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Department of Petroleum Engineering**

**Influence of silica nanoparticles on the surface properties of
carbonate reservoirs**

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**This thesis is presented for the Degree of
Master of Philosophy (Petroleum Engineering)
of
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DEDICATION

To those who suffer in life, but every time they stood stronger and turn every challenge into a strength.

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In the Name of Allah, The Most Gracious, The Most Merciful

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ABSTRACT

In the last decade, nanofluids-based techniques have shown tremendous promise in oil and gas industry. Nanofluids, dispersions of nanoparticles (NPs) in a base-fluid, have shown promises potentials in enhanced oil recovery (EOR), and carbon geosequestration projects. Silica NPs can efficiently decrease the interfacial tension of the oil/water system. Also, NPs can stabilize the oil/water and water/oil emulsions solely or synergistically with other surface-active materials including surfactant. Furthermore, NPs have drastic ability to render the wettability of oil-wet carbonate surface water-wet which is crucial for efficient oil displacement from naturally fractured carbonate reservoirs. From this perspective, one key parameter is the adsorption of NPs on the solid-liquid and liquid-liquid interfaces, which explains the interfacial interaction and the role of NPs in subsurface formations. There have been many studies that investigated the effect on NPs on interfacial tension reduction, wettability alteration, stability of oil/water emulsions, and enhancement of surfactant performance in hydrocarbon recovery applications. However, one crucial aspect which has not been considered in available NPs for EOR studies is the adsorption of such NPs on carbonate surfaces at reservoirs conditions.

This study thus focuses on the adsorption of silica NPs at different initial hydrophilicity onto water-wet and oil-wet carbonate surface. Calcite substrates were used as representative for water-wet carbonate reservoirs while calcite aged with stearic acid were the representatives of oil-wet carbonate reservoirs. Further, the initial hydrophilicity of silica NPs was controlled by treating with 3-aminopropyl triethoxysilane. Treatment of different calcite samples with different silica nanofluids were conducted at typical reservoirs conditions (15 MPa, 323 °K, and 343 °K) to mimic the subsurface behaviour. Initially, the adsorption behaviour of silica NPs at solid-liquid interface was probed via quantification of NPs influence on the structure, composition, and surface morphology of the nano-treated calcite at different treatment conditions. The nano-treated surfaces were analysed by scanning using the electron microscope (SEM), energy dispersive X-ray spectroscopy, and atomic force microscope (AFM). Further, the stability and aggregation behavior of nanofluids was investigated via zeta potential and particle size distribution using the zeta sizer and the dynamic light scattering respectively.

Based on the qualitative analysis, the study reveals that NPs, as a new EOR approach, offer applicable potentials and opportunities that can be implemented successfully at reservoir conditions and show better profits over conventional EOR techniques. By investigating the hydrophilic and hydrophobic NPs adsorption behaviour on water-wet and oil-wet calcite surfaces, the study revealed a key characteristic of NPs in EOR, which is its ability to adsorb into different surfaces at different harsh conditions even at very low NPs load in the liquid phase. Additionally, its capacity to significantly change the morphological properties of the solid surfaces leading to significant change of surface properties into favourable surface conditions that is useful for efficient EOR applications.

PUBLICATIONS BY THE AUTHOR

Published Papers:

1. **Zain-UL-Abedin Arain**, Sarmad Al-Anssari, Muhammad Ali, Shoaib Memon, Masood Ahmed Bhatti, Christopher Lagat, Mohammad Sarmadivaleh. 2019. " Reversible and irreversible adsorption of bare and hybrid silica nanoparticles onto carbonate surface at reservoir condition." *Petroleum*. <https://doi.org/10.1016/j.petlm.2019.09.001>

Conference papers:

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2. Sarmad Al-Anssari, **Zain- UL. Abedin Arain**, Haider Abbas Shanshool, Alireza Keshavarz, and Mohammad Sarmadivaleh. "Synergistic effect of hydrophilic nanoparticles and anionic surfactant on the stability and viscoelastic properties of oil in water (o/w) emulsions; application for enhanced oil recovery (EOR)" *5th Iraq oil & gas conference*, Baghdad, Iraq: Ministry of Oil 27-28 November 2019

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Chapter 1 **INTRODUCTION AND OVERVIEW OF THESIS OBJECTIVES**

1.1 Background

In the past five decades, innovative approach in the technical operations has generally seen the shifting of materials size from regular bulk to smaller materials at the nanometre scale. The possibility to manipulate the surface properties of matter at nano-size supports the rapid development of nanoscience or what is commonly known as nanotechnology. In the last 20 years, nanotechnology researches and applications have experienced a higher trend of growing and the funding of nanotechnology projects increased rapidly from \$22.9 billion in 2013 to \$26 billion in 2014 reaching \$64 billion in 2019 (Nwidae et al. 2018). Nanosized materials cut across different applications to be an elegant solution for many science and engineering issues. Typically, nanotechnology comprises the design, synthesis, modification, and use of nanosized materials. The matter is considered as a nanomaterial when one or more of its dimensions in the order of nanometer (≤ 100 nm) knowing that each nanometer is 10^{-9} meters (Guz et al. 2007). Recently, nanotechnology has motivated advanced applications in all science and industrial fields that spanning from medicine and drug delivery, coating and lubrication, pollution and wastewater treatment, to underground projects such as soil decontaminations, geo-thermal extraction, improving of aquifer quality, and oil industries including drilling, carbon geosequestration, and enhanced oil recovery (EOR).

Energy demand has rapidly increased over the years due to global industrialization and population fast growth (Vatanparast et al. 2011). The deteriorating issue of energy resources has triggered worldwide concerns. Despite the emergence of renewable energy projects, hydrocarbon resources still the main global energy sources. The potentials of different kinds of hydrocarbon including natural and associated gas, and crude oil to meet the global energy needs are subject to new hydrocarbon field discoveries and enhancing the recovery of existing hydrocarbon fields. Most of the current producing hydrocarbon fields in the declining phase (Afolabi and Yusuf 2019). Discoveries of new oil fields, on the other hand, are limited and mostly in reservoirs that are difficult to produce, including high pressure and temperature reservoirs, low permeability reservoirs, naturally fractured oil-wet reservoirs, and viscous oil

reservoirs. Thus, the key to ensure continued production of enough hydrocarbon resources, would mainly be the application of innovative technologies as novel solutions for old issues. These new technologies are necessary for the exploitation of new oil and gas fields and enhancing the recovery from existing hydrocarbon fields. In the last ten years, oil companies, institutions, and universities have been in a competition to implement novel technologies to supply cheap energy. In EOR projects, various techniques have been used to increase oil production. For example; surfactant flooding (Bera et al. 2013, Zendehboudi et al. 2013, Bera et al. 2014), polymer flooding (Al-Manasir et al. 2009, Zhong et al. 2018), and surfactant-polymer combination. Further, the applied technologies in EOR have experienced a transition from the bulk-domain to macro-domain to micro-domain reaching the nano-domain. The success of nano-application in the oil industry may probably shift the EOR technology into pico-domain (Afolabi and Yusuf 2019). There are some preliminary discussions about the Picotechnology where the matter size at the atomic scale.

The use of nanotechnology has suggested as a feasible alternative for tertiary oil recovery. The term Nano-EOR is commonly used to describe the use of nanomaterials in enhanced oil recovery (EOR) projects. Nanotechnology in EOR is mainly based on the injection of NPs or nanofluid which is a dispersion of NPs in a base fluid into subsurface formations to manipulate the interfacial properties and the interactions between rocks, oil, and formation brine. In regard to Nano-EOR, several nano-applications have been suggested; nanoparticle stabilized emulsions (Shen and Resasco 2009, Kumar and Mandal 2018, Maurya and Mandal 2018), different NPs-surfactant (Ravera et al. 2008, Worthen et al. 2014, Maurya and Mandal 2018), nanoparticle-polymer (Yousefvand and Jafari 2015, Cheraghian 2016, Giraldo et al. 2017, Rellegadla et al. 2018, Druetta and Picchioni 2019, Bashir Abdullahi et al. 2019), nanoparticle-surfactant-polymer formulations (Kumar and Mandal 2018), and nanofluids (Li et al. 2007, Karimi et al. 2012, Ogolo et al. 2012, Amraei et al. 2013, Bayat, Junin, Samsuri, et al. 2014, Negin et al. 2016, Zhang et al. 2016, Sun et al. 2017, Al-Anssari, Arif, Wang, Barifcani, Lebedev, et al. 2018, Zallaghi et al. 2018, Ebrahim et al. 2019). Comparing the previously mentioned methods, nanofluids are the most feasible technique that can economically improve the production of hydrocarbon (Ko and Huh 2019, Rostami et al. 2019).

In general, NPs in EOR are mainly classified into three groups including metal oxide, organic, and inorganic NPs (Al-Anssari 2018). Silica NPs, as an example of inorganic, are the most commonly used NPs in oil industry (Youssif et al. 2018). In this context, silica is typically one of the most abundant components in the Earth crust and the fundamental component of sand and sandstone (Negin et al. 2016). Silica can be found naturally as quartz or can be made-up synthetically (Tabellion et al. 2006). Factors including low cost of fabrication, environmentally friendly (Gao et al. 2013), and possibility to functionalize the surface properties for specific usage made silica NPs are commonly used in all field of science and industry. Subsurface industries and particularly EOR and carbon geosequestration (Al-Anssari, Wang, Barifcani, and Iglauer 2017) are examples of underground industries that utilizing silica NPs.

Previous studies in the field of Nano-EOR categorised the roles of NPs in EOR into four groups of effects. Such effects are including controlling the rheological properties (Bashir Abdullahi et al. 2019), interfacial tension reduction (Al-Anssari, Wang, Barifcani, and Iglauer 2017), wettability alteration (Rostami et al. 2019), and governing the permeability of the porous media (Amedi and Ahmadi 2016). Typically, most of the published data in EOR field is based on the ultimate enhancement in oil recovery. Such recovery rate is measured by core flooding tests or some other measurements such as changes in viscosity, interfacial tension, and water contact angle. Although the effect of NPs in subsurface formations is primarily based on the adsorption of NPs into the solid/liquid or liquid/liquid interfaces (Abhishek et al. 2018), there is no comprehensive study has systematically evaluated the adsorption and desorption behaviour of NPs into subsurface formations particularly at reservoirs conditions. Further, most of research in Nano-EOR topic focused on sandstone systems, while only limited number of studies investigated the Nano-EOR in limestone systems.

In EOR, one of the crucial issues is hydrocarbon production from carbonate reservoirs. It is well agreed that carbonate reservoirs hold more than 60% of the discovered gas and 50% of the discovered oil reserves in the world (Kamaei et al. 2019). These carbonate formations are typically naturally fractured intermediate-wet or oil-wet reservoirs (Ali et al. 2019). Oil from such reservoirs is mainly produced from the fractures because injected water during secondary recovery step (water flooding) does not imbibe into the matrix of the rock due to the capillary forces of the oil-wet and

intermediate-wet porous media (Mason and Morrow 2013). Consequently, no more than 25% of original oil in place (OOIP) can be produced by conventional water flooding techniques (Wu et al. 2008) since most of the crude is tightly held in the matrix and not in the fracture (Gupta and Mohanty 2010). Subsequently, a considerable number of carbonate reservoirs are categorised as depleted reservoirs when they still hold 75% of OOIP. It is, therefore, necessary to alter the oil-wet carbonate reservoirs into water-wet to improve water imbibition into the rock matrix to displace the considerable amount of oil and thus increase the recovery rate of EOR process (Rostami Ravari et al. 2011). One of the mechanisms that can sufficiently alter the wettability of oil-wet porous media into water-wet is aging with nanofluid. Mechanistically, mono or multi-layers of NPs adsorb into the carbonate surface changing the hydrophobic status of the porous media into hydrophilic.

In the interim, the harsh condition of underground formations such as high temperature, and high salt concentrations required an adequate understanding of NPs flow behavior and its effect on the rocks surface properties at such severe conditions. The implementation of silica NPs in the chemical EOR methods may open a bright avenue for investing the depleted carbonate oil reservoirs.

