with high aspect ratio to enhance mechanical properties.
3. nanomaterials to reduce permeability/porosity; and,
4. nanomaterials to increase thermal and/or electrical conductivity.

Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of Nano-size ingredients such as alumina and Nano carbon tubes particles. CNT are expected to have several distinct advantages as a reinforcing material for cements as compared to more traditional fibers (Rahimirad et al.,2012).

3.3 PRODUCTION AND STIMULATION

Stimulation is widely used to enhance production in low permeability oil and gas reservoir. Fracturing fluids are used to carry prop pant. Fracturing fluid is very critical to successful fracturing operation. Its treatments used to enhance the well productivity either by hydraulic fracturing and matrix acidizing to increase the permeability or by increasing the well production. During hydrocarbon production, various problems can reduce the production efficiency to alternative. solution of liquid loading problem in deep gas well during the production process. They proved that engineered silica NPs with a temperature resistance up to 150 °C, salinity resistance about 250 g/L, and H2S resistance up to 0.04%, could solve the liquid loading problem by creating stable gas-liquid foams. Its studied for improving oil recovery of traditional chemical processes. For Nano-assisted polymer flooding, adding silica NPs can improve pseudo-plasticity behavior of polymer solutions and stabilize polymer solutions. NPs along with surfactants can result in improving oil recovery and releasing residual oils due to IFT reduction, spontaneous emulsion formation, wettability alteration, and modification of flow characters. Silica NPs are also beneficial in preventing the wax development at pipe during oil and gas production. Recently, Sun et al.

Few investigations showed an improvement in the well stimulation jobs by means of nontechnology. The targeted properties included filtration and rheological properties of the fracturing and acidizing fluid. A short summary of the investigated nanoparticles and their effects is listed in Table 3.2.

Table 3.2 Application of nanoparticles for well stimulation

Investigated NP	Improved parameters	References
Magnesium oxide Zinc oxide	Improving the rheological properties of fracturing fluid	Nasr-El-Din et al. (2013)
Pyroelectric nanoparticles	Improving the filtration characteristic Improving the rheological properties of fracturing fluid	Crews and Huang (2008)
Silicon dioxide	Improving the permeability of un-propped fractures Formation of microencapsulated acid	Singh et al. (2018)
Silicon dioxide	Improving the filtration characteristic Improving the rheological properties of surfactant-based fluids for hydraulic fracturing applications	Fakoya and Shah (2018)
Silicon dioxide	Reducing adsorption capacity Reducing permeability damage	Li et al. (2019)

3.4 ENHANCED OIL RECOVERY

Due to the continuous increase in the world energy demand, technology for finding hydrocarbon source or for enhancing oil recovery needs to be developed. The fact that finding a new source of hydrocarbon is difficult and most of the oil field have 60 to 70 % of non-producible hydrocarbon in place, drives the development of novel technologies in EOR. There are various studies which had been done on the application of nanoparticle on EOR. The use of NPs suspension for EOR has several advantages such as: good stability because surface force is more dominant than gravity; nanoparticle properties depend on size and shape which can be easily modified during the manufacturing process; chemical properties of NPs correlates to the surface coating, that can be simply tailored from hydrophilic to hydrophobic; 99.8% of silica NPs are silicon dioxide which is a dominant substance in sandstone and making it environmentally friendly; the price is much cheaper than any other chemical EOR.

Nanoparticles are small enough to pass through pore throats in typical reservoirs, but they nevertheless can be retained by the rock.

Rodriguez et al., 2009, injected concentrated (up to ~20 wt. %) aqueous suspensions of surface-treated silica nanoparticles (D = 5 nm and 20 nm) into sedimentary rocks of different lithology's and permeability's. The particles generally undergo little ultimate retention, nearly all being eluted by a lengthy post flush.

The Nanoparticles in an aqueous dispersion will assemble themselves into structural arrays at a discontinuous phase such as oil, gas, paraffin, or polymer. The particles that are present in this three-phase contact region tend to form a wedge-like structure and force themselves between the discontinuous phase and the substrate as illustrated in Figure (3.3).

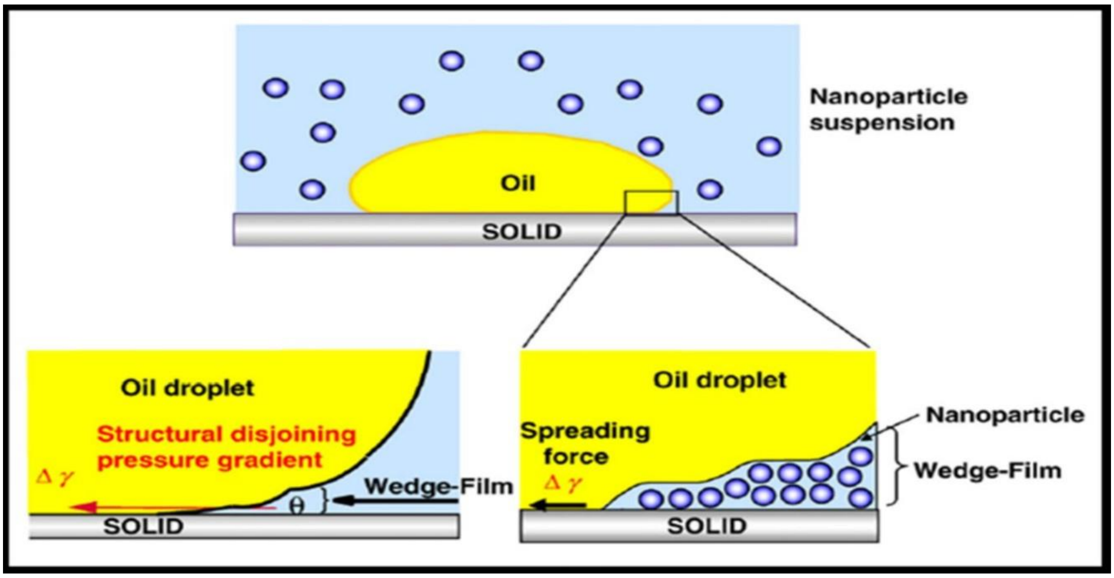

Figure 3.3 Nanoparticle structuring in the wedge-film resulting in structural disjoining pressure gradient at the wedge vertex (Kirtiprakash et al., 2012).

Particles present in the bulk fluid exert pressure forcing the particles in the confined region forward, imparting the disjoining pressure force. The energies that drive this mechanism are Brownian motion, and electrostatic repulsion between the particles (Kirtiprakash et al., 2012).

The force imparted by a single particle is extremely weak, but when large amounts of small particles are present, referred to as the particle volume fraction, the force can be upwards of 50,000 Pa at the vertex as shown in Figure (3.4).

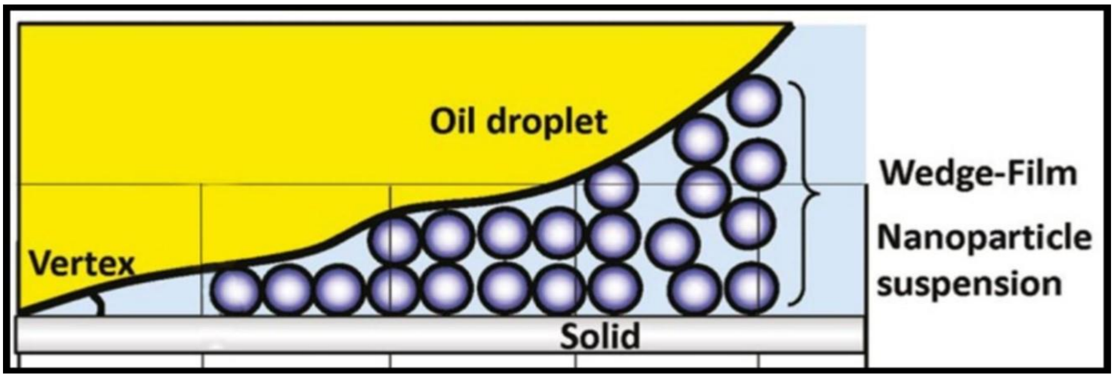

Figure 3.4 Nanoparticle structuring in the wedge-film (Kirtiprakash et al., 2012).

When this force is confined to the vertex of the discontinuous phases, displacement occurs in an attempt to regain equilibrium.

Ogolo et al., 2012, used nanoparticles oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon. It was imperative to find out the effect of these nanoparticle oxides on oil recovery since this is the primary objective of the oil industry.

Metal oxides NPs also potential to be applied in EOR. In 2011, Suleimanov et al. found that the use of non-ferrous NP dispersed in anionic surfactant able to increase oil recovery up to 18%. Interfacial tension reduction due to nanoparticle was observed by Saien et al. when hydrophilic and hydrophobic alumina NPs were applied on the toluene-water system. Esmaelizadeh reported the effect of $ZrO2$ NPs on interfacial tension of surfactant for both air-water and n-heptane-water interfaces, while Moghadam and Azizian studied interfacial tension of anionic surfactant in the presence of ZnO NPs. They concluded that IFT of surfactant-oil could be reduced significantly and in general, dynamic IFT will reduce faster if ZnO NPs are added into the system.

The nanoparticle as novel foam and emulsion stabilization additive had been investigated in the past few years. Zhang et al. observed that nanoparticle could stabilize an emulsion of oil-in-water or water-in-oil in the absence of surfactant. The emulsions with nanoparticles were stable up to 2 years and could stand in harsh condition. A further study had been done by Mensah et al. on the emulsion stability effect by utilizing cooper and aluminum-based NP. They correlated the effect of NPs concentration and water density with the emulsion behavior. Differently, Espinosa et al. concluded that silica NPs dispersion could also stabilize supercritical CO_2 foams in porous media with co-injection of liquid and supercritical CO_2.

Nanoparticle especially metallic based NPs had been projected as the solution for improving heavy oil recovery. Hamedi et al. observed the use of copper and nickel for improving heavy oil recovery by thermal method. Later, Ehtesabi et al. reported that TiO_2 NPs could improve the heavy oil recovery up to 51%.

3.4.1 Chemical Flooding

Mechanism of nanoparticles used for EOR was based on difference in disjoining pressure (Wasan et al., 2003; Chengara et al., 2004). Nanoparticles present in the bulk fluid exert pressure forcing the particles in the confined region forward, and imparting the disjoining pressure force as shown in Figure 3.5 The driving force is Brownian motion and electrostatic repulsion between the particles. The force can be up to 50 KPa with high volume of nanoparticles. The smaller the particle size is, the higher the charge density, and the larger the electrostatic repulsion between those particles will be.

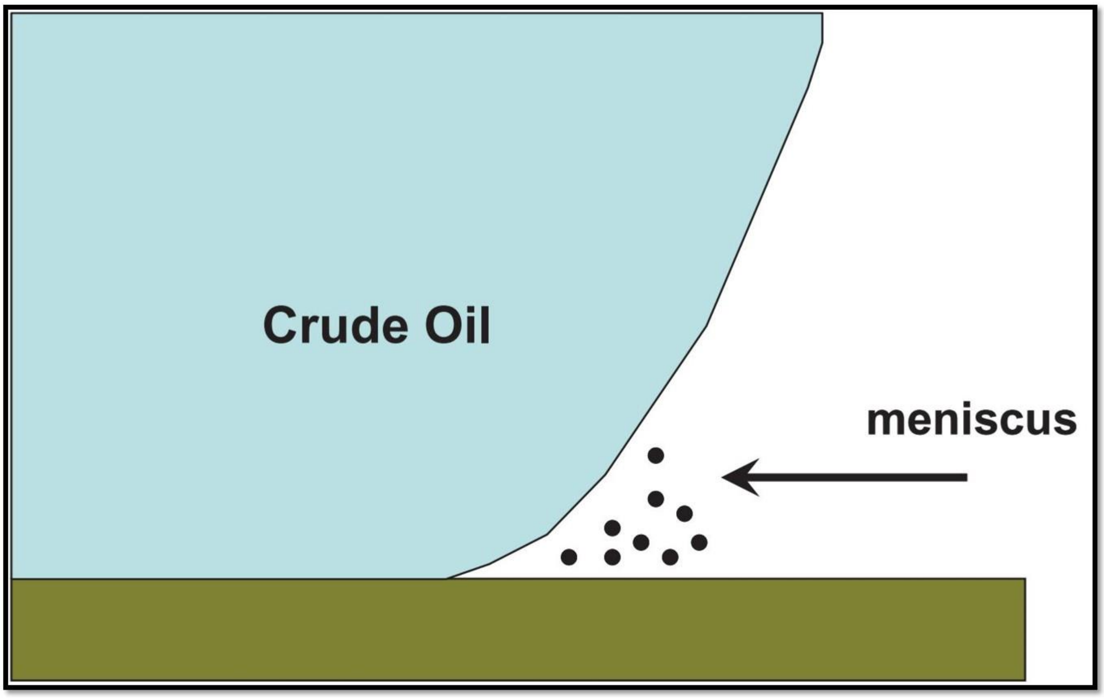

Figure 3.5 Nanoparticles are pushed underneath the discontinuous phase.

The nanoparticles form a self-assembled wedge-shaped film on contact with a discontinuous phase. The force is confined to the vertex of the discontinuous phases; thus, displacement occurs to regain equilibrium. This wedge film acts to separate formation fluids from the formation's surface, thereby recovering more fluids than conventional additives.

Nanoparticles dispersion of silicon dioxide has been used to increase oil recovery (Hendraningrat et al., 2013). Interfacial tensions (IFT) decreased when hydrophilic nanoparticles were introduced to brine. The IFT decreases when nanofluid concentration increases, which enhances oil recovery. Increasing hydrophilic nanoparticles will also decrease the contact angle of the aqueous phase and increase water wetness. Flow testing of Cores saturated with crude oil flow testing were compared. The test showed 10% nanoparticle dispersion can enhance oil recovery by 41-66%. The surface image from scan electronic microscope showed adsorption of nanoparticles at rock surface, which was from the discontinuous phase along the substrate (Mcelfresh et al., 2012).

The nanoparticles are usually mixed with surfactants. Nanoparticles associated with surfactants make the nanofluid can act as wetting agents, non-emulsifiers, and surface tension reducers at the small contact angles, which further enhances the removal of oil, wax, polymer, and leaves the substrate water wet. Suleimanov et al. studied an aqueous solution of anionic surface-active agents with an addition of light non-ferrous metal nanoparticles (Suleimanov et al., 2011). The nanofluid permitted a 70-90% reduction of surface tension on an oil boundary in comparison with surface-active agent aqueous solution and is characterized by a shift in dilution. Application of nano-suspension results in a considerably increase oil recovery.

3.4.2 Water Control

High water production is a serious problem in the oil and gas industry, which affects the economic life of producing wells. Nanomaterials could be used for plugging and sealing water-or-gas-producing zones, such as bottom-water coning, natural fractures, gas coning, etc., thus improving oil recovery. The smaller particle size of nanoparticles generates increased surface area and interface atoms, which in turn increases the surface free energy and associated structural perturbations (Roddy et al., 2009).