1.2 Motivation of thesis

Previous studies have introduced NPs as promising agents in EOR industry (Rostami et al. 2019). Experimental and numerical studies have proven that injection of nanofluid, which is a dispersion of NPs in base liquid, can significantly enhance hydrocarbon production from hard-to-produce hydrocarbon reservoirs. In this context, NPs can drastically alter the wettability of oil-wet and rocks to water-wet (Rostami et al. 2019, Ebrahim et al. 2019) which is key for higher rate of oil recovery. For example, aging oil-wet calcite samples with nanofluid results in vital reduction in water contact angle from 150° to 20° referring to a significant alteration of surface wettability. Mechanistically, adsorption of mono or multi-layers on NPs onto the solid surfaces is the main reason for such dramatic changes of solid surface properties. Moreover, NPs have considerable effects on the interfacial tension of oil/water system. Several studies revealed that NPs, individually or mixed with different surface-active agents including surfactant, can substantially reduce the oil/water interfacial tension which favourably

facilitating the displacement of oil from the porous media. Typically, adsorption of NPs onto the oil/water interface may significantly influence the interfacial tension (Dugyala et al. 2016). Furthermore, NPs can improve the performance of surfactants in the subsurface formations in two different mechanisms. Primary, adsorption of NPs into rock surfaces reduces the loss of surfactant molecules via adsorption on solid surfaces (Esmailzadeh et al. 2011). Further, NPs via its Brownian motion act as carriers to transport surfactant molecules efficiently towards the oil/water interface (Al-Anssari, Arif, Wang, Barifceni, and Iglauer 2017). In addition, NPs can manipulate the viscosity of injection fluids in EOR processes when combined with polymer solutions (Druetta and Picchioni 2019). Typically, adsorption of NPs into rock surfaces reduces the loss expensive polymer after injection to the subsurface formation. Also, combination of NPs-polymer in single solution can significantly enhance the rheological properties of the new solution. Consequently, NPs have great potentials in all chemical enhanced oil recovery methods and mainly the role of NPs in all such methods is based on the adsorption of NPs into the subsurface interfaces including solid/liquid and liquid/liquid interfaces. It is therefore of vital importance to investigate the adsorption behaviour of NPs in subsurface formations to identify the efficiency of NPs as EOR agent at reservoirs conditions.

1.3 Objective of Thesis

Given the above motivation and background, the following objectives are set for this thesis:

1. To examine the influence of initial hydrophilicity of silica NPs on the adsorption behaviour into carbonate surface in order to understand the potential circumstances when the surface properties of hydrophilic silica NPs switch to hydrophobic due to the complex chemistry of reservoirs fluids.
2. To examine the influence of the wetness state of the porous media (oil-wet, or water-wet carbonate surfaces) on the adsorption behaviour of silica NPs.
3. To examine the influence of reservoirs severe conditions (i.e. Hi pressure, high temperature and salinity) on the adsorption behaviour of silica NPs.
4. Probing the mechanism that demonstrating the fundamental effect of NPs on the morphology of carbonate surface via AFM, SEM and EDS to understand the effect of silica NPs on the rock's chemistry and surface properties.
5. To formulate a stable silica NPs dispersion for subsurface applications.

1.4 Thesis Organization

This thesis has five (4) chapters. Chapter 1 provides an overview of the thesis, including background, motivation, and objectives. A comprehensive literature review is given in Chapter 2. Chapter 3 describes the methodology of the thesis and presents the results with discussion. The methodology predominantly comprises procedures to modify the hydrophilicity of hydrophilic silica NPs and to age the calcite samples in stearic acid to mimic the surface properties of underground formations. Chapter 3 also presents the results and discusses morphology measurements of nano-treated calcite samples as a scale of NPs adsorption on the originally very smooth calcite substrates. This chapter may include repeated materials from other chapters of this thesis since it is complete copy of my published paper” *Reversible and irreversible adsorption of bare and hybrid silica nanoparticles onto carbonate surface at reservoir condition*”. Chapter 4 concludes the thesis with future recommendations. Figure 1-1 establishes a pictographic view of the organisation of the thesis.

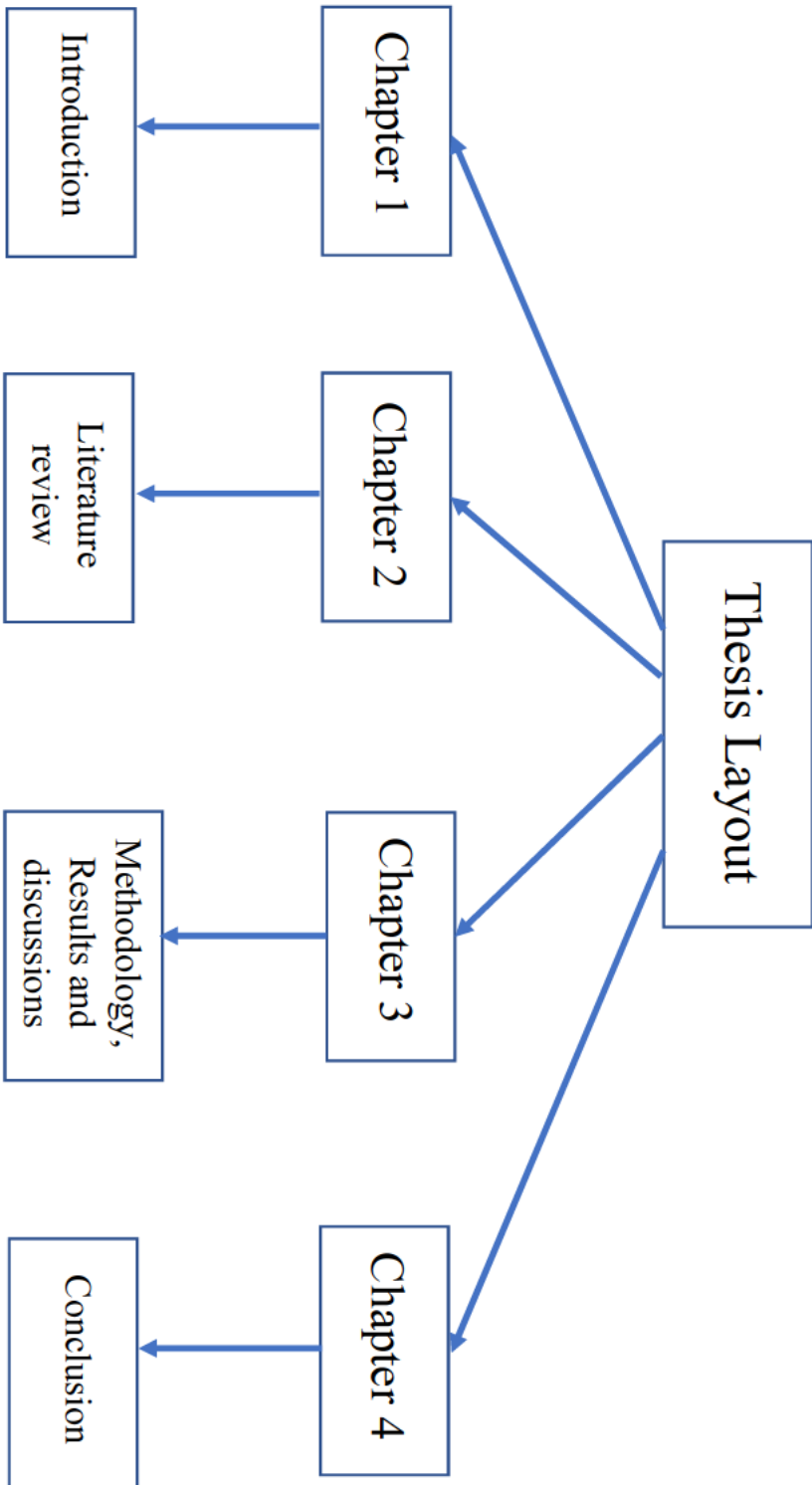


Figure 1-1 Layout of thesis objective and structure

Chapter 2 **LITERATURE REVIEW**

Chemical Enhanced Oil Recovery (CEOR) techniques are being used to increase oil production by modifying some key parameters in porous media such as wettability, interfacial tension, and mobility ratio. Choosing the best applicable CEOR techniques for a particular hydrocarbon field is the most crucial step for a feasible EOR process. In this context, in parallel to conducting experimental studies, it is very important to create a full understanding of the proposed mechanisms that affect hydrocarbon production capacities. CEOR process optimization requires full understanding of the relationship between the increase in oil recovery rate and the behaviour of the used chemicals at reservoirs conditions. Recently, nanoparticles (NPs) with its unique surface properties have shown very promising potentials in EOR projects. This chapter thus provides an insightful analysis of currently applied CEOR techniques in oil reservoirs and how NPs can improve the efficiency of such processes via enhancing the performance of the used chemical agents at reservoirs conditions.

2.1 Introduction

Most of the hydrocarbon fields around the world have entered the mature period of development, while, according to OPEC World Oil Outlook 2014, global energy demand is expected to increase by 60 % of 2010 levels by 2040. To cover this demand, a rise in supply in all forms of energy is expected. Despite several alternative energy sources including renewables, nuclear, biogas, and hydro power, there are yet to be enough energy supplies. The major energy supply is still predominantly from hydrocarbon sources including crude oil, unconventional oil, associate and natural gas (Nwidae 2017). Although the economic impact of oil as the main energy source worldwide is significant, crude oil production from existing fields is expected to decline by about 75% to reach only 16 million barrels per day at 2035. North America, Europe and Eurasia, and Middle East are the main sources for crude oil in the world (Figure 2-1). Consequently, discovery and production of new oil fields are essential to cover the demand growth for energy and possible drop in oil production from existing fields (Sheng 2013). According to the data predictions (OPEC World Oil Outlook 2014), more than half of crude oil production within the next 20 years will be from

new fields that already been discovered now, and the rest will be from fields yet to be discovered. However, most of the newly discovered fields are in challenging and hard-to-produce conditions. For instance, since 2000, most of the newly discovered fields have been in deep water. Enhanced oil recovery (EOR) can considerably reduce the demand for production from unconventional oil fields via increasing the recovery factor from current fields.

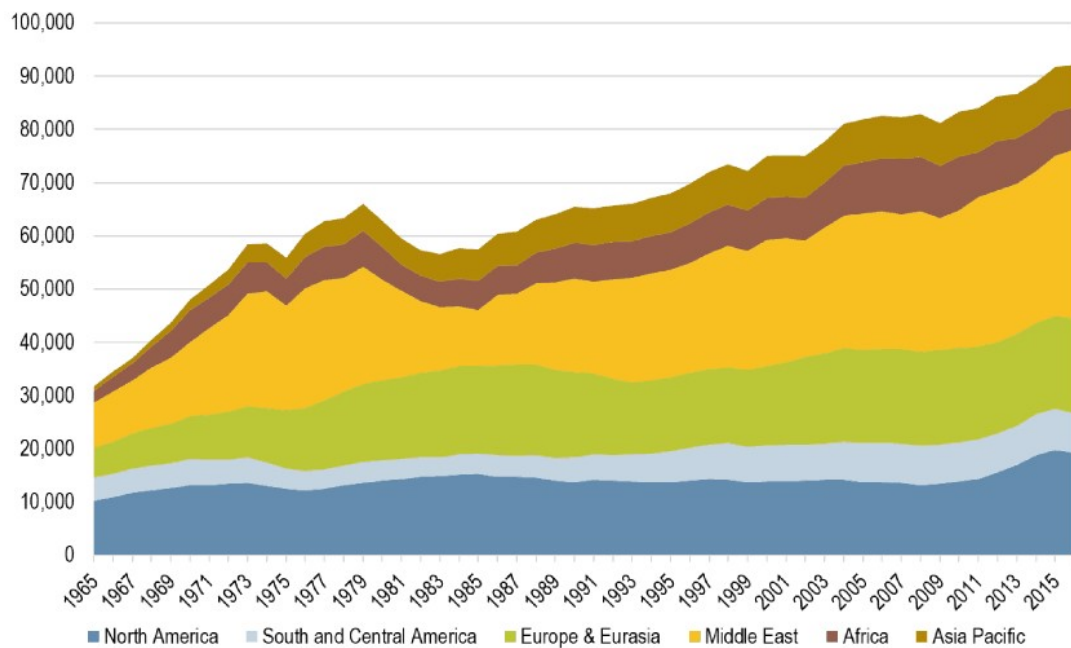


Figure 2-1 World Crude Oil Production and Consumption, 1965-2016 (Rodrigue 2020)

2.2 Characterization of Oil Reservoirs

A common misconception is that hydrocarbons including oil and natural gas are found in underground caverns. Typically, hydrocarbons are found within the microscopic pore of rocks. The underground formations that contains hydrocarbon may be called hydrocarbon-bearing reservoirs. However, oil production from such reservoirs is not always feasible. Characteristically, oil must be able to flow through the pore space of reservoirs rocks via a connected pore network. In this context, the displacement of residual oil is dominated by two important factors at the pore scale including capillary number (N_c) and mobility ratio (M).

2.2.1 Capillary Number (N_c)

Typically, a higher capillary number refers to high oil recovery rate due to the decreasing of residual oil saturation. The capillary number ($N_c = v\mu/\sigma$) is the product of Darcy velocity (v (m/s)) and the viscosity of the displacing fluid (μ (Pa.s)) divided by the interfacial tension (σ (N/m)). The capillary number can be increased by decreasing the interfacial tension of the oil/water system at reservoirs conditions. Such reduction in the interfacial tension is the main target of some thermal or chemical EOR methods. In this context, at the end of secondary oil recovery process (water flooding), the capillary number in the porous media will be very low (i.e. as low as $N_c \approx 10^{-7}$). At such circumstances, no more oil can be produced by pumping more water and oil reservoir is considered depleted (Yarranton et al. 2015). Increasing the capillary number, by one of EOR techniques, by for example three orders of magnitude (i.e. $N_c \approx 10^{-4}$) will reduce the residual oil saturation to the half (Figure 2-2) which typically facilitates the displacement of oil (Keshavarz et al. 2012).

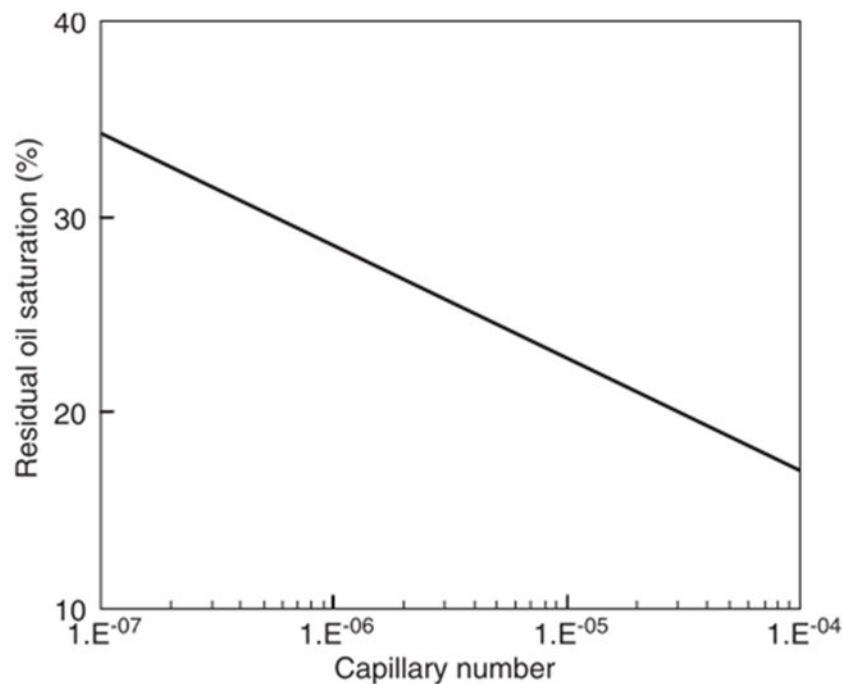


Figure 2-2 The impact of Capillary Number (N_c) on the residual oil saturation (Thomas 2008b).

2.2.2 Mobility Ratio (M)

Mobility ratio is a key parameter in EOR processes, particularly in heavy oil reservoirs (Johannesen and Graue 2007). The ratio of mobility of the displacing fluid such as water (λ_{water}) to the mobility of the hydrocarbon such as oil (λ_{oil}) is called the mobility ratio ($M = \frac{\lambda_{\text{water}}}{\lambda_{\text{oil}}}$). Here, the mobility of each phase is the effective permeability (k) divided by the viscosity of the phase (μ) [$\lambda = \frac{k (m^2)}{\mu (Pa.s)}$]. Thus, the unit of phase mobility is $\frac{m^2}{Pa.s}$. The mobility ratio impacts oil displacement at both macro and micro scale. Characteristically, the best sweeping efficiency is obtained when the mobility ratio is unity ($M = 1$). While, relatively high mobility ratio ($M > 1$; i.e. 10, 100, or 1000) refers to lower sweeping efficiency due to the channelling (fingering) effect of the displacing fluid (Figure 2-3).

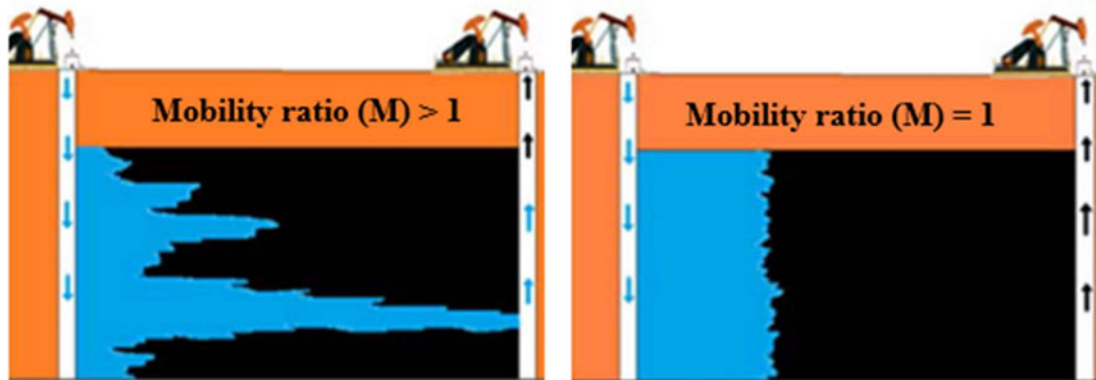


Figure 2-3 Effect of mobility ratio on sweeping efficiency and channelling phenomenon of the displacing liquid. Reproduced after (ShamsiJazeyi et al. 2014).

Such a channelling effect which unfavourably bypass a substantial amount of oil results from the higher readily flow of displacing fluid compared to that of oil (Thomas 2008a, ShamsiJazeyi et al. 2014). In such cases, it is essential to increase the viscosity of the displacing fluid ($Pa.s$) which in turn reduces the mobility of the displacing fluid (λ_{water}) and consequently the mobility ratio (M). Otherwise, a large amount of the displacing fluid will need to be injected to achieve a specific residual oil saturation (Figure 2-4).

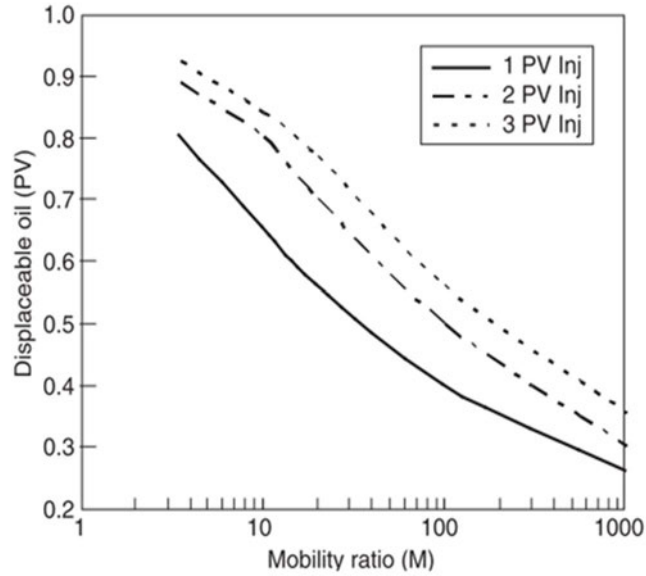


Figure 2-4 Influences of the mobility ratio (M) on oil displacement (Thomas 2008a).

2.2.3 Permeability and Relative Permeability

Permeability is a key property of pore space in subsurface formations which has been widely investigated by engineers and geologists and has a vital role in the oil recovery process. Permeability is basically the ability of fluid to flow within the pore space. Reduction of permeability which is known as formation damage is one of the main challenges in oil industry. In this context, injection of large amounts of fresh or low salinity water during the secondary oil recovery (water flooding) processes can dramatically reduce the permeability of the subsurface formations (White et al. 1964). The formation damage can also be caused by changes in pH (Mohan and Fogler 1997). Mechanistically, expansion and dispersion of subsurface minerals when coming into contact with relatively freshwater (i.e. substantially less saline than the connate water) is the main reason for such formation damages. In addition, to change in pH and salinity, Mungan (1965) showed that the change in temperature is another reason for permeability reduction in oil reservoirs. It has been earlier suggested that permeability reduction results from the blocking of small passages by the moving particles or other mineral fines suspended in the flowing liquid. Permeability is a representative of a single-phase flow in pore space. But, to simulate the case in oil reservoirs where we have a two-phase flow through solid pore spaces, the concept relative permeability should be introduced.

Relative permeability is the ratio of the phase permeability to absolute permeability and it is a direct measure porous media ability to conduct one fluid when one or more fluids are present (Anderson 1987). Thus, relative permeability is typically used to describe the multiphase flow of immiscible fluids in subsurface formations. Characteristically, flow properties in the pore space are the synergistic effect of pore geometry, wettability, fluid distribution, and saturation history. Typically, at a given phase saturation, fluid flow in the pore space is controlled by some macroscopic flow properties including the relative permeability (Figure 2-5) and the capillary pressure. Moreover, fluid flow is also a function of fluid properties including viscosity, density, and composition.

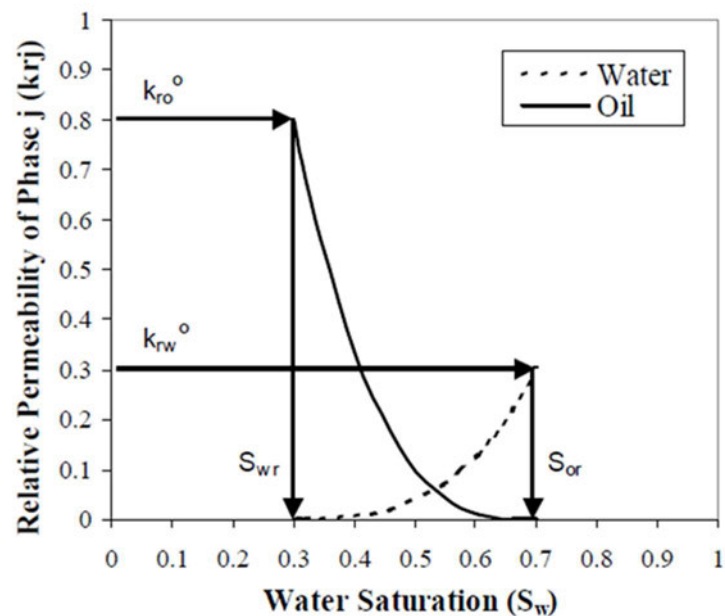


Figure 2-5 Curve of relative permeability of oil/water system (Anderson 1987).