Polymer-coated nanoparticle was used for improving mobility control, altering surface wettability due to improved solubility and stability, greater stabilization of foams and emulsions, and more facile transport through porous media (ShamsiJazeyi et al., 2014). The size of Nano polymer microspheres can be adjusted according to the formation pore throat of formation. After hydration and swelling, the microspheres would reach the designed size and have relatively high intensity. When the size of the microspheres is bigger than that of the formation pore throat or bridged blockage formed, reliable blockage can be formed. The microspheres are elastic, which can deform and move forward under certain pressure, so that fluid diversion can be realized step by step and the request of movable agent is satisfied.

3.5 REFINING AND PROCESSING

Nanoparticle catalysts have been used for almost 100 years in the refinery industry. During the last two decades nanotechnology has made substantial contributions to refining and converting fossil fuels. The oil refining and petrochemical industry is the first area to which Nanotechnology has contributed with lots of applications and potential solution to its challenges Those challenges is facing in the downstream industry such as the limitation on sulfur and CO2 emission to the atmosphere. The development of mesoporous catalyst materials such as MCM-41 has significantly changed downstream refining. Those challenges are reforming refinery industry into cost effective, and energy efficient and technologically focused development. Nano-catalyst is utilizable for low API crude to improve refining potential and efficiency (Fan et al. 2010; Almao 2012; Peng et al. 2017). Crude<20° APl gravity can be upgraded to lighter crude using high temperature and long reaction duration along with severe environmental pollution. Nano-filters and particles have the ability to remove harmful toxic substances such as nitrogen oxides, sulfur oxides, and related acids and acid anhydrides from vapor, and mercury from soil and water with exact precision.

Nanotechnology further provides solutions for carbon capture and long-term storage. Emerging nanotechnology has opened the door to the development of a new generation of nanomembranes for enhanced separation of gas streams and removal of impurities from oil (Kong and Ohadi, 2010). carbon NPs can enhance and improve this cracking process by completing the same reaction at relatively less temperature (about 150 °C) and shorter time (< 1 h) in a cheaper and more environmentally friendly way (Li et al. 2014). Upgrading of bitumen and heavy crude oil has been another important challenge. Because of their high density and viscosity, it is difficult to handle and transport these chemicals to locations where they can be converted into valuable products.

The concept of Nano-catalyst for handling heavy oil production was proposed in 1997 by Ying and Sun. Then, Nano catalyst became more popular in the refinery industry since it has higher surface area to volume ratio than conventional catalyst. The approach in imaging MoS_2 nanocatalyst performed by Kisielowski et al. of NP aggregation for polyether-sulfone (PES)–TiO_2 that can potentially improve the treatment by reducing the fouling effect. reported that TiO_2, ZrO_2, and SiO_2 NPs have potential use for stabilizing asphalting particles via hydrogen bonding between NPs and asphalting at the acidic condition. applied the hyperthermia concept of magnetic induction heating for preventing wax deposition during production and refining. and silica NPs can remove oil droplet from the emulsion significantly faster than conventional demulsifies. In addition, NPs can also be utilized for separating oil-water emulsion that can be a beneficial solution for the refinery industry. It had been studied that magnetic NPs.

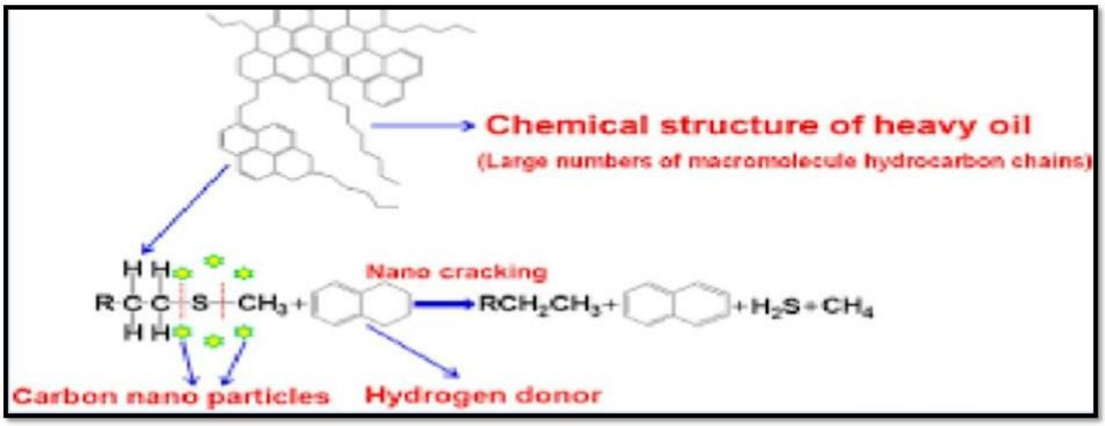

Figure 3.6 Heavy oil cracking using nanotechnology.

CHAPTER 4

EXPERIMENTAL STUDIES OF NANO-EOR

4.1 INTRODUCTION

This chapter covers laboratory experiment conducted on different nanoparticles for EOR purpose. Then, the mechanisms on how NP could improve oil recovery are briefly explained. Then at the end of this chapter the parameters affecting the performance of nanoparticle in increase oil recovery will be discussed.

4.2 LABORATORY EXPERIMENTS

Several laboratory experiments on Nano-EOR had been done in the past few years. From Table 4.1, it can be seen that all experimental research with different NP types and condition indicated the improvement of oil recovery. Various types of NPs had been discovered such as fullerenes, graphene, carbon-nanotube, polymers, metallic and metal oxides. However, only some of them have been tested for EOR application. Negin et al. divided nanoparticle used for EOR into three main categories, metal oxides, organic and inorganic NPs. However, in this section, NPs are discussed with respect to two major categories which are inorganic and organic NP.

Table 4.1 Experimental studies summary.

NP type	NP concentration	Max additional RF	Fluids	Porous Media	Reference
SiO2	0.02-0.03 wt.%	-	Water	sandstone core	Ju et al. (2006)
FeO, CuO, NiO	5 wt.%	14 %	Water	carbonate core	Haroun et al. (2012)
Al2O3, Ni2O3, MgO, Fe2O3, ZnO, ZrO2, SnO, SiO2	0.3 wt.%	12% (Al2O3)	ethanol brine & water	sandstone core	Onyekonwu and Ogolo (2012)
HLP & LHP SiO2	0.1-0.4 wt.%	19.31%	Ethanol	sandstone core	Shahrabadi et al. (2012)
SiO2	0.1 wt.%	10 %	polyacryla mide	glass bed	Maghzi et al. (2013)
LHP SiO2	0.01- 0.1 wt.%	10 %	brine (NaCl 3 wt.%)	berea sandstone	Hendraningrat et al. (2013)
TiO2	0.01 and 1 wt.%	51 %	brine (NaCl 0.5 wt.%)	sandstone core	Ehtesabi et al. (2014)
Fe2O3, Al2O3, SiO2-silane	0.05; 0.1; 0.15; 0.2 and 0.3 wt.%	22.5%	Propanol	sand pack	Joonaki and Ghanaatian (2014)
Al2O3 TiO2, SiO2	0.05 wt.%	7-11%	brine (NaCl 3 wt.%)	sandstone core	Hendraningrat and Torsæter (2014)
SiO2	0.1 wt.%	20 %	Water	carbonate core	Moradi et al. (2015)
SiO2	1 wt.%	21 %	surfactant and polymer	berea sandstone	Sharma et al. (2015)
SiO2	0.01; 0.5 and 3 wt.%	29 %	Water	sandstone core	El-Diasty (2015)
Nanoclay	0.9 wt.%	5.8%	Water	sandstone core	Cheraghian (2015)
ZrO2, TiO2, MgO, Al2O3, CeO2, CNT, CaCO3, SiO2	5 wt. %	8-9%	brine (3, 8, 10, 12 wt.%)	sandstone core	Nazari Moghaddam et al. (2015)
TiO2	1.9; 2.1; 2.3; and 2.5 wt.%	4 %	polymer and water	sandstone core	Cheraghian (2016)
SiO2	5 wt. %	25 %	water and surfactant	carbonate core	Ahmadi et al. (2016)
MWCNT	0.01; 0.05 and 0.10 wt%	31.8%	MWCNT fluid	glass bed	Alnarabiji (2016)
SnO2	0.1 wt%	22 %	Brine	Carbonate core	Jafarnezhad et al.(2017)
Complex nanofluid	1 wt%	16%-21%	water, brine, surfactant	Tensleep core	Towler et al. (2017)

4.2.1 Organic Nanoparticles

In this article, the word organic refers to the traditional definition that embraces all the compounds that contain carbon in their structure.

a. Carbon NP

According to America Element online glossary carbon is the sixth element in the periodic table and one of the most abundant elements in the universe. This black powder consists of spherical shape nanoparticles with unique properties that generally are synthesized through a hydrothermal process. These particles can be desirably surface modified, with organic molecules or polymers chemically bound to the particle's surfaces. A study was conducted by Yu et al. using Berea Sandstone and dolomite cores at room temperature and in the presence of salt ions for the purpose of comparing the breakthrough times of water and various type nanomaterial. The results of this study revealed that the breakthrough time and retention when nanoparticles were used were adversely affected by salt ions. Also, the study concluded that the retention can be improved by controlling nanoparticle surface properties by using different coatings. The retention was higher for dolomite cores because of the attraction between the negatively charged nanoparticles and the positively charged surface of the dolomite core. Therefore, in positively charged formation in carbonate reservoir using surface modifications is highly recommended. For the purpose of determining the suitability of carbon nanoparticles for harsh reservoir conditions Kanj et al. conducted an extensive research using the challenging conditions of a carbonate reservoir called ArabD, with reservoir temperatures greater than 100 C and high salinity formation water (120,000 ppm). The outcome of this research was the design of a new modified carbon nanoparticle formula commercially known as A-Dots.

These particles are carbon based fluorescent nanoparticles and are considered as an example of carbon nanoparticles family group. Based on the results achieved in the above-mentioned research, the application of these particles in carbonate samples increased the oil recovery factor to more than 96%. Carbon nanoparticles are only one of the many types of nanomaterial made out of carbon atoms. Among others diamond nanoparticles, fullerene-C60 (Buckeyballs), fullerene-C70, fullerene C76, fullerene C78, fullerene C84, graphene, graphite nano-powder have attracted the most attention. Carbon nanotubes are the second member of this family and their potential use for EOR has only recently come to the notice of scientists.

b. Carbon nanotubes (CNT) NP

Carbon nanotubes are good candidates for building various instruments since they are light, strong and resistant to corrosion. Donaldson et al. in their book classified these nanotubes under Fullerene family. The nanotubes can be single or Multi-walled. Each wall is made from graphene. Each carbon atom in this wall forms three sp2 hybridized bonds and extra electron from each carbon atom can move through the atom network. Therefore, these tubes exhibit astonishing properties regarding electrical, mechanical and thermal conductivity. These nanotubes are enormously hydrophobic, and thus they have a non-wet water surface. Toluene is a good solvent for carbon nanotubes. There have not been many studies done on using the CNT itself as an EOR agent. However, Chandran carried out a research study on the potential use of Multiwall Carbon Nanotubes (MWNT) fluid as an EOR agent for high-temperature and high-pressure reservoirs. The core-flooding tests were conducted in two different ways, first in the absence and then in the existence of electromagnetic waves. The result of the first test type showed 36% oil recovery after injection of the MWNT nanofluid. The assistance of electromagnetic fields in the second test type almost doubled the recovery. The higher results have been directly related to the oil viscosity reduction associated with the electromagnetic field. Also, the application of these nanotubes has been reported to increase the efficiency of drilling fluids (see Fig. 4.1).

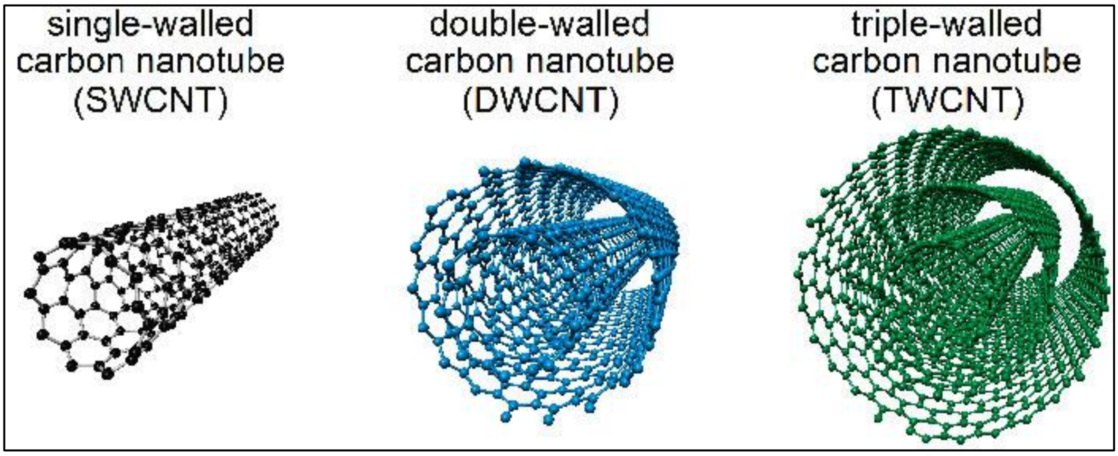

Figure 4.1 Ball and stick illustrations of single (left), double (center) and triple-walled carbon nanotubes.

c. Polymer and polymer-coated

Polymers are mainly used as stabilizer or coating to improve the stability of the nanofluids. Nanoparticles with at least contain one polymer as a component are considered as polymer NPs (PNP). PNP can be fabricated from pre-formed polymers or direct polymerization of monomers. Several processes such as solvent evaporation, salting-out and dialysis, are used for preparing PNP from pre-formed polymers. It can also be directly fabricated by polymerization of monomers by implementing various methods such as mini-emulsion, micro-emulsion, surfactant free emulsion and interfacial polymerization. PNPs are suggested to improve the mobility control and wettability alteration during EOR process.

Several types of research on using nano-size polymers for EOR purpose had been done to improve the injection efficiency and reduce the injection cost . Wang et al. conducted an experimental study on the effect of polyacrylamide (PAM) microgel nanospheres on the recovery improvement. By using PAM nanospheres, they were able to recover 20% additional heavy oil recovery. PAM nanospheres could enhance the viscosity of the nanofluid and improve the sweep efficiency of the EOR.

However, more research needs to be done for PNP since only a few literatures were available on the potential of polymer and polymer-coated NPs as EOR agents.