In the last five decades, most experimental studies investigated the fluid distribution and relative permeability as a function of wettability for sand packs and/or other micro models. Recently, however, studies have used reservoir rock (Figure 2-6) in oil displacement measurements via X-ray medical computed scan (i.e. medical scan Figure 2-7). Further, to measure fluid distribution using X-ray micro-computed tomography μ CT scan a micro core plug (5mm diameter and 10 -15mm length) is drilled from rock samples (Figure 2-8). These technologies make use of computer-processed combinations of many X-ray measurements taken from different angles to

produce cross-sectional images of specific areas of the scanned core (Figure 2-9). CT scan and μ CT scan allow the user to see inside the core spaces and investigate the fluids distribution without cutting (Zhang et al. 2016). In this context, extracted images via μ CT (Figure 2-9, and Figure 2-10), are analyzed to visualize cluster morphologies and initial and residual fluid saturations (Rahman et al. 2016).



Figure 2-6 Core plug samples (Nwidee 2017).

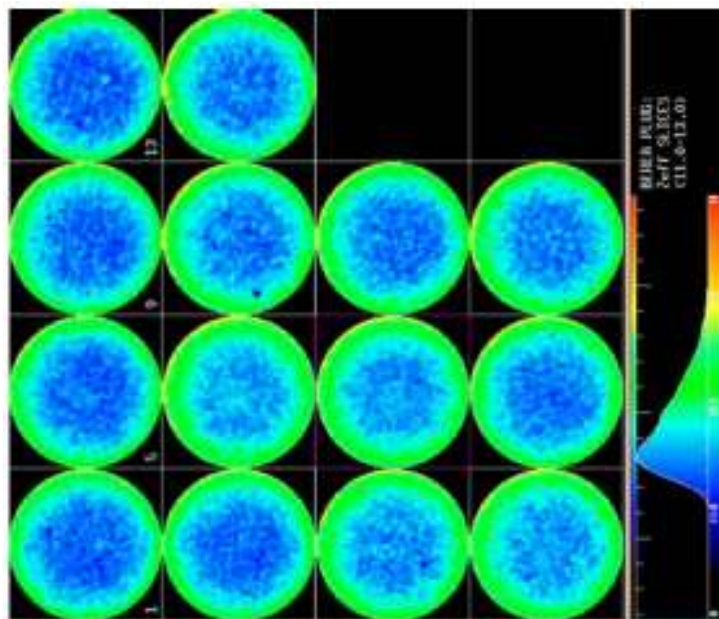


Figure 2-7 X-ray medical scan images for slices of Berea plug (Siddiqui and Khamees 2004)

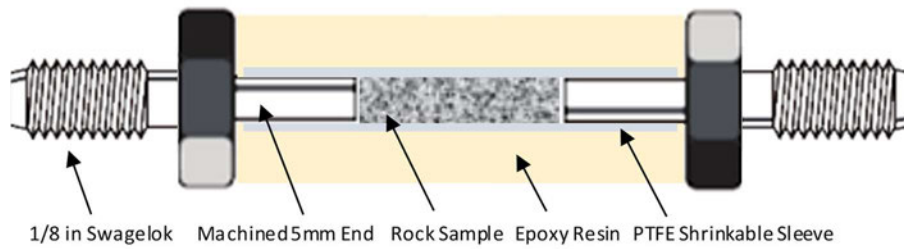


Figure 2-8 Flow cell before and after covering with resin. The length of the core is 17mm and the diameter is 4.8 mm (modified from Al-Anssari, Nwideo, Ali, et al. (2017)).

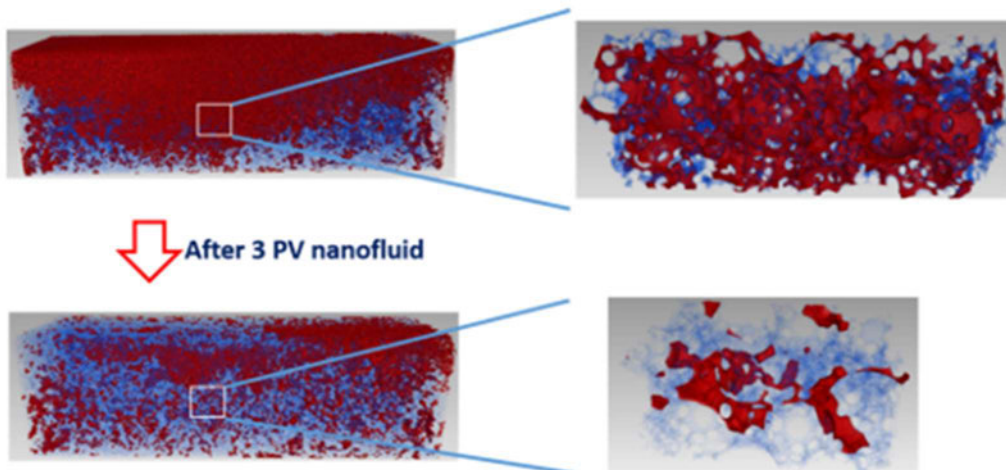


Figure 2-9 μ CT scan images of oil blobs (red) before and after 3 pore volume nanofluid flooding (Zhang et al. 2016). This figure shows smaller oil blobs in the porous medium after nanofluid injection. Mechanistically, nanofluid injection breaks the large structures into small disconnected oil blobs.

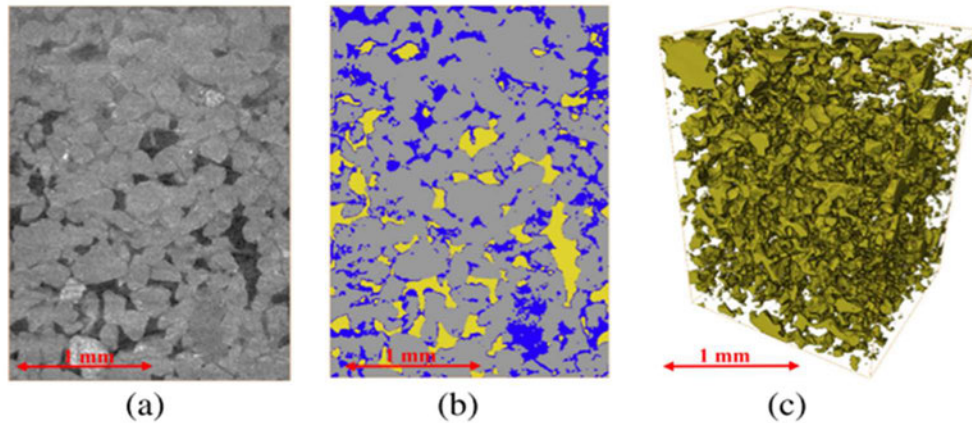


Figure 2-10 μ CT scan images of Bentheimer sandstone at 10 MPa pore pressure and 318 K: (a) water-wet initial CO_2 saturation, raw image; (b) water-wet initial CO_2 saturation, segmented image; (c) CO_2 clusters in 3D for the water-wet initial CO_2 saturation, a volume of 3 mm^3 is shown (Rahman et al. 2016).

2.2.4 Wettability and Wettability Alteration

In a rock/oil/brine system, wettability measures the preference that rock has for either the oil or water. Thus it is a major factor controlling the location, flow, and distribution of fluids in a reservoir (Anderson 1986). During water flooding, wettability is a key in oil displacement. Typically, in water-wet formation, aqueous phase occupies the relatively smaller pores while oil occupies the bigger pores (Rahman et al. 2016). The residual oil saturation depends on wettability. Minimum oil saturation refers to higher oil recovery and it is usually the case of mixed wettability, lower than the cases of strong water- or oil-wetness. In the oil-wet formations, aqueous phase showing earlier breaks through. In contrast, in a water-wet rock, aqueous phase breaks through later due to the low water permeability compared to that of oil (Sharma and Mohanty 2013). Thus, wettability alteration of oil-wet formations into water-wet is essential for efficient and feasible water flooding process in the oil recovery.

More than 50% of the discovered crude oil is stored in carbonate reservoirs (Gupta and Mohanty 2010). Carbonate oil reservoirs are mainly naturally fractured oil-wet or mixed-wet reservoirs which makes hydrocarbon production from such reservoirs a very challenging practice (Gupta and Mohanty 2010). Typically, oil production from naturally fractured oil-wet and mixed-wet reservoirs can significantly be improved via

rendering the wettability of rocks formations into water-wet (Mason and Morrow 2013).

Mainly, there are two methods to alter the wettability of oil-wet carbonate reservoirs. The first technique is via manipulating the ionic composition of the aqueous phase. The addition of sulfate ions, for example, can shift the wettability of hydrophobic characteristics of chalk cores (Tabrizy et al. 2011). In this context, seawater includes, among other ions, Mg^{2+} , and SO_4^{2-} which have been proven to shift the wettability of water flooded reservoir formations (Ding et al. 2010). Such alteration in wettability is most likely due to the potential adsorption/exchange process between Mg^{2+} from the sea water and Ca^{2+} on calcite. Further, the rate of ion exchange increases with temperature (Tabrizy et al. 2011). In line with this, Yousef et al. (2010) have revealed that the injection of low salinity brine in to oil reservoirs at high temperature and high salinity condition induce the shifting of wettability favourable water-wetness states and produce 20% more hydrocarbon.

The second technique involves the injection of chemicals such as surfactant, polymer, polymer-surfactant combination, or nanoparticles, either solely or in combination with other surface-active materials (Maerker and Gale 1992, Sharma et al. 2014, Zargartalebi et al. 2014b, Al-Anssari et al. 2016). In this context, a large number of publications studied the influence of different chemicals of the wetting status of carbonate reservoirs and the potential improvements oil production using CEOR methods.

2.2.5 Interfacial Tension and Interfacial Tension Reduction

The interfacial tension of the hydrocarbon-water/aqueous phase system is one of the basic physical properties required to be manipulated in hydrocarbon producing fields. Reducing of the interfacial tension is one of the ongoing topics since it plays a major role in wide areas of science and engineering for many important applications such as foam and emulsion stability, EOR, carbon geosequestration, etc (Arif et al. 2016, Biswal et al. 2016). The reduction of interfacial tension is key in facilitating the displacement of oil from the pore space. Typically, surface-active materials including surfactants were utilized to reduce the interfacial tension of oil/water system.

Mechanistically, the adsorption of surfactant monomers at the oil/water interface is responsible for the efficient reduction of the interfacial tensions by tenths of orders. Characteristically, surfactants are mainly classified into two categories; non-ionic and ionic surfactant. The ionic surfactants are on two types; cationic with positive head group and tail group, an anionic surfactant with negative head group and tail group. The choice of surfactant type in interfacial tension reduction applications, particularly in oil recovery industry, depends on the type of reservoirs and composition of the aqueous phase and the oil (Ahmadi and Shadizadeh 2012). Injection of surfactant into oil reservoirs, however, includes series limitations including the high cost of surfactant, the loss of surfactant due to adsorption into rocks surfactant, and the dramatic impact of reservoirs harsh condition on surfactant stability. Recently, nanotechnology has drawn attention to its high potentials in interfacial tension reduction applications. In this context, hydrophilic NPs can synergistically induce the ability of surfactants to reduce the interfacial tension (Zargartalebi et al. 2015, Al-Anssari, Wang, Barifcani, and Iglauer 2017, Kumar and Mandal 2018). Mechanistically, NPs can act as a carrier via its Brownian motion to transport to surfactant molecules to the oil/water interface (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). Also, NPs may lessen the loss of surfactants due to adsorption into rocks and thus increase the number of surfactant monomers in the liquid phase (Zargartalebi et al. 2014b). Thus, NPs have promising potentials in interfacial tension reduction applications.