4.2.2 Inorganic Nanoparticles

In this article, the word inorganic refers to the traditional definition that embraces all the compounds that are lacking carbon in their molecular structure. This group is further sub-classified to particles with and without silica.

a. Silica containing nanoparticles (SiO_2) NP

i. SiO_2 NP.

In the book published by the Society for Mining, Metallurgy and Exploration it is explained that silicon dioxide also known as silica is one of the most abundant compounds on earth and is the principal constituent of the sand and sandstone. Therefore, this has made silica to be one of the most commonly used and cost-effective nanoparticles. Silica can be obtained naturally from quartz or can be created synthetically. Experimental studies done by Ogolo et al. on the application of SiO2 in water-wet sandstone reservoirs showed that it could be considered as a suitable EOR agent for this type of rock. In the presence of ethanol as a dispersing agent, it altered the wettability to intermediately -wet in addition to IFT reduction. Wang et al. through their research revealed that the specific surface area of the SiO2 powders barely changes even when they are heated to various temperatures up to 650 C. This proves the SiO2 has good thermal stability. Hendraningrat and Torsæter suggested that Silica nanoparticles form a more stable emulsion in 3%wt NaCl brine compared to metal oxides and does not need a stabilizer. The results achieved by Hendraningrat and Torsæter (2015) showed that this mixture, despite having a higher oil-brine IFT compared to a mixture of brine and stabilizer on its own, resulted in higher oil recovery from Berea sandstone. This proves that the wettability alteration from water wet Berea sandstone to intermediately -wet is the dominant mechanism for oil recovery. By analyzing the various literature, it becomes apparent that although under specific circumstances such as the use of water-wet or intermediate wet rock cores. The use SiO2 nanoparticles during core-floods conducted at room temperature resulted in less recovery, however, generally, it is still considered as a suitable EOR agent in all different wettability conditions from water wet to intermediate and oil wet. In 2011, Nhu et al. studied the synergistic blends of SiO2 nanoparticles and surfactants for EOR in high-temperature and high brine hardness sandstone reservoirs. They performed experiments combining different types of anionic surfactants with SiO2 nanoparticles. Some of the blends showed high potential for EOR application because of their resistance to adsorption onto the rock surface, thermostability as well as IFT reduction to ultra-low values. Miranda et al. have discussed some other benefits of using silica nanoparticles for EOR purposes. As described by the authors, one of the advantages is the ease with which the physical chemistry properties of this inorganic compound could be influenced. Also, using salinization with hydrophilic hydroxyl groups, hydrophobic sulphonic acid, and hydrophilic polyethylene glycol, the surface property of SiO2 can be switched between hydrophobic and hydrophilic states. Furthermore, Miranda added one main drawback in using this nanoparticle is its tendency to aggregate to larger sizes. Subsequently, this may prevent them from flowing through the pores and pore throats inside a rock (typically measured in microns) and may block the pores. Therefore, the stability of this nanofluid especially in high salinity and high temperatures is always a concern while used as an EOR agent. In Mirandas' et al. studies the emulsion properties of SiO2 nanoparticles were measured at 300 K and 0.1 MPa pressure and ($CaCl_2$ and NaCl) 1 wt% salinity. Miranda et al. observed the diffusion coefficient increased by increasing salt concentration. The oil/nanoparticles IFT measurements showed the lowest value for hydroxylated nanoparticles and highest value for Functionalized PEG nanoparticles. However functionalized PEG Nanoparticles caused the higher nanoparticles mobility. This was because of higher repulsion with the double band of aromatic ring and also higher contact angle between the nanoparticles and the oil/brine interface, which overall led to higher oil recovery (see Fig. 4.2).

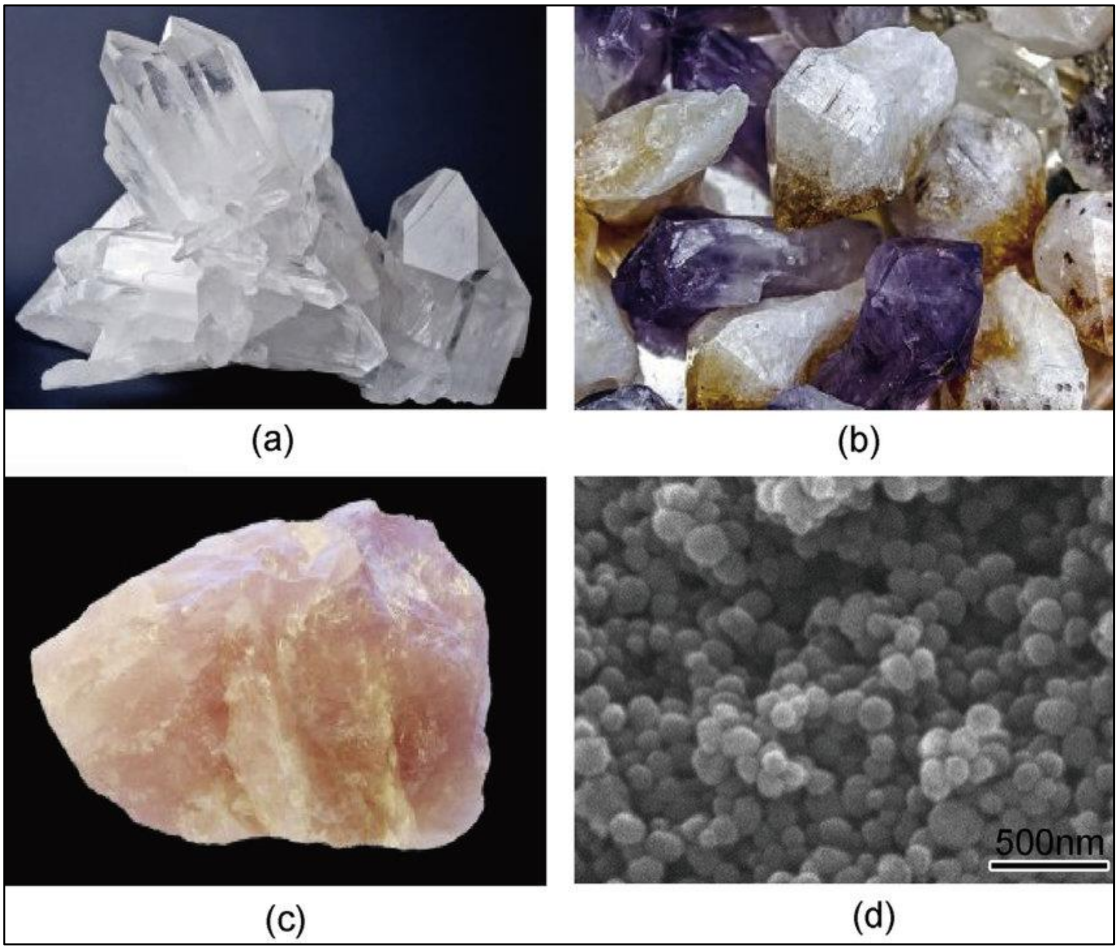

Figure 4.2 From left a) Quartz in the most abundant mineral found on Earth, b) Amethyst is a colored type of quartz, c) Rose quartz is often used in jewelry, (a, b and c, courtesy) d) SEM image of mesoporous silica: courtesy.

ii. Alumina coated silica NP.

Hoeck et al. (2011) explained that alumina coating on the SiO_2 nanoparticles entirely alters their properties. The coating creates a positive charge on the surface of this nanoparticle. The Result of their work showed that Alumina coated SiO_2 nanoparticles have a higher surface area compared to the bare SiO_2 nanoparticles however if released into the environment, they show lower toxicity than bare SiO_2 nanoparticles at concentrations 46 mg/l, except at pH 6.0. At low concentrations, no clear pH effect was observed for alumina coated SiO_2 nanoparticles. While at higher concentrations phosphate insufficiency could have caused the higher toxicity of those particles at pH 6.0e6.8 compared to higher pH values. Over years, many researchers have used a nanoparticle with the commercial name of LUDOX® CL colloidal silica (Sigma-Aldrich) in their EOR related studies. However, in one study the Propyl Gallate (PG) (Sigma-Aldrich) is used to modify the surface area of the 20 nm nanoparticles to make them partially hydro-phoebe. The study revealed that the alumina coated silica nanoparticles with modified surface formed a more stable foam and could recover more oil from sandstone cores compared to nanoparticles or surfactant flooding's alone on their own (see Fig. 4.3).

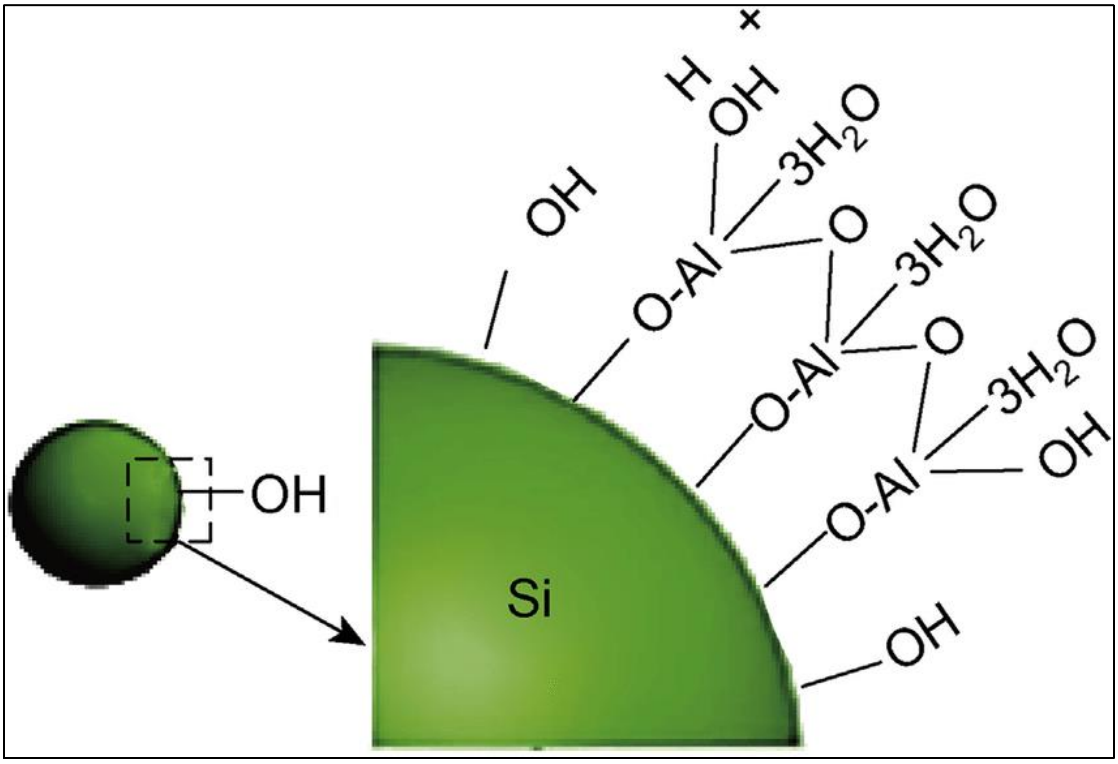

Figure 4.3 Sketch of alumina coated nanoparticle.

iii. Hydrophobic silicon oxide (SiO2) NP.

Salyer demonstrated that one common way of synthesizing silica is the addition of silanol (Si-OH) groups on the surface of the Silica nanoparticles which creates hydrophilic particles, originally. Later, if these particles are processed further through a chemical reaction with other reagents, hydrophobic silica particles could be produced. Often the required further process involves adding hydrocarbon group coatings such as alkyl or dimethyldi-chlorosilane and hexamethyldisilazane chains to the silanol group. Furthermore Salyer classified hydrophobic silica nanoparticles as fumed silica, precipitated silica, and aerosol assisted self-assembly. Studies completed by Ogolo et al. showed that this nanoparticle can be a good EOR agent for sandstone reservoir when ethanol is used as the dispersing agent. The recovery factor was higher for this nanoparticle comparing to aluminum oxide, magnesium oxide, iron oxide, nickel oxide, zinc oxide, zirconium oxide and tin oxide. Zhang et al. (2010) suggested that these nanoparticles form stable water in oil emulsion and the contact angle at water-oil interface is greater than 90 C The viscosity of the water in oil emulsion decreased with increasing the salinity from 0 to 10 NaCl wt.% and there was an opposite trend for the hydrophilic nanoparticle's emulsion. For the unit volume of stable emulsions, the hydrophilic nanoparticles emulsions which are oil in water produced a higher amount of oil comparing to water in oil emulsions made by hydrophobic nanoparticles. For hydrophobic nanoparticles increasing the nanoparticles concentration from 0.1 to 5 wt.%, dispersed more water with a smaller droplet in the emulsion.

iv. Spherical fumed silica NP.

Zhang et al. defined these particles as the most frequently used type of nanoparticles as a stabilizing agent for oil/water emulsions. The wettability of the surface of the particles depends on the degree of coating using silanol groups. High degree of coating (greater than 90%), helps to forms a hydrophilic surface around the particles that is necessary for creating a stabilized oil-in-water emulsion. On the contrary, covering only 10% of the surface with the silanol coating, does not disturb the hydrophobic behavior of the surface and makes the particles suitable for the water-in-oil emulsion. Partially covering the surface creates nanoparticles with inter-mediate hydrophobicity. To the best of the authors' knowledge, the application of this nanoparticle in EOR studies has been limited to using them as stabilizing agents and its direct application in other EOR related work such as flooding experiments, has not been studied yet. However, the small size of these particles in the range of several to tens of nanometers reduces the risk of blocking the pore in an EOR process.

v. Inorganic silica-core/polymer-shell nano composite.

These nanoparticles are SiO2 nanoparticles in the core that have been covered with a shell of synthetic polyacrylamide polymer. Nguyen et al. showed that these nanoparticles with a composite nature, are suitable for high temperature and high salinity applications in the presence of hard ions commonly found in offshore reservoirs. The particles are efficient in reducing the IFT, increasing the viscosity at critical concentrations. They also have high thermostability and salt tolerance. Based on the results obtained by Nguyen et al. (2012), injecting mixtures of 200 ppm core-shell nanoparticles and 800 ppm blends of two surfactants (anionic and nonionic) in a fractured granite sample at 92 C and 3.44 wt.% salinity could increase the oil recovery by 6.2%.

vi. Silicon oxide treated with silane NP.

Different types of silane functional group can be found in the market. Jian-Shu (2009) used aminopropyltriethoxysilane, 3-glycidoxypropyl-trimethoxysilane and 3-methacryloxypropyltrimethoxysilane to modify SiO_2 particles that resulted in "increasing the final monomer conversion, decreasing the particle size, and narrowing the particle size distribution of the poly (MMA-HEMA)/SiO_2 composite emulsion". Lin et al. (2011) also have used other silane coupling agents such as glycidyloxypropyltrimethoxy silane (GPTMS), aminopropyltriethoxy silane (APTES), trimethox-ysilylpropyl methacrylate (TMPM), and dichlorodimethyl silane (DCMS) to treat the surface-activated nano-silica. Ogolo et al. (2012) have explained that this nanoparticle can be an excellent EOR agent for sandstone reservoirs, especially when dispersed in ethanol. Experiments with this nanoparticle resulted in the highest recovery compared to other nanoparticles such as aluminum oxide, magnesium oxide, iron oxide, nickel oxide, zinc oxide, zirconium oxide, tin oxide and hydrophobic silicon oxide.

b. Aluminum oxide (Al_2O_3) NP

Ogolo et al. explained that Al_2O_3 nanofluid is capable of reducing the oil-brine IFT and oil viscosity. However, the oil viscosity reduction is the dominant effect, especially when the particles are dispersed in brine. The results of the conducted core-flood in sandstone with this nanofluid showed that the highest recovery achieved was when brine or distilled water was chosen as a dispersing agent. The researchers recommended this nanofluid as an EOR agent for heavy oil reservoirs. Ogolo et al. also separately investigated the spontaneous imbibition recovery in sandstone cores that showed the highest recovery when Al_2O_3 nanoparticle was dispersed in diesel. Later Hendraningrat and Torsæter researched the emulsion stability of 0.05% wt. Al_2O_3 when dispersed in 3% NaCl wt.% brine and its effect on oil recovery factor. Their initial measurement showed that Al_2O_3 has the closest specific surface area to titanium (TiO_2) and silica (SiO_2) nanoparticles comparing to other metal oxide nanoparticles. The experiments conducted by these researchers showed that the solution of this nanoparticle in brine was not stable, and it started to precipitate in the first hour. To minimize this problem, they added Polyvinylpyrrolidone (PVP) also known as Povidone with a chemical formula of (C_6H_9NO) to the solution. Results revealed that the PVP successfully stabilized the emulsions. In the second section of their experimental work, the emulsion stabilities of Al_2O_3, TiO_2, and SiO_2 nanoparticles were observed while increasing the temperature up to 80 C. Inter-estingly, the results revealed that the aggregation behavior of the emulsions to be almost independent of the temperature. Finally, the core flooding tests conducted by Hendraningrat and Torsæter using the Al_2O_3 nanofluid on Berea Sandstone cores with different wettability at room temperature resulted in the highest recovery for the intermediate wet, the lowest recovery for oil-wet and an in-between recovery for the water-wet rocks. They reported the wettability alteration as the dominant mechanism despite of the fact that it reduced the IFT value as well. Hendraningrat and Torsæter reported Aluminum Oxide, as a good agent for EOR in a sandstone reservoir.

c. Magnesium oxide (MgO) NP

Huang el al. investigated the application of nanoparticles to control fines migration in reservoir formation. In their study, they used a particular type of coated crystalline MgO nanoparticles that had been mentioned previously in the literature by its commercial name of nanoparticle 20/40 US mesh. The results obtained by these researchers using this metal oxide are promising. However, MgO nanoparticles effects on EOR requires greater investigation. Later on, other researchers showed that magnesium oxide and zinc oxide used during core-flood tests while dispersed in brine or ethanol can cause permeability impairment in sandstone rocks. On the positive side, Ogolo et al. found that soaking the rock samples in ethanol and magnesium oxide nanoparticles solution could reduce the oil viscosity significantly. This study concluded that overall, MgO nanoparticles are weak recovery agents for EOR in sandstone reservoirs.

d. Titanium oxide (TiO2) NP

The potential use of titanium oxides NPs for EOR has been proposed by several researchers. Ehtesabi et al. employed TiO_2 NPs in water for enhancing oil recovery in sandstone core plug. They discovered that TiO_2 NPs could improve recovery from 49% to 80% by altering the wettability due to uniform adsorption, as proved by SEM study. Similar experiments with lower concentrations of TiO_2 (0.01 and 0.05 wt. %) showed that TiO_2 was not significantly affecting viscosity and interfacial tension, but will change the wettability from oil-wet to water-wet. Hendraningrat and Torsæter studied the effect of Al_2O_3 and TiO_2 on Berea sandstone. They showed that combined TiO_2 NPs with PVP as dispersant yield highest recovery compared with Al_2O_3, SiO_2, brine-only and dispersant-only. They concluded that TiO_2 NPs is the most effective nanoparticle for

EOR compared to the other metal oxides NPs with wettability alteration as the dominant mechanism.

The possibility of combining TiO_2 NP with surfactants or polymer in chemical EOR had been investigated. Cheraghian proved that oil recovery was increased by 4.85% when using 2.2 wt. % TiO_2 in surfactant compared with only surfactant. Similarly, by combining polymer with 2.3 wt.% TiO_2, the recovery of oil was improved by 3.9% than conventional polymer flooding due to the viscosity improvement of the displacing fluid. Moreover, Sedaghat et al. observed the effect of TiO_2 on polymer-surfactant flooding which showed positive recovery improvement than conventional polymer-surfactant flooding.

e. Zirconium oxide (ZrO_2) NP

As explained by Myloslavskyyl zirconia nano powders have recently been applied extensively in the industry. He listed these applications as catalysis, ceramics, thermal barrier coating, solid oxide fuel cell components, drug delivery, microelectronics such optical storage and stereo television glasses, high-temperature and corrosion resisting components, temperature and pressure transmitters, transmitting elements, electrode used for magnetic-current generator, heating elements and etc.

However, this nanoparticle is not common in the oil and gas industry particularly in EOR process. In 2012, Ogolo et al. injected this metal oxide as an EOR agent at room temperature into a sandstone core sample. The results showed a small increase in oil recovery compared to injection of distilled water alone. On the other hand, when brine or ethanol were used as dispersing agents, it actually reduced the recovery factor to less than that achieved in the absence of nanoparticles.

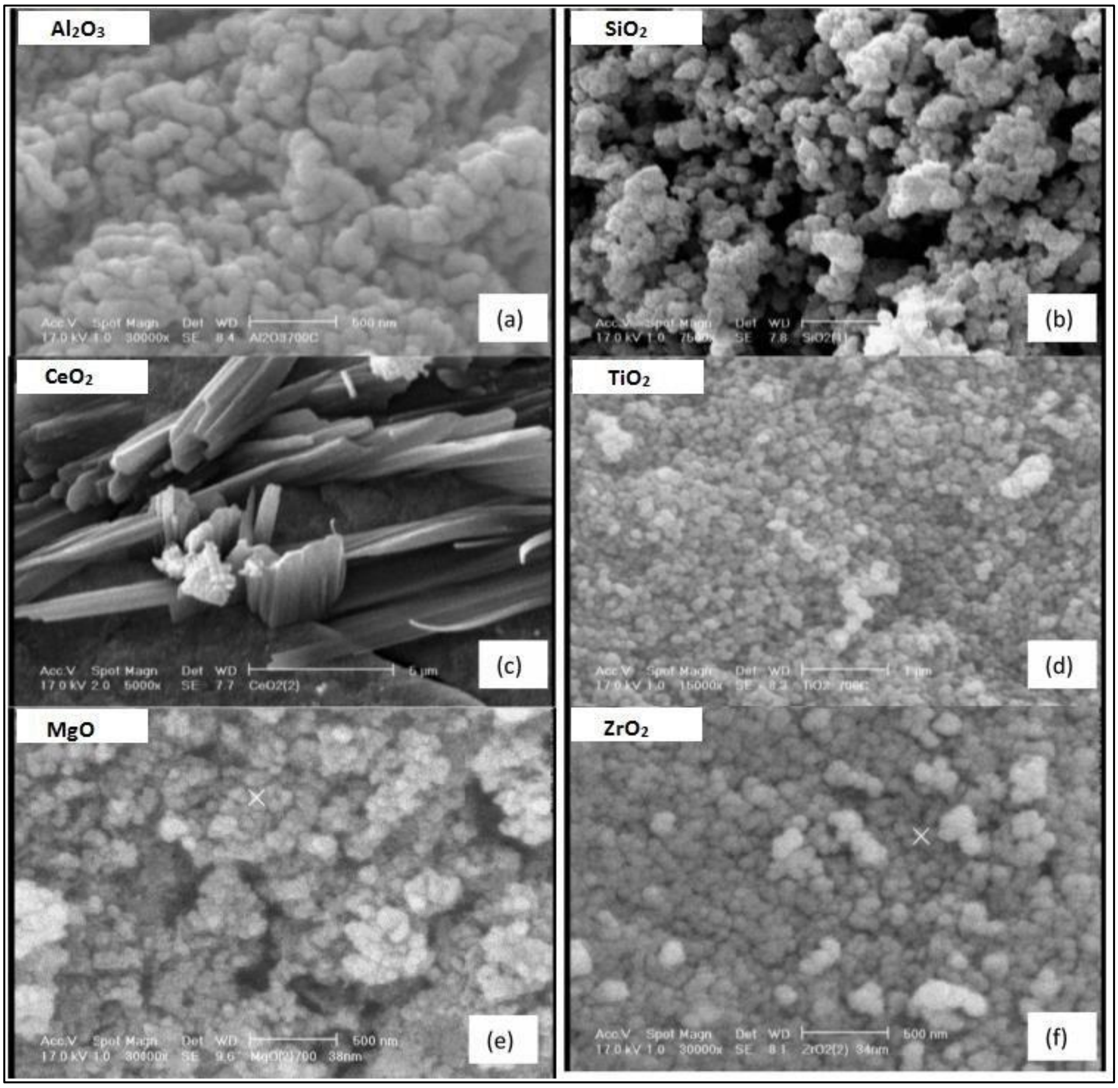

Figure 4.4 ***SEM*** *image of different nanofluids (a) Al2O3, (b) SiO2, (c) CeO2, (d) TiO2, (f) MgO and (f) ZrO2.*

f. Zinc oxide (ZnO) NP

Zinc oxides (ZnO) has been widely studied for wettability change in EOR in the past few years. Ogolo and Onyekonwu showed that zinc oxides dispersed in brine and water caused permeability reduction due to the agglomeration of ZnO into larger particles, which blocked the pore throat of the core. Differently, Zaid et al. proved that ZnO could be a good candidate for EOR agent. They found out that ZnO has better performance in oil recovery than Al2O3 (72% ROIP for ZnO vs. 53% for Al2O3) with lower IFT value. They also concluded that larger particle size of ZnO gives higher recovery for about 145%

higher than smaller sizes. Similarly, Tajmiri et al. investigated oil recovery by 0.2 wt.% ZnO NPs over heavy oil saturated sandstone and carbonate core samples. Improvement of oil recovery with both carbonate (8.89% of OOIP) and sandstone (up to 20.68% OOIP) core plugs was achieved. ZnO NP was able to reduce the heavy oil viscosity and alter the grain surface wettability.

Latiff et al. proposed to use ZnO combined with non-invasive electromagnetic (EM) transmission. They investigated the effect of ZnO particle dispersed in water, on the oil recovery from glass micromodel saturated with heavy oil (viscosity 12.31 CP). They successfully recovered 26% remaining oil by 30 minutes EM exposure with a simultaneous nanofluid injection.

Adil et al. studied the stability of zinc oxides NP dispersed in water. By using different anionic surfactants as the stabilizer with various NPs concentration, they concluded 0.1 wt. % ZnO stabilized with 0.025 wt. % sodium dodecyl benzenesulfonate (SDBS) has the highest stability at 95°C with viscosity enhancement up to 11%. The combination of surfactant, pH and ultrasonication for ZnO nanofluid preparation to adjust their mobility properties were suggested.

Also, Feng in his book explains that ZnO can have polar and non-polar structure. He relates the a-plane ZnO film to non-polar and c-plane to polar. As indicated by Jelinek, ZnO nanoparticles have been used considerably for applications such as stabilizers for rubber material, ceramics, food, semiconductors, ointments and photocatalysis. There has been some ongoing research on a particular shape of ZnO called ZnO nanorods (NRs). Feng further explains that NRs shows better physical properties compared to ZnO nanoparticles. Investigations about the applications of this inorganic compound in EOR processes have been very limited. Ogolo at al. explain that, similar to magnesium oxide, when ZnO was implemented as an EOR agent in sandstones, it negatively affected the permeability of the samples used. Evidently, this was more significant when brine or ethanol were used as dispersing agents. The study claimed that the problem initiated by agglomeration of the zinc oxide nanoparticles at the injection point can block the pores. Therefore, due to this problem zinc oxide nanoparticle could lower the overall oil recovery factor.

g. Iron oxide, (Fe_2O_3/Fe_3O_4) NP

With unique magnetic and electrical properties, iron oxides (Fe_2O_3/Fe_3O_4) NP is proposed by many researchers as sensor tracker (nano sensor). However, there is only a few researches on the potential use of iron oxides for EOR. Haroun et al. studied several metal oxide NPs such as Fe_2O_3, CuO, and NiO on carbonate core plugs. The result on the iron oxides NPs was not so promising since it could only reach 57% ultimate recovery while other NPs can achieve up to 85%. However, others have shown that iron oxides were able to increase the recovery up to 24% (additional) when they are dispersed in water. Iron oxide has the possibility to increase the viscosity of the displacing fluid which also improves of sweep efficiency. Joonaki et al. reported that iron oxides were only able to recover 17% extra oil while other NPs i.e., Al_2O_3 and SiO_2 recovered around 20% additional oil.

Ferrofluids (Fe_3O_4) were proposed for magnetic heavy oil recovery by Shekhawat et al. Magnetic recovery is done by having an in-situ injection of magnetic NPs and pushing the NPs towards the reservoir using magnetic downhole tools. Then, inward magnetic forces are applied towards the borehole to recover magnetic NPs that already soaked with oil. Iron oxides NPs is shown to stabilize CO_2 foam which can improve sweep efficiency during the CO_2 injection process.

It seems that iron oxides NPs are not the best candidate for EOR. However, they still give a decent performance on recovery and viscosity enhancement.