2.3 Enhanced Oil Recovery (EOR)

When primary and secondary oil recovery processes produce no more oil, EORs, also called tertiary oil recovery methods, are employed to harvest more oil. It is well agreed that the primary recovery is driven by the internal energy (pressure) of the reservoir and can produce around 10% of the original oil in place (OOIP). Secondary oil recovery which drives by water flooding can rise the ultimate amount of recovery to 25 – 28% of the OOIP leaving considerable amount of oil trapped in the pore spaces. The estimated increase of recovery by tertiary techniques (EOR) varies from 7 – 25% more oil. Typically, EOR includes a number of processes in various stages of development and of varying utility (Thomas 2008a). Generally, EOR is divided into

two main sectors including thermal, and non-thermal methods (Figure 2-11). The non-thermal methods mostly comprise techniques that use various chemicals (i.e. CEOR). Here, and before presenting EOR techniques in detail (Figure 2-11), it is important first to distinguish between improved oil recovery (IOR) and enhanced oil recovery (EOR).

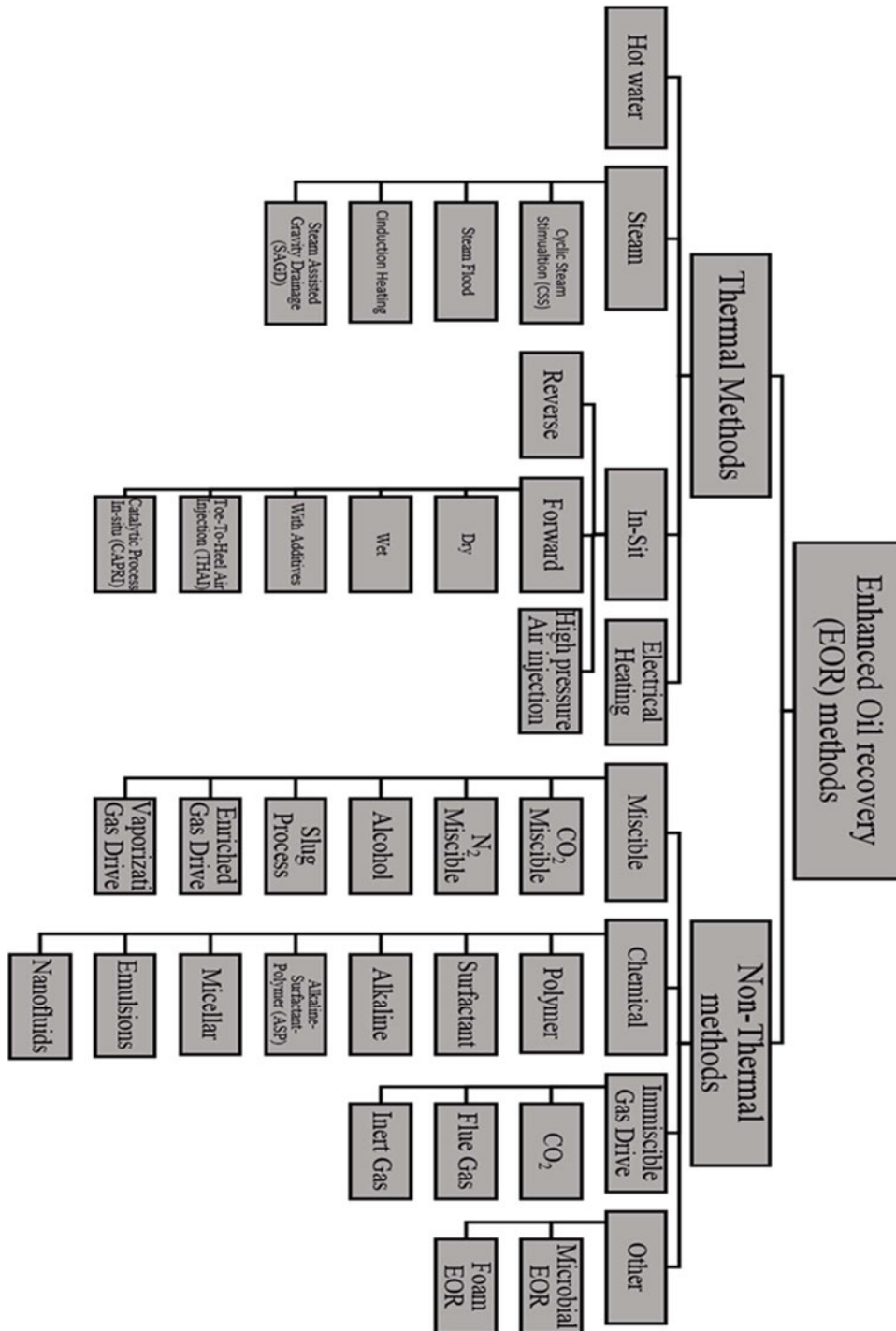


Figure 2-11 Categories of enhanced oil recovery (EOR) techniques (Al-Ansari 2018).

2.3.1 IOR and EOR

The terms IOR and EOR have been used randomly and interchangeably on many occasions. Generally, IOR refers to all the applied means and operational strategies including infill drilling and horizontal wells as well as improve vertical and areal sweep that in total result in improving oil recovery. On the other hand, EOR is a subcategory of IOR and precisely indicates the lessening of oil saturation under the residual saturation (Thomas 2008a). In general, the trapped light oils, after primary and secondary oil recovery, by capillary forces and the hard to produce (heavy) oils due to viscosity can only be recovered by reducing the oil saturation of such oils below the residual oil saturation using of the EOR methods. The applied techniques and the expected efficiency of the EOR process are mainly depend on the type of oil formations types (see Figure 2-12). EOR typically applicable after the water flooding process to produce more oil (around 60% of OOIP). Differently, heavy oils and tar have extensively poor responses to primary recovery and water flooding processes. Subsequently, the majority of oil from such hard-to-produce oil reservoirs result from EOR applications via in-situ manipulation of the capillary number (N_c) and/or mobility ratio (M) of reservoir fluids utilizing different EOR techniques including nanofluid injection (Druetta and Picchioni 2019).

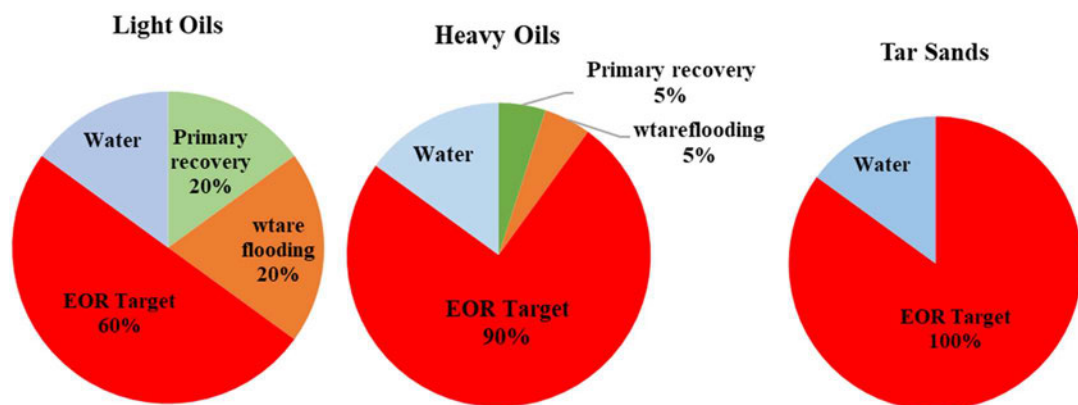


Figure 2-12 Enhanced oil recovery (EOR) target for different hydrocarbon, based on 15% pore volume water saturation and 85% oil. Reproduced after (Thomas 2008a).

2.4 Affiliation of Nanotechnology in EOR

Nanofluid flooding for enhanced oil recovery (EOR) has feasible potentials in the oil industry. The proposed recovery mechanisms following the injection of NPs include wettability alteration and interfacial tension reduction. The nanofluid is a NPs dispersion in a liquid phase. The liquid phase can be water, brine, or surfactant solution. The physicochemical properties of nanofluids are controlled by the type of NP and the component of the base fluid. The efficiency of nanofluids in EOR depends on the stability of nanoparticles and the proper selection of nanofluid. The optimum selection of nanofluids depends on the on-site properties of the oil reservoir including pressure, temperature, salinity, and mainly rock type. Incorrect selection of nanofluid; on the other hand, can lead to significant damage to the rocks including blockage of the pore space, rock dissolution, and reduction of permeability (Amedi and Ahmadi 2016). Despite the promising potential of NPs in subsurface industry, there is still severe lack of understanding on infiltration of these NPs in the subsurface formation and its potential to reach the underground water supplies. Moreover, depleted oil reservoirs are strong candidates for carbon geo-storage projects which may be affected by the existing of nanoparticles. Thus, keeping the amount of injected nanofluids at its lower limits is of primary importance. This section presents in detail the most commonly suggested NPs and their nanofluids in EOR projects at different operation conditions.

In oil recovery projects, once primary and secondary oil recovery techniques don't yield economical oil production, enhanced oil recovery (EOR) techniques, also known as tertiary oil recovery, can be utilized to produce the oil. EOR projects use thermal energy, miscible gas injection or chemical flooding methods. Since 2006 forward, nanofluids which are dispersions of nanoparticles in a base liquid have been suggested as a smart solution for the chemical flooding method. Furthermore, extensive research on the implementation of NPs and its nanofluids in enhanced oil recovery has started since 2010 and continue to date to be the new phenomenon of oil recovery technology.

Nanotechnology introduces a novel concept to facilitate the displacement of oil from porous media. Typically, the capillary force in the pore-scale controls the displacement of oil droplets from the pore throat via reducing the water-oil interfacial tension (IFT) and altering the wettability of pore towards more water-wet. Due to the high surface

energy which results from a high surface to volume ratio (Figure 2-13), the nano-sized material contributes to the EOR process by modifying the status of geological formations including wettability and surface chemistry. Characteristically, the adsorption of nanoparticle onto liquid-liquid interfaces reduce the oil-water interfacial tension. On the other hand, NPs adsorption into the solid-liquid interface significantly reduces the water contact angle which alters the wettability of oil-wet formations towards water-wet. The ability of NPs to reduce the water contact angle mainly depends on the type and initial size of the NPs (Bayat, Junin, Samsuri, et al. 2014). Mechanistically, the nano-arrangement of single and multilayers of nanoparticles into the solid-oil edge creates a pressure that acts to detach the oil droplet from the solid surface (Nikolov et al. 2010). The pressure that results from these single and multi-nanolayers is called a structural disjoining pressure (Zhang et al. 2014). The ability of NPs to adsorb on the liquid-liquid and solid-liquid interfaces depends on the surface properties of these nanoparticles.

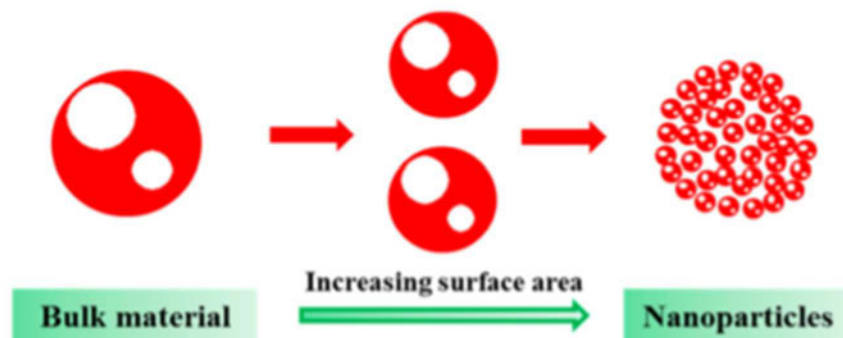


Figure 2-13 A schematic diagram of the high surface to volume ratio of NPs (Sun et al. 2017)

In-situ NP applications for full-scale oil fields is limited by crucial challenges such as stability of NPs in the dispersion after injection, retention of NPs at early stages after injection, reduction of relative permeability and porosity of reservoirs and the relatively high production cost of NPs compare to the same materials at the bulk size. Consequently, extensive research has been devoted to overcoming the practical challenges of implementing NPs in the oil recovery industry. Subsequently, large number of studies in the field of nanotechnology and particularly NPs applications in

subsurface formations was introduced (Ju et al. 2006, Lan et al. 2007, Zhang et al. 2007, Hernández Battez et al. 2008, Ju and Fan 2009, Onyekonwu and Ogolo 2010, Suleimanov et al. 2011, Amraei et al. 2013, Hendraningrat et al. 2013, Esmaeilzadeh et al. 2014, Roustaei and Bagherzadeh 2014, Sharma et al. 2014, Zargartalebi et al. 2014a, Zhang et al. 2014, Ponmani et al. 2015, Al-Anssari et al. 2016, Amedi and Ahmadi 2016, Nwidee et al. 2016, Zhang et al. 2016, Abdelfatah et al. 2017, Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017, Al-Anssari, Arif, Wang, et al. 2017a, b, Al-Anssari, Nwidee, Ali, et al. 2017, Al-Anssari, Nwidee, Arif, et al. 2017, Al-Anssari, Wang, Barifcani, and Iglauer 2017, Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017, Al-Anssari 2018, Al-Anssari, Arif, wang, Barifcani, Maxim, et al. 2018, Al-Anssari, Barifcani, et al. 2018, Al-Khdheawi et al. 2018, Nwidee et al. 2018). Table 2-1 lists the most important studies in the field during the last decade. Further, several literature reviews on NPs potential for EOR have recently been published (Cheraghian and Hendraningrat 2016, Negin et al. 2016, Sun et al. 2017, Afolabi and Yusuf 2018, Kazemzadeh et al. 2019, Ko and Huh 2019, Rezaei Gomari et al. 2019). In this review, we aim to compile comprehensive NPs researches in subsurface projects and particularly EOR which provides the first insight into criteria for selecting a specific type of NP for an oil reservoir.