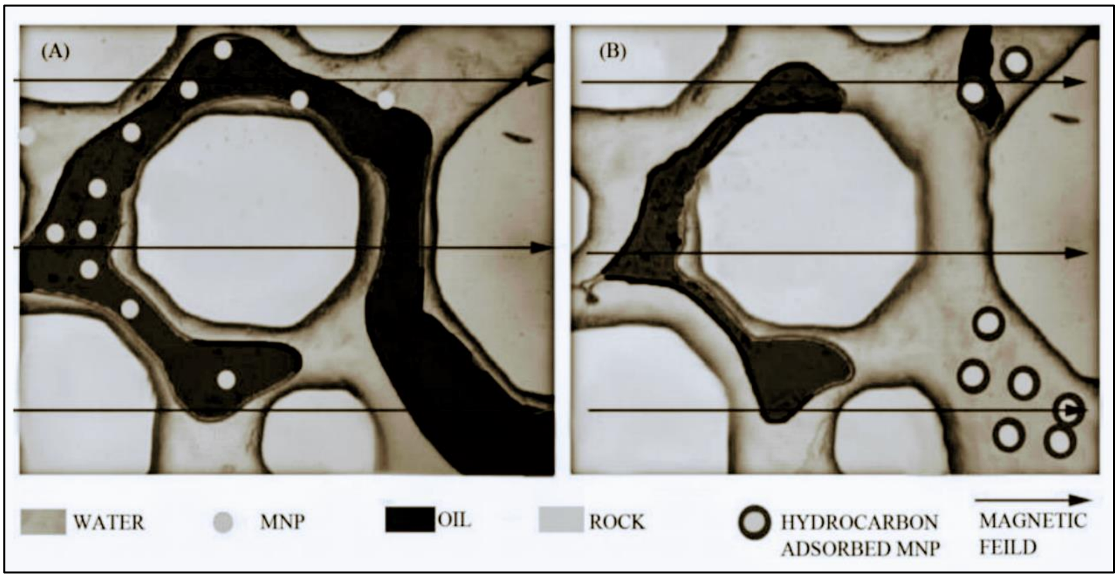

Figure 4.5 Oil recovery mechanism by magnetic nanoparticle (MNP).

h. Nickel oxide (Ni2O3) NP

Nickel oxides (NiO/Ni2O3) as one of hydrophilic metal oxides has potential use for EOR . Ogolo et al. found out that nickel oxides NPs dissolved in diesel and brine had positive result towards the improvement of oil recovery due to wettability alteration of the rock surface and viscosity enhancement of the brine. Nwidee et al. studied the effect of NiO and ZrO2 NP with fractured limestone core samples. They concluded that even though ZrO2 gave the best result, NiO has potential use as EOR agent since it is able to reduce the water contact angle with increasing concentration, injection time and salinity. Therefore, it has been shown NiO is not the best compared to other metal oxides (Al2O3 and ZrO2) for EOR, but it still gave a positive improvement in recovery with its ability to alter wettability and enhance viscosity.

4.3 MECHANISM

Understanding the EOR mechanisms of nanoparticles is fundamental to their application in EOR processes. and understand the EOR of nanofluid flooding. The change in reservoir wettability and the reduction of the interfacial tension are the two well accepted mechanisms of NPs and reduction of oil viscosity and plugging of pore channels and increasing the disjoining pressure and different nanoparticle types that they could improve hydrocarbon recovery in EOR process. Its Several mechanisms for the recovery improvement are proposed, such as interfacial tension reduction, wettability alteration, viscosity control, disjoining pressure, those mechanisms take place because adsorption, desorption and transport of NP occur inside the pore throat. and these follow:

4.3.1 Alteration Wettability

Alteration is a well-known practice for oil-wet and mix-wet formation enhanced oil recovery and preventing asphaltene precipitation wettability alteration, improvement in the mobility of trap of oil. The definition of rock wettability is the tendency of a fluid to adhere to the rock surface competing with another immiscible fluid . It is directly related to the fluid-fluid and fluid-solid interaction which involves interfacial energy.

Wettability is a rock property that depends on the type of minerals, pore distribution, and surface area. and is also the function of fluid composition and temperature. Several studies have revealed that wettability is an important factor for understanding the multiphase flow during hydrocarbon accumulation until production and achieving the highest oil recovery significantly affects capillary pressure and relative permeability, the oil flow inside the porous media can be improved considerably . It also leads to the spontaneous imbibition of water that helps to push the hydrocarbon out of the matrix blocks during water flooding The wettability alteration was attributed to disjoining pressure ascribed to NPs wedged between the oil and the core sample. To further confirm the effect of NPs on the SDS surfactant, a spontaneous imbibition test proved the ability of NPs to shift the wettability from oil wet to water wet. is usually measured in the laboratory by using the contact angle method, the Amott test and ore displacement test. The young equation is commonly used to distinguish the wettability type of the system by adopting the contact angle methods.

$$\cos \theta = [(\frac{\sigma sw - \sigma so}{\sigma wo})] \tag{4.1}$$

Where σsw is the solid-water interfacial tension, σso is the solid-oil interfacial tension and σwo is the water-oil interfacial tension. This equation used to distinguish the wettability type of the system by adopting the contact angle methods. its valid under equilibrium conditions with assumption on smooth, homogenous, rigid, and nonreactive surface. Based on the contact angle, wettability of rock in oil-water system can be classified into three main types, i.e., water-wet (θ<90°), neutral-wet (θ=90°) and oil-wet (θ>90°). This is illustrated in Figure (4.6)

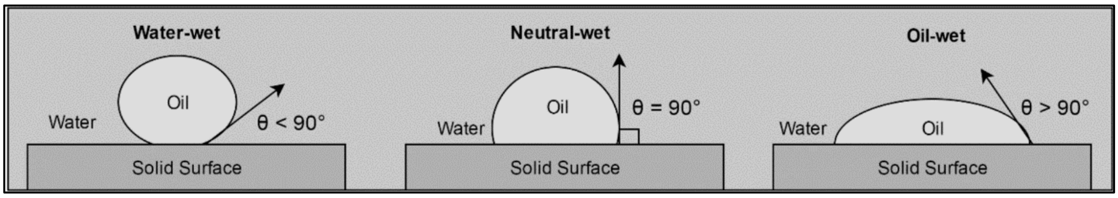

Figure 4.6 Wettability variation on oil-water system.

The Amott test mainly uses the wettability index (Iw) to determine wettability that combines spontaneous and forced displacement at room condition. The definition of Iw is as follows:

$$IW = \left(\frac{VO1}{VO1 + VO2} - \frac{Vw1}{Vw1 + Vw2}\right) \quad (4.2)$$

Where Vo describe oil volume from imbibition process, Vw describe water volume from drainage process, respectively. Subscript ‘1’ means spontaneous displacement process and ‘2’ means forceddisplacement process. Iw ranges from −1, as completely water-wet, to 1, as completely oil wet and 0 is considered as neutral wettability.

The core displacement test also can be used to determine wettability alterations by comparing the changes in residual water saturation (Swr), oil relative permeability (kro) and the point where the water and oil relative permeabilities are equal (crossover point) before and after nanofluid treatment.

Wettability alteration on the polished-synthetic-silica surface in different concentration. As shown in Figure (4.7).

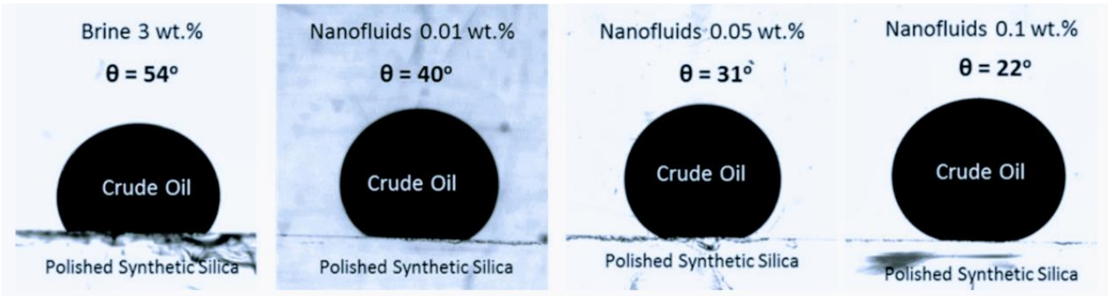

Figure 4.7 Contact angle variation of oil-brine system in different concentration.

Figure shows. the increasing concentration of NPs will reduce the contact angle of crude oil and change the wettability towards more water-wet, and that the smaller size of NPs tends to decrease the contact angle more than bigger size particles, due to the higher electrostatic repulsion on smaller sizes wettability alteration is the function of salinity, ionic composition, initial wettability, a solid system and the exposure time.

Surfactant and nanoparticle have similarity in the mechanism of wettability alteration. Recently, some authors try to analyze the reasons why the NPs can result in wettability alteration of rock surfaces by some novel characterization techniques. For example, Hammond and Unsal proposed two most possible mechanisms, the adsorption on the solid surface (coating mechanism) and removal of the absorbed molecule from the rock surface (cleaning mechanism). The adsorption process of NPs on the grain surface resulted in the formation of composite nanostructure-surface which improves the water-wetting behavior. The SEM images in (Figure 4.8) shows the adsorption of silica NPs on the calcite surface which forms a layer of the nanostructure with some agglomerated particles after 1-hour nanofluid treatment. Also, Karimi et al. proved that NPs adsorbed on the calcite forming of nano textured surfaces by scanning electron microscopy (SEM) images and energy dispersive X ray (EDX) (Figure 4.8).

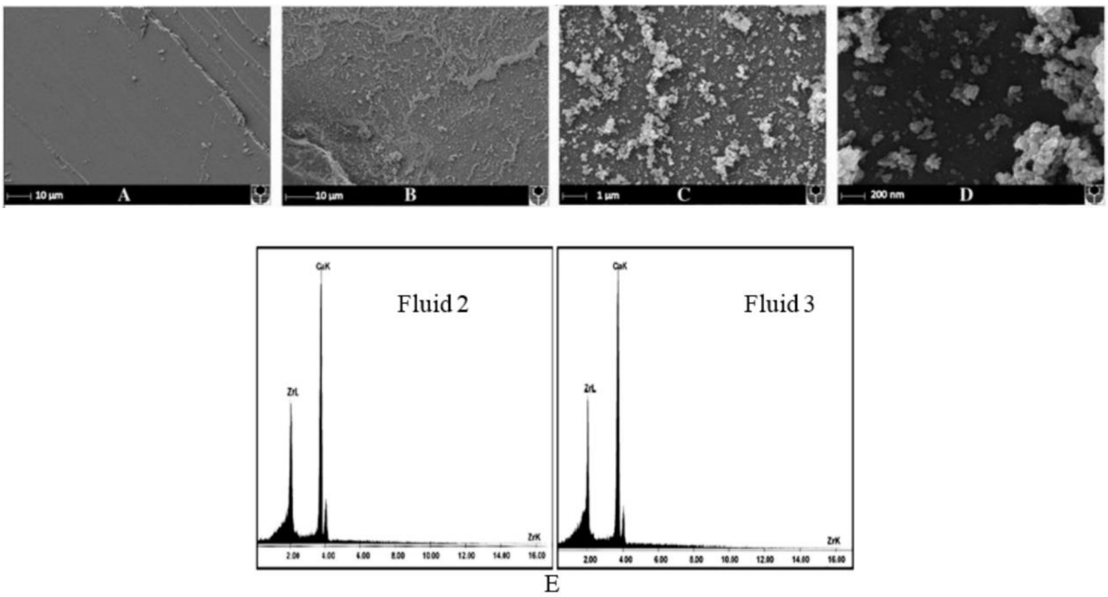

Figure 4.8 SEM images of the measured calcite surface: (A) Calcite surface before; (B) Calcite surface after nano-modification (nanofluid treatment); (C) High resolution; (D) Maximum resolution; and (E) EDX Analysis of carbonate rocks aged in fluids.

Al-Anssari et al. tested the surface modification with SEM–EDS and atomic force microscopy (AFM) measurements. It was observed that the distribution of the NPs on the surface were homogeneous after nano-modification (Figure 4.9). The surface modification by nanoparticles also increases the roughness of the surface as can be seen in (Figure 4.9). Karimi et al. added that the main factors on the wettability alteration are the area fractions of the nanostructure, partition coefficient and surface roughness.

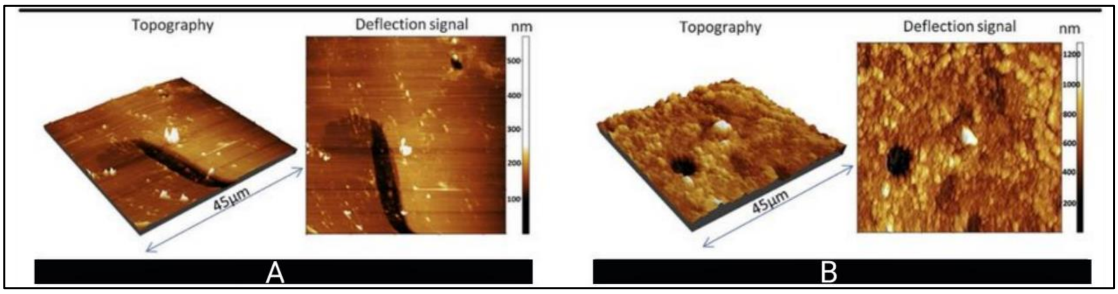

Figure 4.9 Atomic force microscopy (AFM) images of the measured calcite surface: (A) Topography picture before; and (B) Topography picture after nano-modification (nanofluid treatment).

4.3.2 Interfacial Tension Reduction

Interfacial tension (IFT) is the surface free energy at the interface of two immiscible fluids and so is a fundamental parameter for the EOR process. exists between immiscible fluids in the pores of reservoir rocks due to capillary force where Capillary force is one of the most essential forces in reservoir system which restricts the oil recovery. The value of capillary force is determined by interfacial tension (IFT) between the reservoir fluids and rock wettability. When the system is characterized by high capillary pressure, the oil is trapped within the pore but with reduction in the IFT, capillary effect is minimized, and oil recovery is enhanced So when Decreasing interfacial tension will make it easier for oil droplets to move through pore throats by decreasing work of deformation needed. Reducing interfacial tension rising the capillary number. A higher capillary number causes an increase in oil displacement efficiency. the NPs create a thin layer on the surfactant that distributes between oil and injected fluids. This process leads to a significant reduction in the interfacial tension parameter. In fact, in this process, the capillary numbers increase and capillary forces significantly decrease. A mixture of surfactants and NPs, depending on the surface charges and the formation type, may cause IFT reduction, and a decrease in capillary forces. alumina NPs reduction of interfacial tension from 19.2 MN/m with brine to approximately 11 MN/m or to 12.8 MN/m, while silica based NPs are only able to reduce to 15.7 MN/m and reduction in interfacial tension, from 26.3 MN/m to 1.75 MN/m and 2.55 MN/m for HLP and NWP respectively To increase oil recovery ratio, one of the common strategies is to reduce the oil–water interfacial tension is a standard parameter to be used for surfactant characterization. The lowest oil–water interfacial tension by molecular surfactant can reach 10−3 to 10−2 MN/m. Although nanofluid systems cannot achieve that small interfacial values, researchers try to reduce interfacial tension between oil and water by nanomaterials. added, that the magnitude of IFT reduction is directly related to nanoparticle concentration, with higher concentration favorable for lower IFT.

Table 4.2 Measured interfacial tension data of certain nanofluid.

Fluids	**n-Heptane-fluid Interfacial tension (MN/m)**	**Air-fluid surface tension (MN/m)**
Water	51.4	72.1
10mg/l ZrO_2	37.2	71.8
100mg/l ZrO_2	37.2	71.3
500mg/l ZrO_2	36.4	71.1
1g/l ZrO_2	36.8	71.2

Zirconium oxides mixed in a surfactant solution had been proven to reduce the IFT of heptane-fluid and air-fluid significantly, as shown in Table 4.2 found out that zinc oxides could improve the efficiency of sodium dodecyl sulfate (SDS) surfactant in reducing IFT. The pH of the fluid had a significant effect on IFT with acidic and neutral pH favored. In addition,]. Moreover, carbon nanotubes (CNT) were also proven to reduce interfacial tension significantly (Figure 4.10), demonstrating a good potential for EOR agent.

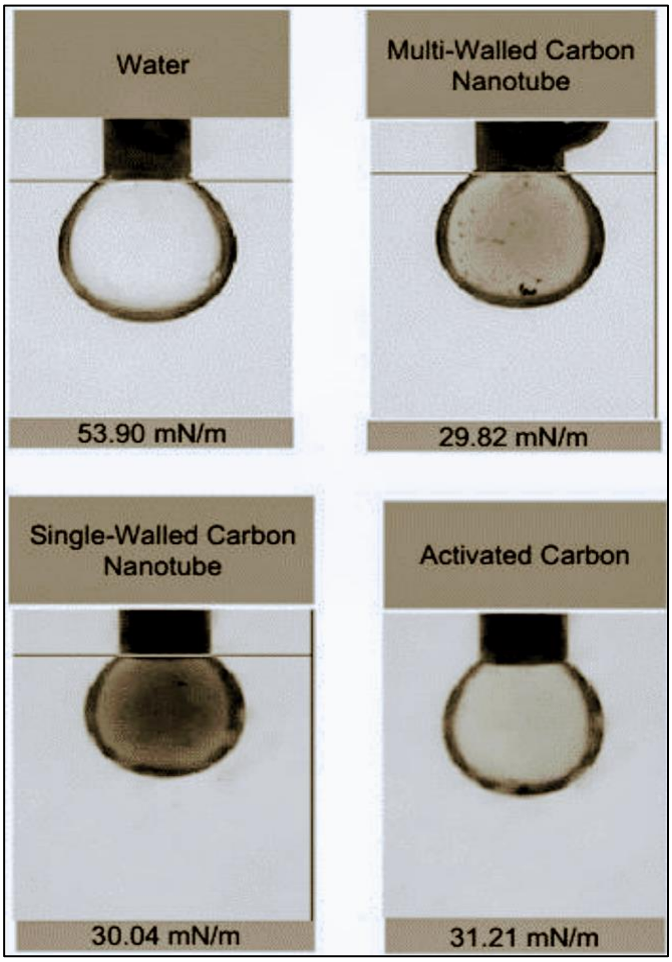

Figure 4.10 The effect of carbon nanotube and activated carbon on the interfacial tension.

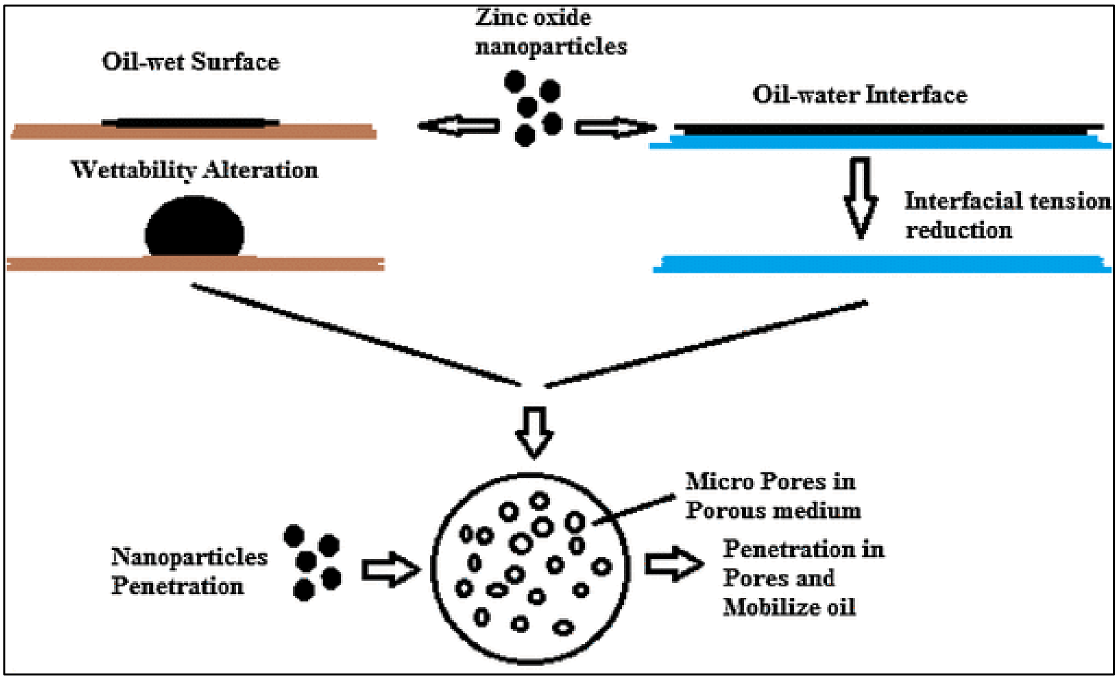

Figure 4.11 Wettability alteration and interfacial tension reduction by nanoparticles.

Oil recovery is directly related to a dimensionless capillary number (Nca), which is defined as a ratio of viscous forces to capillary forces. Mathematically, it can be represented by

$$Nca = \left(\frac{Viscousel\ force}{Capillary\ force}\right) = \left[\frac{Vu}{\sigma cos\theta}\right] \quad (4.3)$$

Where V is the velocity, u is the dynamic viscosity, σ is oil-water IFT, and θ is the contact angle. A higher capillary number is essential in order to reduce residual oil saturation significantly. To obtain such a higher capillary number, IFT must be decreased to an ultra-low value (10−3 MN/m).

4.3.3 Disjoining Pressure

Disjoining pressure that defines the attractive and repulsive forces that exist between two thin layers of fluid films, is another mechanism proposed for effective nanoparticle-EOR process and define it can remove fluids attached to the rock surface due to adhesion force of fluids/solid surface (Jiang et al., 2017). the oil–water–solid contact region has been observed and studied during nanoflooding, which is one of the driving forces to expel oil from rock surface. and forms at the interface between displacing and displaced phases (i.e., nanofluid and oil, respectively) and solid substrate.

The investigations, regardless of theoretical or experimental type, demonstrated that the nanofluids directly affect oil adsorption on a rock surface toward reducing pattern by entering a structural disjoining force (film) between the oil and the rock surface and then creating a wedge film structure on the rock surface which means a smaller NPs leading to stronger repulsion forces (Kopanichuk et al., 2017;Lim and Wasan, 2017) When the rock surfaces are in contact with nanoparticles solution, the particles will adsorb on rock surfaces and form a wedge film that exact an extra pressure (disjoining pressure) on oil droplets. that showed that reduction in the diameter of nanoparticles from 30 nm to 18.5 nm resulted in 4.3 times increase in the structural disjoining pressure.

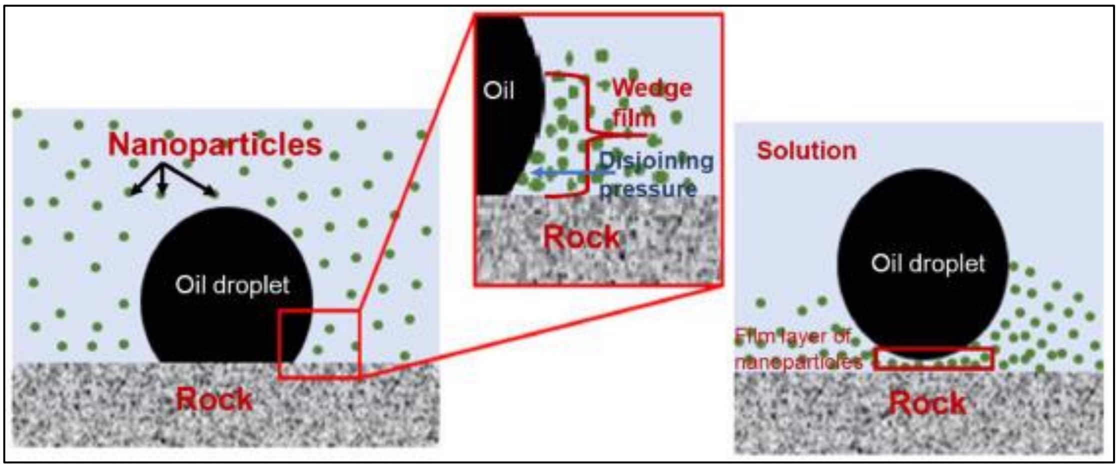

Figure 4.12 Schematic of disjoining pressure and wettability alteration.

Displayed their work on crude oil displacement with nanofluid. They concluded that disjoining pressure is the mechanism underlying their successful oil displacement with sandstone experiment.

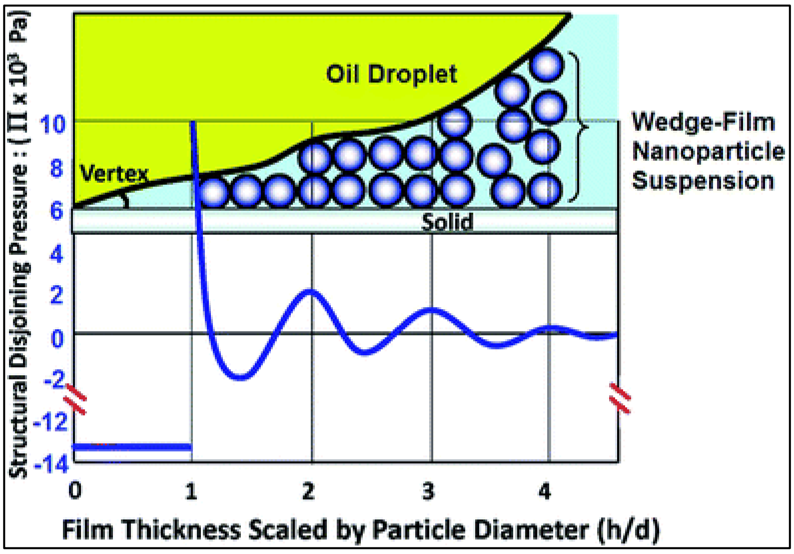

Figure 4.13 Schematic shows nanoparticle wedge film confined by solid surface and oil-nanofluid interface and relationship between disjoining pressure and film thickness.

The demonstrated with a calculated disjoining pressure near the vertex for SiO2 nanoparticles which showed that the disjoining pressure of the nanoparticles layer near the contact point was high enough to advance on the surface and remove the oil from the surface. This was further corroborated by the study done by Kondiparty et al. Wasan and Nikolov showed that the structural disjoining pressure exponentially increases with a decrease in film thickness or number of nanoparticle layers between the solid and oil, Disjoining pressure can directly increase the displacement efficiency of crude oil in the porous media.

This is mostly due to the wettability alteration, but ineffective in changing the interfacial tension. Chengara et al. The positive enhanced oil recovery effects of the application of CaCO3 and SiO2 nanoparticles observed by Moghaddam et al.

Additional adsorption of nanoparticles due to increase in their concentration or increase in their contact time with the rock surfaces will increase this pressure against the oil droplets and thin layer of nanoparticles will cover the rock surfaces and modify their wetness toward water-wetness stated that nanoparticles form a thin film on a rock surface which is forced by injection pressure, and tend to arrange themselves in well-ordered layers. Consequently, an additional disjoining pressure would be exerted in an interface more than that in the bulk liquid. Additionally, Mc-Elfresh et al. reported that a developed film of nanofluids on the surface of the rocks has the ability to separate and release the reservoir hydrocarbon. Hence, the wetting system can be changed from oil-wet to water wet. On the other hand, Aveyard et al.

It is the high structural disjoining pressure that enhances the spreading of the phase containing nanoparticles and can lead to wettability alteration of an oil-wet surface to more water-wet states. Matar et al. showed this theoretically by applying the mass and momentum conservation equations under the lubrication approximation.

4.3.4 Viscosity Control

The last few years, some literature deals with oil viscosity reduction using nanoparticles. These nanoparticles will act as a catalyst during steam injection. In this research, seven different nanoparticles types investigated to study their effect on crude oil viscosity reduction. These nanoparticles comprise Potassium Aluminum Sulphate, Nickel oxide, Zeolite, Silica, Ferric oxide, Tungsten. During the EOR process, high mobility of displacing fluid often results in viscous fingering, which leads to poor sweep efficiency and conformance. Another important dimensionless number in EOR is mobility ratio, which is the ratio between the displacing fluid and displaced fluid. A lower mobility ratio is desired for more oil displacement, under which has a higher sweep efficiency.

Nanofluids have been reported to be used to reduce oil viscosity and increase displacing fluid viscosity. These factors will contribute to decrease mobility ratio and as a result, boost oil recovery ratio where the Nan emulsion also has high viscosity that helps with the control of mobility ratio during flooding and they can penetrate the pore throats without much retention due to their small size. Many researchers have used nanomaterials to reduce the viscosity of bitumen and heavy and semi-heavy oil. Based on some experimental results, NP concentration, size and type are different parameters that affect the reduced viscosity mechanism of heavy oil NPs also cause more enhanced viscosity in Nano suspensions than polymer solutions. In fact, Nano suspensions are a suitable option as they can be applied instead of polymeric solutions to EOR. Therefore, nanoparticle has been proposed to enhance the viscosity of the polymers in the injection fluid, since it improves the thermal stability of the polymer solution and prevent the degradation.