Table 2-1 list of the most important studies in the field of NPs in EOR for the last decade

References	NPs type	NPs con.	Rock type	T (C)	P (MPa)	Studied variables for EOR
(Ju and Fan 2009)	Hydrophilic and hydrophobic silica NPs	≤ 1 wt%	Sandstone	80	ambient	Change in wettability and permeability
(Suleimanov et al. 2011)	Non-ferrous metal NPs	0.001 wt%	quartz	ambient	ambient	Change in IFT and wettability
(Karimi et al. 2012)	Zirconium oxide	5 wt%	Carbonate cores	70	ambient	Change in wettability
(Hendraningrat et al. 2013)	Hydrophilic silica	0.01 -0.1 wt%	Berea sandstone cores	ambient	ambient	Change in IFT and wettability

(Bayat, Junin, Ghadikolaie, et al. 2014)	Aluminum oxide (Al ₂ O ₃)	0.005 wt%	limstone	ambient	ambient	Mobility of NPs in limstone
(Bayat et al. 2015)	Aluminum oxide (Al ₂ O ₃) and Titanuim oxide TiO ₂	0.005 wt%	clay	ambient	ambient	Transport and retention of NPs
(Zhang et al. 2015)	Surface coated silica NPs with polyethylene glycol	5 wt%	sandpack	ambient	ambient	Adsorption of NPs in the porous media
(Al-Anssari et al. 2016)	Hydrophilic silica (SiO ₂) NPs	0.5 -2 wt%	calcite	70	ambient	Change in wettability
(Nwidee et al. 2017)	Zirconium ZrO ₂ and nickel oxide (NiO) NPs	0.004 - 0.05 wt%	calcite	70	ambient	Change in wettability
(Al-Anssari, Arif, wang, Barifcani, Maxim, et al. 2018)	Hydrophilic silica (SiO ₂) NPs	0.1 – 0.5 wt%	calcite	70	20 MPa	Change in wettability
(Liu et al. 2019)	Silica (SiO ₂) NPs	0.2 wt%	carbonate	ambient	ambient	Transport and adsorption in carbonate reservoirs
(Rostami et al. 2019)	Silica (SiO ₂) NPs	0.2 wt%	sandstone	ambient	ambient	Change in IFT, wettability, and recovery factor

2.5 EOR Mechanisms by NPs

Four different mechanisms have been suggested for NPs function in EOR including structural disjoining pressure, wettability alteration, interfacial tension reduction, and reduction of heavy oil viscosity.

2.5.1 Structural Disjoining Pressure (SDP)

The structural disjoining pressure (SDP) is the force that resists and contrasts the adhesion force of oil into the solid surface. Nikolov et al. (2010) were the pioneers in suggesting that the SDP is a key in oil separation from solid surfaces by NPs. Mechanistically, a mono or multi-layer film of NPs is created at the oil-solid interface (Wasan et al. 2011). Thus, the initiation of SDP requires the existence of an in-between wedge between oil droplets and solid surfaces, consequently, it only functions when the water contact angle is less than 90° (Al-Anssari, Nwidee, Arif, et al. 2017). Further, the force of separation due to structural disjoining pressure increase with increased nanoparticle load in the liquid phase and water-wetness of the solid surface (Figure 2-14). Typically, the energy of the structural disjoining pressure is a function of NPs size, salinity, and temperature of the medium and surface properties of the rock (Nikolov et al. 2010).

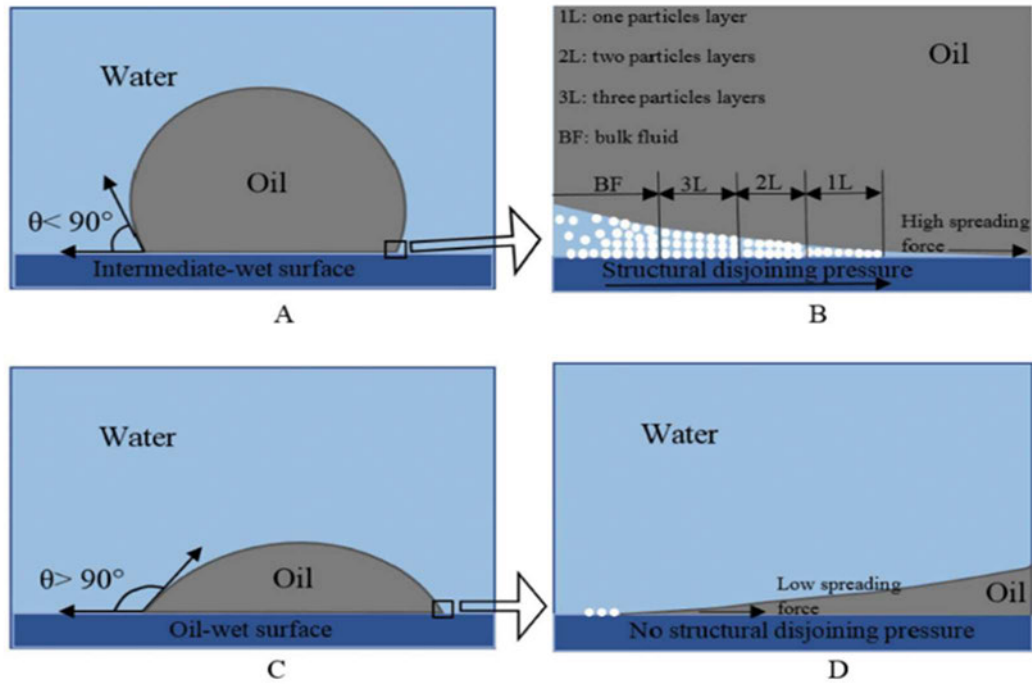


Figure 2-14 The proposed impact of initial water contact angle on the structural disjoining pressure of NPs at water and intermediate-wet ($\theta \leq 90^\circ$) surfaces (A, and B) and oil-wet ($\theta > 90^\circ$) surfaces (C, and D) (Al-Anssari, Nwidee, Arif, et al. 2017).

2.5.2 Alteration of Wettability

NPs have a drastic ability to alter the wettability of oil-wet surfaces to water-wet and thus allows water to penetrate the solid matrix of the rocks and produce more oil (Karimi et al. 2012). In this context, most of the oil in carbonate reservoirs, which contains more than 50% of the discovered oil, is stored in the rocks matrix while less oil is located in the fractures (Sharma and Mohanty 2013). During water flooding, oil can only produce from the fracture because the aqueous phase does not simultaneously imbibe to displace oil from the matrix (Mason and Morrow 2013). The presence of NPs through nanofluid flooding can alter the wettability of oil-wet matrix into water-wet, thus water spontaneously imbibe into the matrix and sweep a large amount of oil from the rock pore space (Figure 2-15) (Al-Anssari et al. 2016). Adsorption of NPs into oil-wet surfaces is the main mechanism to shift the wettability towards less oil or water-wet status (Dehghan Monfared et al. 2015, Abhishek et al. 2018). Factors including NPs concentration, NPs initial size and hydrophilicity, temperature, pressure, salinity, pH, and initial wettability of the porous media control the efficiency

of NPs as wettability modifiers (Al-Anssari et al. 2016, Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017, Al-Anssari, Arif, Wang, Barifcani, Lebedev, et al. 2018).

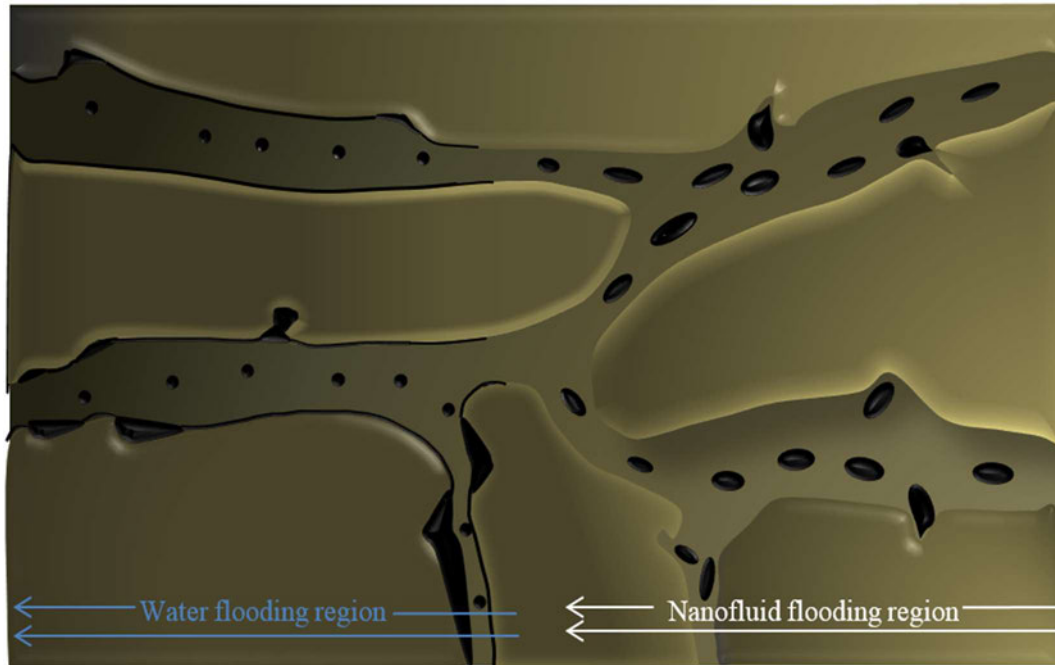


Figure 2-15 Impact of nanofluid flooding on the wettability, fluid distribution and oil displacement in the porous media

2.5.3 Interfacial Tension Reduction

The reduction of oil/water interfacial tension is key to a high displacement efficiency of oil. Although the surfactant is a well-known chemical agent to reduce the interfacial tension between crude oil and formation brine, some types of NPs (e.g. silica NPs) have also shown a significant potential for reducing the interfacial tension (Al-Anssari, Wang, Barifcani, and Iglauer 2017). Further, the combination of surfactant-NPs has thus a significant potential in oil recovery due to the synergistic effect between these two surface activating materials in the porous media (Al-Anssari, Wang, Barifcani, and Iglauer 2017, Xu et al. 2016). In this context, Zargartalebi et al. (2015) stated that the presence of NPs reduces the losses of surfactant monomer by adsorption on the rock surface thus keeps high surfactant concentration in the liquid phase leading to ultra-reduction of interfacial tension. Synergistically, the presence of a surfactant is essential to achieve stable NPs in the nanofluid leading to more efficient wettability alteration process (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017).