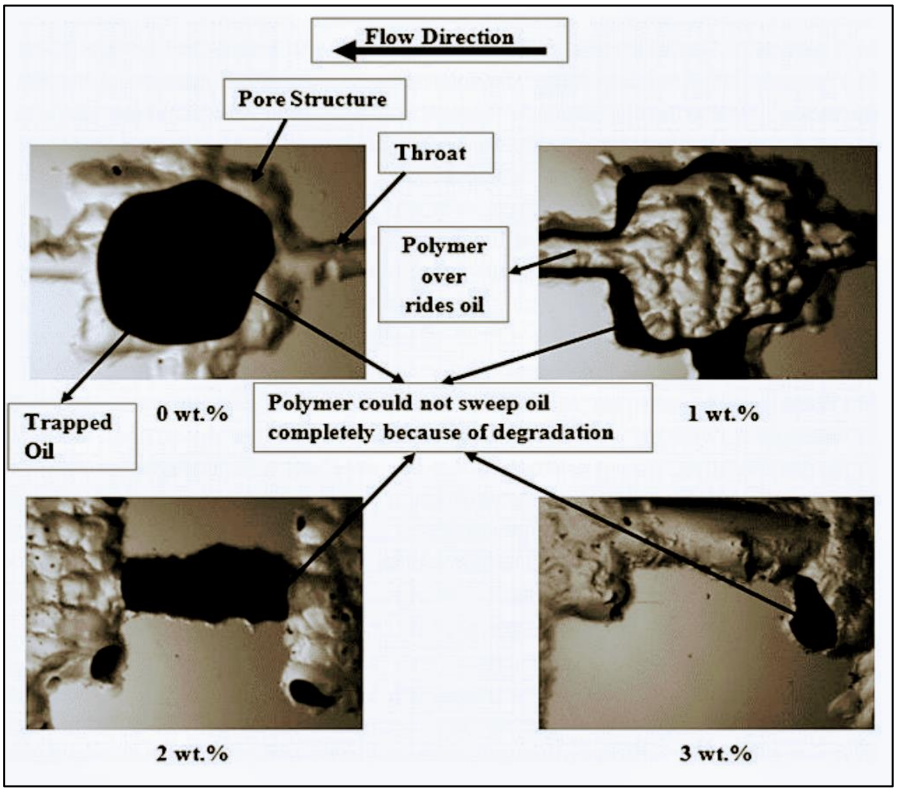

Figure 4.14 Glass micromodel picture of the oil displacement process with nano-polymer solution at different NPs concentrations.

Thickening of the solution occurs due to the ability of NP to form a network structure via hydrogen bonding, which will directly affect the fluid shear stress. Zeyghami et al. showed that viscosity enhancement by silica NPs in water solution is relatively low due to the high polarity of water. However, in the polymer solution, NPs seem to be able to enhance pseudoplasticity behavior considerably even in low shear rate.

Increase in concentration of the nanoparticles improves the displacement efficiency due to the enhanced viscosity of the nanofluid and the spreading of the nanoparticles on the rock surface where the TiO2 nanofluid increases the water viscosity so, providing favorable mobility ratios, which in turn improve macroscopic displacement proficiency , and revealed that combining 1% CuO nanoparticles with CO2 increased the viscosity of the resulting nanofluid 140 times of the normal CO2. Yousefv and Jafari also investigated the effect of combining silica nanoparticles with polymer on oil recovery in comparison with conventional water and polymer flooding's and the highest recovery was observed with the combined process, and necessary to control the mobility of the injected fluid to achieve better sweep efficiency for higher oil recovery. The mobility ratio of the displacing fluid and reservoir fluid is the function of permeability and viscosity, and can be expressed as:

$$\boldsymbol{M} = \{\boldsymbol{Krinj}/\boldsymbol{\mu o}/\ \boldsymbol{Kro}/\boldsymbol{\mu inj}\} \qquad (\mathbf{4.4})$$

Which M is the mobility ratio; $krinj$ and kro are relative permeability of injection fluid and oil; μinj and μo are the viscosities of both injected fluid and oil. Polymer flooding has been successfully used as a viscosity control agent for increasing sweep efficiency.

4.4 THE EFFECT OF NANOPARTICLE PARAMETERS

4.4.1 Nanoparticle Size

The size of nanoparticles has a direct effect on wettability alteration and is considered one of the several essential factors in the application of nanoparticles in EOR. This importance stems from the adoption of a wettability alteration mechanism such as disjoining pressure or log-jamming as a function of the application of various sized nanoparticles in the nanofluids.

In very small throats of rock pores, nanoparticles are stacked at the entrance of those throats owing to their large particle size compared with a pore channel entrance, leading to channel plugging. This process is defined as mechanical trapping (Fig. 4.15a). The log-jamming mechanism illustrated in Fig. 4.15b has been interpreted as a result of the differences between particle and solvent densities. Due to the smaller size of pore throats and the continuous differential pressure, the flow velocity increases in pore throats compared to that in pore bodies.

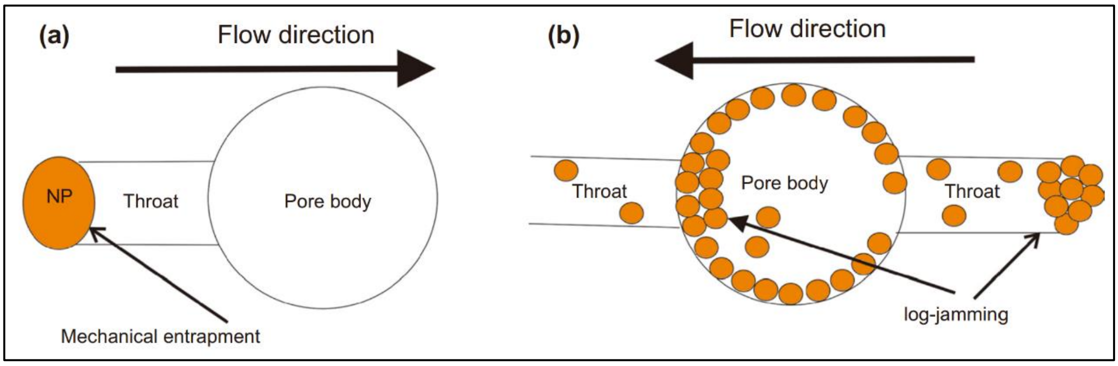

Figure 4.15 The mechanisms causing pore channel plugging: a mechanical trapping and b log-jamming mechanism.

The size of NPs and its associated charge density have a significant effect the disjoining pressure strength. McElfresh et al. concluded that smaller particles would result in higher charge density and the stronger electrostatic repulsion, assuming the particle is in stable condition. According to Hendraningrat et al. smaller particles are proven to increase the recovery considerably as can be seen in Figure 4.16. The result shows that not only oil recovery but also displacement efficiency is increasing due to the smaller size of NPs. Similarly, several other experiments concluded that smaller particles would lead to the higher ultimate oil recovery. Another study proved that by decreased NPs' diameter from 30 nm to 18.5 nm, the structural disjoining pressure would increase for about 4.3 times.

For a similar mass, smaller NPs will give higher particle density and lower contact angle between fluid and rock surface. Higher particle density improves the structural disjoining pressure significantly. For less hydrophilic surface, smaller NPs will spread more readily than a bigger particle. The size of the particle should be small enough not to be mechanically trapped, but big enough to avoid extra log-jamming . Therefore, smaller particles are favorable for the higher oil recovery.

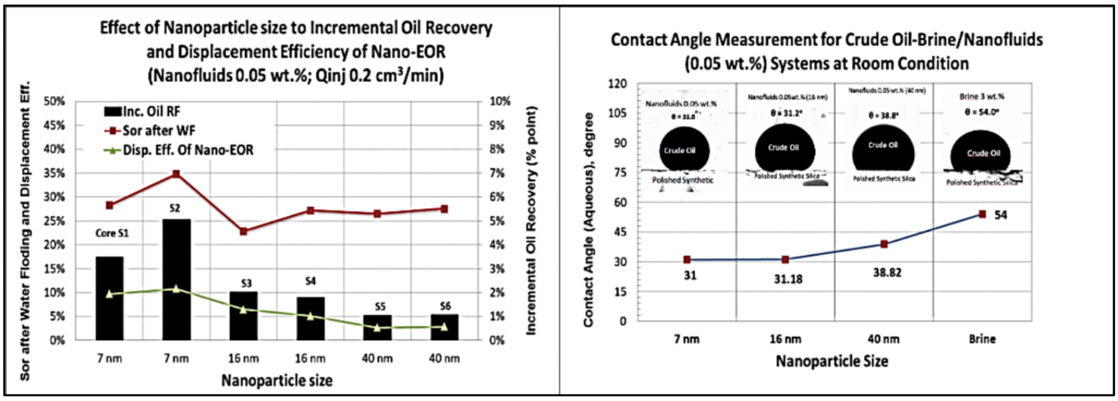

Figure 4.16 The effect of nanoparticle size.

4.4.2 Nanoparticle Concentration

Nanofluid concentration is one of the crucial factors in applications of nanofluid flooding, where nanoparticles become more efficient with increased concentration. In some investigations, the researchers focused on determining the nanoparticle concentration ranges in addition to their effect on wettability alteration. The impact of nanoparticles on wettability alteration has been studied in a wide range of concentrations; the outcome of the most studies was that the rock wettability enhancement increases with an increase in nanoparticle concentration due to the impact of repulsion forces (Bhuiyan et al. 2015).

Also, the concentration of injected NPs is one of the key parameters that determine EOR process. According to Chengara, disjoining pressure and Brownian motion will increase with increasing concentration which also increases the repulsion forces. Increasing concentration will also improve the displacement efficiency due to the viscosity enhancement of the nanofluid and the spreading of NPs on the grain surface. The effect of concentration on the displacement efficiency and IFT can be seen in Figure 4.17. The interfacial tension between reservoir fluids was reported to significantly decrease by increasing concentration of injected NPs. High concentration also leads to the higher wettability alteration effect. Based on the facts above, a higher concentration is favorable for higher oil recovery.

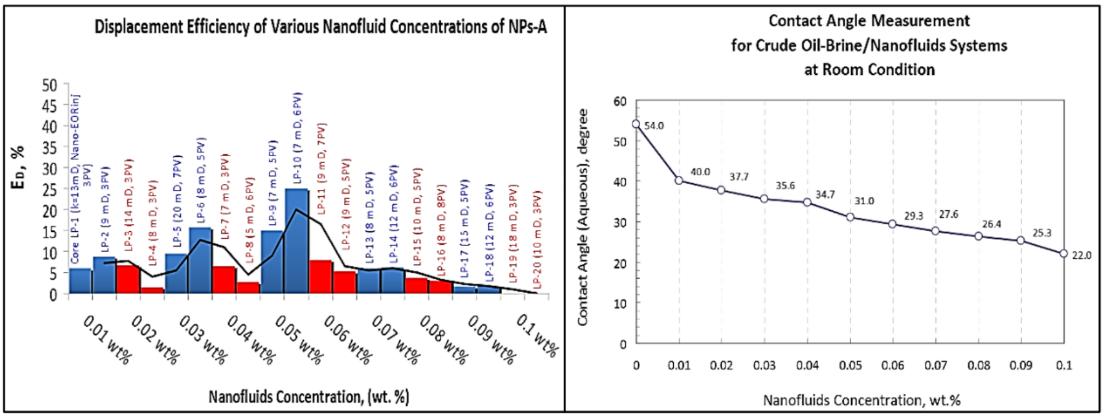

Figure 4.17 Concentration Effect on nano-EOR.

However, there is a certain limit on the concentration of injected NPs, since above that limit NPs will tend to block the pore throat and reduce the ultimate oil recovery. Hendraningrat et al. reported the permeability and porosity impairment of Berea core for about 2% after injecting 0.5 wt.% of silica NPs. A higher concentration will improve the displacement efficiency, the wettability alteration and the IFT reduction. However, when the concentration is too high, the aggregated NPs were found to accumulate around the inlet and reduce the displacement efficiency.

Therefore, an optimum injected concentration is necessary to get maximum oil recovery. It is varied based on the type of nanoparticle, porous medium and the environmental condition.

4.4.3 Temperature

Working at high temperatures is considered a challenge in most chemical methods, including nanofluids. This cross-study review found that all nanofluid researchers recognize temperature as the most significant and substantial parameter and have found a consistent, prevalent downward trend in the viscosity of nanofluids as a function of an increase in temperature (Belhaj et al. 2019). In other words, the stability of nanoparticles decreases with an increase in temperature; therefore, the performance of nanofluids in high temperature reservoirs needs to be improved, especially on wettability alteration.

Since the temperature of the reservoir is always higher than the temperature at the surface, nanofluid should be able to operate at relatively high temperature for effective nano-EOR application. According to Caldelas, the temperature has an insignificant effect on the nanoparticle retention due to the weak temperature dependence for adsorption and desorption of nanoparticle. Differently, a set of experiments by Hendraningrat et al. showed that temperature significantly influences the oil recovery as can be seen in Figure 4.18. The higher temperature is favored for higher oil recovery than lower temperature. The higher temperature condition could possibly alter the reservoir fluids at the molecular level, which reduces the contact angle between the fluids.

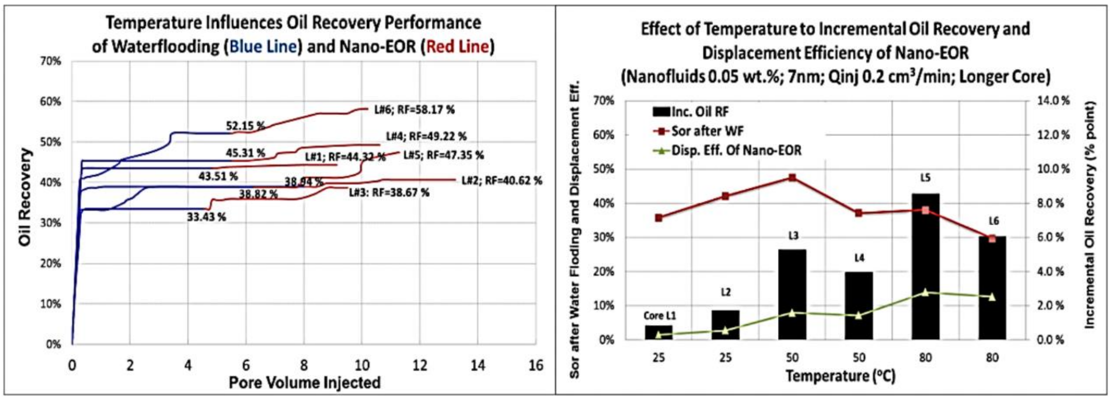

Figure 4.18 Temperature effect.

However, the mechanism of the temperature effect is complex and difficult to explain since it involves several variables. One of the reasons is increasing the temperature tends to decrease the zeta potential of the particles. This means decreasing the stability of the nanofluid and will likely reduce the oil recovery. The increment on recovery could probably be ascribed to decreasing IFT at high temperature since it weakens molecular interaction or to the increasing Brownian motion and a reduction in viscosity. Since changing temperature will affect both nanofluids and the reservoir system, the effect of temperature on the recovery cannot be generalized. Therefore, further study on the temperature effect should be done to get a better understanding of the nano-EOR mechanism.

4.4.4 Wettability

Wettability alteration and its applications are known as the main and most challenging subjects in subsurface engineering. It has been reported that increasing water wetness of the rock will increase oil recovery and vice versa. According to Morrow, strong water wetness and associated high capillary imbibition are favorable for more efficient oil displacement. However, at special cases, it had been reported that oil-wet reservoir and neutral wettability were proven to give higher oil recovery. Thus, wettability is playing an important role in the hydrocarbon mobility. It affects distribution and displacement process of hydrocarbon and other reservoir fluids within the matrix.