2.5.4 Manipulation of Viscosity

In the last decades, the world sources of light, and sweet crude oil are decreased. Consequently, the abundant stocks of heavy oils and bitumen, about 70% of the remaining discovered oil, become an important part of the world's hydrocarbon production. However, the viscosity and density of heavy crude oil are higher than that of conventional crude oil in addition to the higher contents of sulfur, nitrogen, oxygen, and metals. Recovery of heavy oil is a complex and challenging practice thus viscosity reduction of heavy oil is essential for heavy oil production. Typically, steam stimulation (gurge and disgorge or Huff and puff) is the main technique to recover heavy oil. Mechanistically, the injected steam acts as a heat carrier to raise the temperature and thus reduce the viscosity of the heavy oil which mitigates the flow resistance of heavy oil through the pore space. Li et al. (2007) were the first to synthesis and utilize nano-nickel catalysts in the viscosity reduction process of heavy oil by aqua-thermolysis. Their results showed that the mean molecular weight of the non-treated heavy oil was less comparing to the original crude sample. Characteristically, the contents of sulfur and asphaltene were reduced from 0.45% to 0.23% and from 15.83% to 15.33% respectively. Subsequently, the viscosity of the nano-treated heavy crude oil was reduced from 139800 mPa.s to 2400 mPa.s at 50°C. A similar effect of other NPs including Copper oxide (CuO) NP and Iron oxide (Fe₂O₃/Fe₃O₄) NP was noticed on the viscosity of heavy oil (Negin et al. 2016).

2.6 Most Common NPs Employed for EOR

Modern manufacturing technologies allow the synthesis of materials at the nanometre scale including nano-fibres and NPs. Generally, NPs are categorized as carbon nanotubes, graphene, polymeric, metal oxide, and metallic NPs. However, depending on economic and environmental requirements, only limited types of NPs were tested for their potential in the oil industry (Negin et al. 2016). NPs in EOR are mainly classified into three groups including metal oxide, organic, and inorganic NPs (Al-Anssari 2018).

2.6.1 Metal Oxide Nanoparticles

Metal oxide NPs are frequently applied in various industries due to the cheap price of manufacture and the possibility to control their surface properties for a specific application such as EOR. Metal oxides including Aluminium oxide (Al_2O_3), Copper oxide (CuO), Iron oxides (Fe_2O_3 , and Fe_3O_4), Nickel oxide (Ni_2O_3), Magnesium oxide (MgO), Titanium oxide (TiO_2), Zinc oxide (ZnO), Zirconium oxide (ZrO_2) are mainly polar or hydrophilic molecules depending on the electronegativity difference of the atoms that forming the molecules. In this context, metallic elements are typically low ionization potential and low electronegativity which make these elements very reactive and unstable (Hendraningrat and Torsæter 2015, Rezaei Gomari et al. 2019). Consequently, metallic elements have a high potential to react with oxygen, when they come into contact, to reach a stable state after losing electrons easily (Höpfner 1997). Characteristically, molecules with a high electronegativity difference of its atoms are hydrophilic molecules while hydrophobic molecules are that with a low difference of electronegativity between their atoms. Rankin (2013) reported that when the electronegativity difference ranging between 0.5 – 1.7 the molecule is considered as hydrophilic or polar. On the other hand, a molecule with an electronegativity difference less than 0.5 is non-polar or hydrophobic. Subsequently, the metal oxide is strongly hydrophilic molecules which gave it high potentials in the oil industry and particularly EOR applications.

2.6.1.1 Aluminium oxide (Al_2O_3) NPs

Aluminium oxide NPs are being utilized in a wide range of applications including EOR (Bayat, Junin, Ghadikolaie, et al. 2014). Al_2O_3 has been tested for both limestone (Bayat, Junin, Samsuri, et al. 2014) and sandstone (Ogolo et al. 2012, Hendraningrat and Torsæter 2015) oil reservoirs. Compared to other types of NPs such as TiO_2 , SiO_2 , and Al_2O_3 has the lowest absorption rate into the limestone surface however it shows the highest efficiency in EOR due to its ability to reduce the capillary forces of the porous media and also reduce the viscosity of the oil at all temperatures (Bayat, Junin, Samsuri, et al. 2014). In this context, Ogolo et al. (2012) demonstrated that despite the

measured reduction of oil-brine interfacial tension during Al_2O_3 injection, the reduction in oil viscosity is the dominated effect to displace oil from the porous media. Consequently, Al_2O_3 suspension is the recommended nanofluid to produce more oil from heavy oil reservoirs. Also, the initial wettability of rocks can dramatically impact the efficiency of nanofluids in EOR. Hendraningrat and Torsæter (2015) revealed that the highest oil recovery rate via nanofluid flooding can be achieved from the intermediate-wet core while the lost recovery rate was recorded from the oil-wet core. The results confirm the dominating role of the structural disjoining pressure on oil recovery by nanofluid flooding (Zhang et al. 2016). Typically, NPs accumulate in the indeterminate space sandwiched between the oil droplet and the rock's surface. This in-between edge can only exist in the intermediate surface when the contact angle is less than 90° (Al-Anssari, Nwidee, Arif, et al. 2017). Like other types of NPs, Al_2O_3 is unstable when solely dispersed in water, and it tends to flocculate, aggregate, and precipitate directly after the formulation of nanofluid. Stabilizer such as Povidone ($\text{C}_6\text{H}_9\text{NO}$) can be added to the nanosuspension to minimize instability of the dispersion at all temperatures (Hendraningrat and Torsæter 2015). Thus, Al_2O_3 NPs can be classified as a successful agent for EOR projects for heavy crude oil from sandstone reservoirs.

2.6.1.2 Titanium oxide (TiO_2) NP

The use of this NP as an EOR agent was investigated for both sandstone (Hendraningrat and Torsæter 2015, Ehtesabi et al. 2014, Zargartalebi et al. 2015) and limestone (Bayat et al. 2015) reservoirs. Comparison studies revealed that TiO_2 NP is less effected as EOR agent than another type of NPs such as Al_2O_3 , ZrO_2 , and SiO_2 (Bayat et al. 2015, Hendraningrat and Torsæter 2015). In line with that, Ehtesabi et al. (2014) stated that TiO_2 has no significant influence on the water viscosity or the oil-water interfacial tension which makes the effect of these NPs on EOR process limited by the alteration of surface wettability. Further, core flooding experiments with 0.01% concentration TiO_2 nanofluid into sandstone core revealed a substantial pressure drop indicating a blockage of the pores. Probing the porous media after injection with TiO_2 NPs showed dramatic sedimentation and over-deposition of NPs on the surface which explained the huge reduction in water contact angle and thus shifting of wetness to

more water-wet. Reported data in the literature showed a higher ability of nanofluid to alter the wettability of oil-wet surfaces when the base fluid is brine and not DI-water. This can be explained by the effect of salt ions on NPs stability and the subsequent precipitation of NPs in the pores media. The contentious precipitation of NPs in the porous media, due to reservoirs harsh conditions including high temperature and salinity, can block the pores and decrease the recovery factor dramatically. Thus, in the oilfield, it is essential to use a minimum concentration of NPs and control the deposition to avoid blockage issues.

2.6.1.3 Zirconium oxide (ZrO₂) NP

Nwidee et al. (2017) studied the effect of zirconium oxide (ZrO₂) NPs on wetting preference of fractured limestone formations during EOR process and compared it with Nickel oxide (NiO) NPs. Results showed a significant increase in oil recovery from limestone core after immersing in ZrO₂ nanofluid for a specific time and according to specific core/nanofluid weight ratio. The enhancement in oil recovery was related to the wettability alteration of oil-wet core samples to water-wet. This was confirmed by contact angle measurement on oil-wet calcite samples that immersed in a nanofluid. Measurements reported a drastic reduction of contact angle after immersing in ZrO₂ nanofluid refereeing to alteration of wettability of the porous medium. Compare to NiO at the same NP concentration and immersing condition, ZrO₂ demonstrated a better efficiency while NiO was not useful as a wettability modifier. Literature has reported more types of metal oxide NPs including NiO₂, MgO, SnO₂, CuO, Fe₂O₃. However, studies revealed that the overall oil recovery using these types of NPs was decreased despite the probable effect on wettability or interfacial tension. This reduction in oil recovery is most likely due to the instabilities agglomeration of NPs in the porous media (Dastvareh and Azaiez 2017) and the associated reduction in permeability.

2.6.2 Organic NPs (Carbon NPs and Carbon nanotubes (CNT))

In general, the term organic materials refer to all compounds with carbon in their structure. Typically, carbon NPs and Carbon nanotubes (CNT) are the most popular organic nanomaterials. Other diamond NPs that made of carbon atoms such as fullerene-C60, C70, C76, C78 and C84, graphene, and graphite nanopowder have gained less attention in science and industry than Carbon NPs and CNT due to difficulties in controlling the surface properties of that materials. Carbon NPs are mainly synthesized via a hydrothermal process and the surface of the produced NPs can be desirably modified to be applicable for specific applications. Also, the CNT can be single or multi-walled carbon nanotube (MWCNT). These CNTs are strongly hydrophobic. Several studies have introduced carbon NPs and CNT as an EOR agent. Most recently, Ghalamizade Elyaderani et al. (2019) have conducted systematic study on using different concentration of functionalized MWCNT (0.01,0.05, and 0.1 wt%) to investigate the effect of these NT on the interfacial tension, wettability, viscosity and the stability of nanofluid in the presence of brine (NaCl) during EOR process. Results showed that the interfacial tension is decreased with increased NPs concentration (from 0.01 to 0.1 wt%) due to the adsorption of NPs on the oil/nanofluid interface. Also, as expected, the viscosity of the nanofluid was increased with NPs concentration which improves the displacement efficiency of water to oil and prevents the unfavourable fingering action in the pore space. Further, a significant shifting of wettability towards more water-wet was indicated via a drastic reduction of water contact angle with the presence of MWCNT. The created emulsion was water-in-oil (W/O) emulsion where the size and number of water droplets in the oil phase increase with NPs concentration. Interestingly, the nanosuspension was stable for 10 days without the addition of any surfactant or surface-active materials. Eventually, the study showed that the addition of 0.005 wt% sulfonated polymer to the nanosuspension keeps it stable even in the saline environment. Thus, functionalized MWCNT is a promising agent to enhance heavy-oil recovery via mechanisms of interfacial tension reduction, wettability alteration of oil-wet reservoirs, increasing the aqueous phase viscosity and creation of water-in-oil emulsion.