During nano-EOR, initial wettability will determine the magnitude of the wettability alteration. An experimental study using silica NPs showed that the highest incremental oil recovery was yielded from intermediate-wet core. In intermediate-wet, oil and brine are in the equal state which reduce the possibility of the disconnected and trapped oil phase in the matrix. Li added that wettability affects the adsorption quantity of NPs. Water-wet and neutral-wet have higher adsorption than oil-wet media. In an oil-wet medium, the adsorption area is very close to the desorption area, which means that desorption will likely to happen.

The wettability of reservoir rocks has a considerable effect on the fluid distribution in oil reservoirs and impacts oil recovery during EOR process. Figure 4.19 is an appropriate description of the effect of wettability on EOR in a micromodel system. The effect of silica NPs on wettability alteration is that this phenomenon causes increased oil recovery. Kuang et al. indicated that a water-wet surface increases the imbibition process into medium and small-sized pores, and lower IFT increases the drainage process and reduces entry pressures (see Figure 4.19e). Figure 4.19f–h show brine, simple SiOx nanofluid and complex SiOx nanofluid injection in medium and small-sized pores. The brine has weak performance in displacing oil; however, SiOx nanofluid due to lower IFT produces more oil from medium and small-sized pores.

There are several experimental works in the oil recovery field with hydrophilic silica NPs, most of use silica NPs to achieve wettability alteration. Silica NPs are one of the most used materials for changing wettability. Skauge et al. investigated the oil mobilization properties of nanosized silica particles. They also studied the flow diversion microscopic mechanism by colloidal gel dispersion. In a serial experimental investigation, Hendraningrat used NPs for wettability alteration for use in EOR in reservoirs with different degrees of permeability. In another work, Onyekonwu and Ogolo found that polysilicon NPs (PSNP) have the suitable ability to change rocks’ wettability. Their results showed that organically treated hydrophobic and lipophilic PSNP (HLPN) compounds improve oil recovery by more than 50% in water-wet rocks. In similar research, Ju and Fan studied the ability of nano powders to change wettability for EOR. The results showed that the wettability of reservoir rocks can change from oil-wet to water-wet by the use of lipophobic and hydrophilic polysilicon NPs. In addition, absolute permeability decreases while an improvement in effective permeability occurs. In another study by Hendraningrat , IFT and contact angle were analyzed to investigate displacement mechanisms in a chemical EOR process. The results showed that nanofluid with 0.05 wt.% of hydrophilic NPs changes wettability by between 15% and 33%, while NPs had no considerable effect on IFT reduction. Moreover, it was observed that hydrophilic NPs (in an optimized range) with wettability alteration have an effective role in oil displacement in porous media.

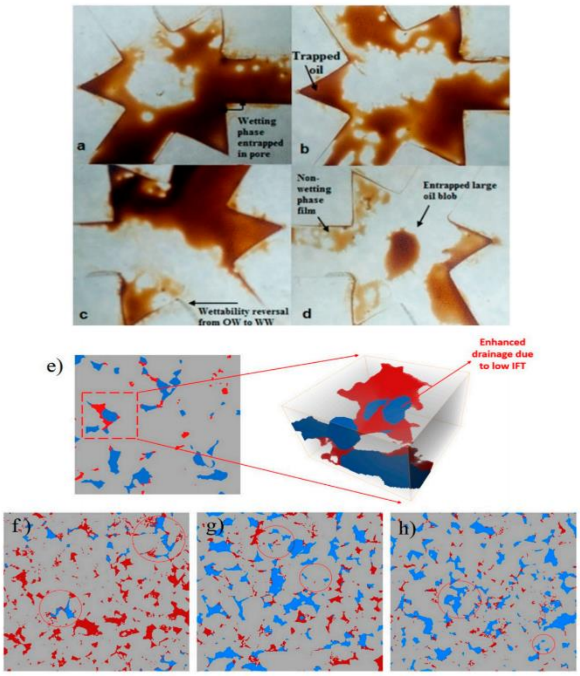

Figure 4.19 Digital microscope images of solution injection in the micromodel showing the pore-scale configuration and distribution of wetting and non-wetting phases within an initially preferential oil-wet medium for (a, b) surfactant solution and (c, d) surfactant and NP solution; (e) 3D illustration of enhancement of the drainage process after a complex nanofluid injection and (f–h) 2D cross-sectional fluid occupancies for nanofluids in oil-wet systems.

4.4.5 Salinity

Among different EOR methods, low-salinity water (LSW) flooding has attracted considerable attention due to the availability of natural water resources and also being environmentally friendly (Sheng 2014). Currently, researchers have observed that injecting low-salinity water (LSW) produced a persistent wettability alteration of the rock (towards water wet), facilitating additional oil recovery (Rivet et al. 2010). Nanofluids have an inverse relationship with salinity, where the nanofluids become less stable when salinity increases accordingly, which in turn is an indicator of the occurrence of the agglomeration of particles in the fluid.

Mansouri et al. (2019), reported the effect of nanofluid on fines migration in low-salinity water. The results showed that the SiO2 nanofluid could reduce the production of fines when mixed with low-salinity water. In other literature, experiments on wettability alteration and incremental oil recovery were conducted to understand the performance of nanoparticles mixed with low-salinity water.

The salinity of the reservoir fluid and the nanofluids have a significant effect on the stability of the dispersion. Increasing salinity is proven to reduce the zeta potential of each particle which leads to easy agglomeration. High ionic strength in the fluid due to the presence of salt will lead to the lower electrical repulsion between particles and allows the vdW attraction forces to dominate. As most of the rock surface are charged, it is expected that the attraction and collision will happen for particle-particle but not particle-surface. Thus, in high salinity environment modification on nanoparticle is necessary to maintain the stability which can be achieved by surface modification, ionic control via surfactant, or the combination of both.

However, the result of a laboratory study had shown that the oil recovery increases at high salinity environment. By using high stability silica NPs, Hendraningrat et al. proved that high salinity nanofluid injection could improve the wettability alteration to be more water-wet. At high salinity, the adsorption of NPs is improved due to the increasing physicochemical interaction. Similarly, Kanj et al. concluded from their research that increasing salinity on the dispersion did not hinder the NPs transport, but increased the adsorption on the grain surface. Increasing salinity seems to increase the adsorption of NPs and improve the recovery of the oil. However, at the same time, the stability of NPs will reduce in the high salinity environment. Therefore, the correct salinity level and surface coating are important aspects to be considered to prevent agglomeration of NPs.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION REMARKS

Massive studies on the application of nanotechnology in petroleum industry especially for EOR have been done and shown promising results. Nano-EOR is proposed to substitute the existing chemical EOR for improving the oil recovery efficiency with several advantages:

(1) NPs can improve the fluid performance by only using small amount of materials.

(2) improvement in heat and mass transfer lead to the possible application in high-temperature condition.

(3) high flexibility for combining with other materials such as surfactant and polymer.

Various types of NPs (organic and inorganic) are confirmed to be able to increase the oil recovery up to 20% additional in oil recovery. They can improve the oil recovery through several mechanisms such as IFT reduction, wettability alteration, disjoining pressure, and viscosity control. Some parameters, like NPs' concentration, size, temperature, wettability, and salinity, are proven to affect the performance of nano-EOR.

5.2 RECOMMENDATIONS

1. The retention can be improved by controlling nanoparticle surface properties by using different coatings, where the retention was higher for dolomite cores because of the attraction between the negatively charged nanoparticles and the positively charged surface of the dolomite core. Therefore, in positively charged formation in carbonate reservoir using surface modifications is highly recommended. For the purpose of determining the suitability of carbon nanoparticles for harsh reservoir conditions.

2. To enhance the stability of the nanofluids, the following steps are recommended;

   a. Changing the pH value: Isoelectric point (IEP) is the value of pH at which a particular molecule carries no net electric charge, or hydration forces are negligible. When the pH of nanofluids is equal or close to the IEP, nanofluids become unstable. Zeta potential is zero at the isoelectric point, repulsive forces between NPs suspended in base fluid are zero and there is a tendency of coagulation Hydration forces between NPs must be high in order to enhance the stability of nanofluids .A stable nanofluid must have pH around 7 because very high or low pH values may damage the heat transfer surface due to corrosion especially at high temperature.
   b. Using surfactants: Surfactants can act as a bridge between NPs and base fluids which creates continuity between NPs and base fluids Hydrophilic NPs such as oxides NPs will be easily dispersible into the polar base fluids like water. However, when there is a need to disperse hydrophobic NPs into polar base fluids and hydrophilic into non-polar base fluids, then addition of surfactants is required to stabilize the nanofluids. It should be mentioned that the addition of surfactant which affect the thermophysical properties of nanofluids.
   c. Using ultrasonic vibration: Ultrasonication is an accepted physical technique to disperse agglomerated NPs into the base fluid to disperse the aggregates of NPs, ultrasonication bath- or probe-based ultrasonic devices are most commonly used. The probe based ultrasonic devices operates at very high frequency. So, there may be the probability of contamination of nanofluids due to the detachment of very minute metal particles from the surface of metal probe. This may affect the stability of nanofluids adversely. The use of these techniques depends on the required application of the nanofluid. Selection of suitable surfactants depends

mainly upon the properties of the solutions and particles. Stability of NP dispersion in base fluid is indicated by zeta potential value, high zeta potential value indicates good stability.

3. It is recommended that the optimum concentration of the injected nanoparticles is needed to get the maximum oil recovery as the higher concentration is better to improve the displacement efficiency which will change the wettability and reduce the surface tension. But when the concentration of the injected nanoparticles is higher than the finite concentration or when the concentration exceeds the finite concentration, the nanoparticles tend to clump together and accumulate and cause agglomeration around the pore entrance and cause a decrease in the displacement efficiency.

4. In high salinity environment modification on nanoparticle is necessary to maintain the stability which can be achieved by surface modification, ionic control via surfactant, or the combination of both.

5. In Alumina coated SiO2 nanoparticles must the decreasing concentrations phosphate While at higher concentrations phosphate insufficiency could have caused the higher toxicity of those particles at pH 6.0e6.8 compared to higher pH values.

6. Al2O3 nanoparticle in brine was not stable, and it started to precipitate in the first hour. To minimize this problem, must added Polyvinylpyrrolidone (PVP) also known as Povidone with a chemical formula of (C6H9NO) to the solution. Results revealed that the PVP successfully stabilized the emulsions.

REFERENCES

[1] An Overview of Oil Production Stages Enhanced Oil.

[2] A Literature Review and Transport Modelling of Nanoparticles for Enhanced Oil RecoveryCredits (ECO)

[**3**] History of nanotechnology – Wikipedia.

[**4**] History and development of nanoparticles and nanostructured materials.

[**5**] Nanoparticle – ScienceDaily.

[**6**]. Summarized in The History of Nanoscience and Nanotechnology: From Chemical–Physical Applications to Nanomedicine.

[**7**]. Bawarski, W.E., et al., Emerging nanopharmaceuticals. Nanomedicine: Nanotechnology, Biology and Medicine, 2008. 4(4): p. 273-282.

[**8**].. Marcato, P.D. and N. Durán, New aspects of nanopharmaceutical delivery systems. Journal of nanoscience and nanotechnology, 2008. 8(5): p. 22162216-2

[**9**] Application of Nanotechnology in Enhanced Recovery Oil and Gas.

[1**0**]. Best EOR Methods Best Method for Enhanced Oil Recovery from Sarvak Reservoir and Analyse Sensitive Parameters.

[1**1**]. Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress.

[1**2**] Methods for Enhancing Recovery.of Heavy Crude Oil.

[1**3**] Application of Nanoparticles for Oil Recovery.

[1**4**] Materials for buried plastic tension to improve oil extraction.

[1**5**] surfactant–Polymer Flooding: Influence of the Injection Scheme.

[16] Low Salinity Water Injection for EOR.

[17] Mohajeri, A., et al., Hydrodesulphurization Nanocatalyst, Its Use and a Process for Its Production. 2009, Google Patents.

[18] Gavrielatos, E., R. Mohan, and O. Shoham, EFFECT OF INTERMEDIATE WETTABILITY NANOPARTICLES ON OIL-WATER EMULSION STABILITY. Journal of Petroleum Science and Engineering, 2017.

[19] Microbial Enhanced Oil Recovery | IntechOpen.

[20] Microbial Enhanced Heavy Oil Recovery by the Aid of Inhabitant Spore-Forming Bacteria: An Insight Review.

[21] Md. Amanullah, Mohammad K Al-Arfaj and Ziad Al-Abdullatif; Preliminary Test Results of Nano-based Drilling Fluids for Oil and Gas, the SPE/IADC Drilling Conference and Exhibition held in Amsterdam, The Netherlands, 1–3 March 2011, SPE/IADC 139534.

[22] Soma Chakraborty, Gaurav Agrawal, Anthony DiGiovanni and Dan Scott; The Trick Is the Surface – Functionalized Nanodiamond PDC Technology, SPE International Oilfield Nanotechnology Conference held in Noordwijk, The Netherlands, 12–14 June 2012, SPE 157039.

[23] Zhihui Zhang Zhiyue Xu and Bobby Salinas; High Strength Nanostructured Materials and Their Oil Field Applications, SPE International Oilfield Nanotechnology Conference held in Noordwijk, The Netherlands, 12–14 June 2012, SPE 157092.

[24] Bobby J. Salinas, Zhiyue Xu, Gaurav Agrawal, and Bennett Richard; Controlled Electrolytic Metallics - An Interventionless Nanostructured Platform, SPE International Oilfield Nanotechnology Conference held in Noordwijk, The Netherlands, 12–14 June 2012, SPE 153428.

[25] Al-Anssari, S., et al., Wettability alteration of oil-wet carbonate by silica nanofluid. Journal of colloid and interface science, 2016. 461: p. 435-442.

[**26**]. Al-Anssari, S.; Barifcani, A.; Wang, S.; Maxim, L.; Iglauer, S. Wettability alteration of oil-wet carbonate by silica nanofluid. J. Colloid Interface Sci. 2016, 461, 435–442. [CrossRef] [PubMed].

[**27**]. Nikolov, A.; Kondiparty, K.; Wasan, D. Nanoparticle self-structuring in a nanofluid film spreading on a solid surface. Langmuir 2010, 26, 7665–7670. [CrossRef] [PubMed]

[**28**]. Winkler, K.; Paszewski, M.; Kalwarczyk, T.; Kalwarczyk, E.; Wojciechowski, T.; Gorecka, E.; Pociecha, D.; Holyst, R.; Fialkowski, M. Ionic strength controlled deposition of charged nanoparticles on a solid substrate. J. Phys. Chem. C 2011, 115, 19096–19103. [CrossRef].

[**29**] Karimi, A.; Fakhroueian, Z.; Bahramian, A.; Khiabani, N.P.; Darabad, J.B.; Aniz, R.; Arya, S. Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. Energy Fuels 2012, 26, 1028–1036. [CrossRef]