2.6.3 Inorganic NPs (Silica NPs)

Inorganic material is the traditional definition of any compounds that are free of carbon in their molecular structure. Silica also is known as silicon dioxide is one of the most abundant components in the universe and it is the fundamental component of sand and sandstone. Silica can be found naturally as quartz or can be made-up synthetically. Silica NPs are cheap price, environment friendly, and possibility to functionalize the surface properties for particle usage. Thus, silica NPs are commonly used in many industrial applications such as subsurface industries and particularly EOR. In 2002, silica was the first suggested NPs for EOR applications by (Ju et al. 2002). This study starkly revealed for the first time that oil recovery can be enhanced by flooding with silica NPs despite the slight reduction effects on the permeability. Following the announcement of Ju et al. (2006), tremendous number of studies have investigated the role of silica NPs and their different types in EOR applications. Types of silica NPs that applicable in EOR may embrace Alumina coated silica NPs, Hydrophobic silica NPs, Spherical fumed silica NPs, silica-core/polymer-shell NPs, Silanized-silica (silica grafted with silane) NPs, Polysilicon (PSNPs), Hydrophobic and lipophilic polysilicon (HLP) NPs, and Lipophilic and hydrophilic polysilicon (LHP) NPs (Negin et al. 2016, Al-Anssari 2018). After the pioneered work of Ju and his co-researchers (Ju et al. 2002, Ju et al. 2006, Ju and Fan 2009), the use of silica NPs to improve oil recovery became the most significant discussion topic in petroleum industry. Zhang et al. (2010) formulated NPs-stabilized emulsions for EOR applications. Their results showed that oil-in-water (O/W) and water-in-oil (W/O) emulsions augmented with surface-coated silica NPs remain stable for several months without coalescence. Results also declare that the initial wettability of silica NPs (bare or surface-coated NPs) determines the type of emulsion formed (O/W or W/O). Metin et al. (2011) studied the stability of silica NPs suspension and the role oil reservoirs conditions including the pH, temperature, and salinity on the stability of NPs after nanofluid injection. Using spectral analysis of the Si-O bond at wave number of 111cm^{-1} with the Attenuated total reflection-Fourier-transform infrared (ATR-FTIR), results indicated a structural change of NPs surface with pH change. These results were confirmed by zeta potential measurements at different pH. For the first time, Metin et al. (2011) introduced the critical salt concentration (CSC) and report its data for different salts including NaCl, CaCl₂, BaCl₂, and MgCl₂. Literally, the CSC is the salt

concentration in the nanofluid above which the silica suspension becomes unstable. Amraei et al. (2013) found silica NPs can strongly shift the wettability status of hydrophilic carbonate surface into water-wet and reduce the oil/water interfacial tension. Up to date, a large body of studies were investigating the application of silica NPs in EOR. Recently, Al-Anssari, Arif, Wang, Barifcani, Lebedev, et al. (2018) conducted a series of contact angle measurement experiments at reservoirs pressure, temperature, and salinity. They announced that what has been approved at ambient conditions is also applicable at reservoir conditions including 20Mpa, 70°C, and harsh salinity. In their experimental work, they used CO₂ gas to raise the pressure in the optical cell during wettability assessment and that has attracted the attention to the potential of silica NPs on carbon capture and storage projects (Al-Anssari, Arif, Wang, et al. 2017a, b).

2.7 Field Implementation of NPs

The first field implementation of NPs injection flooding was performed in the Liauhe field of China. Practically, NPs were fed to the reservoir via steam injection through the injection well (Kazemzadeh et al. 2019, 2018). Also, in 2012 five kilograms of A-Dot NPs was dispersed in 255 barrels of seawater and injected to one of the observation wells in the Ghawar field of Saudi Arabia. The flooding procedure was continued until NPs had advanced about 6 meters in the reservoirs. The well was closed for 72 hours and the hydrocarbon production was the start again. The tested samples indicated that only 10% of the injected NPs had been trapped in the well (Kazemzadeh et al. 2015).

2.8 NPs Adsorption-Desorption into carbonate reservoirs

In the last decade, contact angle measurement was the main measurement method to evaluate NPs influence on the properties of the rock of oil reservoirs. Typically, more reduction of water contact angle of nano-treated oil-wet surfaces refers to higher effect in terms of wettability alteration (Hendraningrat and Torsæter 2015, Zhang et al. 2016, Al-Anssari, Nwideo, Arif, et al. 2017, Al-Anssari, Arif, Wang, Barifcani, Lebedev, et al. 2018, Rezaei Gomari et al. 2019, Rostami et al. 2019). Such higher effect reflecting

a higher adsorption rate of NPs into the solid surface. However, the reduction in contact angle is not always related to chemical surface treatment including nano-treatment. For example, the decline in contact angle might be related to the effect of water on the carboxylic groups on oil-wet carbonate surface. Moreover, it is well agreed that the surface charge dramatically changes due to the addition of even a little amount of NaCl to the surrounding solution. Thus, the amount and chemistry of aqueous solution control the surface charge on the mineral, and it is logical to affect the surface wettability (contact angle) with or without the presence of NPs. Thus, contact angle measurement is not typically the perfect scale for NP adsorption into solid surfaces.

The electrostatic interactions control NP behaviour in underground applications. Such surfaces normally carry ionic charges depending on the surrounding water chemistry. The electrostatic forces between high surface energy NPs, and between NPs and rock surfaces govern the circumstances of NPs combined, suspended, adsorbed, or desorbed into the rocks. Naturally, the salinity and acidity govern the electrostatic interactions in hydrocarbon reservoirs. Salinity has a screening effect on the electrical double layer of NPs which reduces the repulsive activity between adjacent NPs. Since the repulsive forces mitigate the effect of the collision and coalescence and thus aggregation of NPs as well as particle settlement in the pore space, extensive ionic strengths thus increase the van der Waals attraction force (Saleh et al. 2008) leading to vital aggregation and adsorption rate of NPs into rock surfaces (Kobayashi et al. 2005). Such complexity in aqueous phase chemistry, NP charges, and reservoir conditions make it unpractical to consider the change in wettability (contact angle) as a successful practice to evaluate NP adsorption. (Espinasse et al. 2007). Different techniques and properties can be more valid for NP adsorption evaluation such as SEM, EDS, and AFM which this study concentrated on.

2.9 Conclusion

Efficient displacement of oil from underground formations is key in helping to meet the unceasing worldwide energy demand. Oil can be recovered via three recovery stages including primary, secondary (water flooding), and tertiary (EOR) oil recovery processes (Thomas 2008b). However, due to the fact that most of the discovered oil reservoirs are in the matured stage, the conventional recovery methods such as primary

and secondary oil recovery will not recover majority of remaining oil. Studies reported that primary and secondary oil recovery process can produce no more than 30% of the original oil in place (Wu et al. 2008) leaving drastic amount of oil in the geological formations of carbonate reservoirs. Typically, the remaining amount of hydrocarbon can be partially produced via tertiary oil recovery (Gupta and Mohanty 2010) including chemical EOR (Sharma and Mohanty 2013). Nevertheless, some critical challenges may limit the efficiency of chemical EOR processes such as high materials cost, high potentials of chemical mismatches, and losing of chemicals via trapping or adsorption in the porous media. Thus, smart chemicals are extensively required to overcome such potential issues in EOR applications. Nanotechnology, and particularly nanofluid, have been suggested as an elegant solution for EOR issues. The dispersed NPs in such nanofluids can significantly alter the wettability of oil-wet surfaces into water-wet, reduce the oil/water interfacial tension, and influence the viscosity of the displacement fluids. Mostly, adsorption of NPs into the liquid-liquid or solid-liquid interfaces is the key for NPs role in EOR applications. Understanding the adsorption behaviour of NPs into the carbonate surface is crucial as it controls the ability of nanofluids to alter the wettability of oil-wet carbonate reservoirs into water-wet and thus facilitate the displacement of hydrocarbon and increase the recovery rate. The aim of this work is to demonstrate the adsorption scenarios of silica NPs into calcite surfaces at reservoir conditions such as high pressure and temperature. The practical applicability of the prepared nanodispersions was studied via systematic testing of NPs adsorption via probing the nano-treated surfaces and the stability of NPs.

Chapter 3 Experimental Methodology with Results and Discussions (Reversible and irreversible adsorption of bare and hybrid silica nanoparticles onto carbonate surface at reservoir condition)

Realistic implementation of nanofluids in subsurface projects including carbon geosequestration and enhanced oil recovery requires full understanding of nanoparticles (NPs) adsorption behaviour in the porous media. The adsorption behaviour of NPs into porous media is controlled by the physicochemical interactions. These interactions include the interaction between each two adjacent NPs and between the NP and the porous media grain surface. This study investigates the reversible and irreversible adsorption of silica NPs onto oil-wet and water-wet carbonate surfaces at reservoir conditions.

Each carbonate sample was treated with different concentrations of silica nanofluid to investigate NP adsorption in terms of nanoparticles initial size and hydrophobicity at different temperatures, and pressures. Aggregation behaviour and the reversibility of NP adsorption onto carbonate surfaces was measured using dynamic light scattering (DLS), scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) measurement.

Results show that the initial hydrophilicity of the NP and the carbonate rock surface can influence the NPs adsorption onto the rock surfaces. Typically, oppositely charged NP and rock surface are attracted to each other, forming a mono or multilayers of NPs on the rock. Operation conditions including pressure and temperature have shown minor influence on nano-treatment efficiency. Moreover, DLS measurement proved the impact of hydrophilicity on the stability and adsorption trend of NPs. This was also confirmed by SEM images. Further, AFM results indicated that a wide-ranging adsorption scenario of NPs on the carbonate surface exists. Similar results were obtained from the EDS measurements. This study thus gives the first insight into NPs adsorption onto carbonate surfaces at reservoirs conditions.

This chapter illustrate all materials, devices, and equipment used in this study. Moreover, all the obtained results are presented and discussed here. Initially, the chapter gives a brief introduction for the topic and then describes the used materials and fluids including their functional and other physicochemical properties. The calcite surface aging procedure is then outlined, and the stability of the formulated nanodispersion demonstrated. Eventually, the influences of aging with nanofluid on the surface properties including surface roughness is extensively discussed.

3.1 Introduction

Inorganic fillers, particularly silica nanoparticles (NPs), have a wide potential application in many industries including cosmetics, food products, drug delivery, and geological industries including aquifer decontamination, carbon capture and storage, and enhanced oil recovery (EOR) (Al-Anssari et al. 2016). In the oil and gas industry, once primary and secondary oil recovery methods can no longer produce sufficient amount of hydrocarbon, EOR (also called tertiary recovery method) can be utilized for more hydrocarbon production (Li 2011). Nanofluid flooding is regarded as a potential EOR technique in oil-wet reservoirs. Nanofluids, dispersion of NPs in a base fluid (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017), have been suggested to facilitate oil displacement from the porous media (Nikolov et al. 2010, Kondiparty et al. 2011). Reduction of water contact angle on the oil-wet solid surfaces in addition to the interfacial tension reduction is the main NPs mechanisms in EOR (ShamsiJazeyi et al. 2014, Al-Anssari, Nwidee, Ali, et al. 2017). In this context, NPs (i.e. silicon dioxide; SiO₂) can enhance hydrocarbon recovery via rendering the wettability of oil-wet surfaces to water-wet (Al-Anssari et al. 2016, Nwidee et al. 2017) which in turn promotes the spontaneous imbibition of brine into the low-permeability rock (Gupta and Mohanty 2010). Although NPs efficiency as wettability modifier is limited by the adsorption of these fine particles onto the fluid-fluid interface (Dugyala et al. 2016) and solid surface (Zhang et al. 2016), there is a dramatic lack of understanding about NPs adsorption onto rock surfaces at reservoirs conditions. According to the available literature, no previous study concerning nanoparticle adsorption has been conducted at subsurface pressure, temperature, and salinity.

Recently, there have been several studies on the application of silica NPs to render the oil-wet rock surfaces water-wet for the enhanced oil recovery. Moghaddam et al. (2015) have compared the effectiveness of different NPs on wettability alteration of oil-wet calcite surfaces. Their results showed that SiO₂ nanoparticles are more efficient in terms of contact angle reduction. Zhang et al. (2015) proposed that NPs mutually experience reversible and irreversible adsorption on the solid surfaces. In their study, nanofluid was injected into columns packed with a crushed sedimentary rock at

ambient condition. The NPs concentration in the effluent stream showed that NPs adsorbed onto the solid surfaces until the adsorption capacity was reached i.e. when the NPs in the effluent equals to that in the injection stream. Subsequent injection of DI-water into the columns led to dramatic desorption of nanoparticle, which was indicated by the significant concentration of NPs in the effluent stream. More recently, Al-Anssari, Wang, Barifcani, Lebedev, et al. (2017) reported the influence of nanofluid concentration and treatment temperature on the reduction of water contact angle on nano-treated calcite samples. Using technologies including scanning electron microscopy (SEM) images, energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) measurements, the researchers investigated the adsorption of silica NPs onto calcite samples and the formation of nanotextured surfaces.

Understanding of adsorption behaviour of NPs on rock-solid surfaces is one of the critical issues in the oil and gas industry. Physicochemical interactions between NPs and treated surfaces (Metin, Baran, et al. 2012) and between NPs itself (Metin et al. 2011) are the main controlling factors for the potential irreversibility of NPs adsorption in the porous media (Petosa et al. 2010, Mondragon et al. 2012). Typically, physicochemical interactions are mainly controlled by the surfaces charge (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). While the surfaces charge of NPs depends on the surface type of such NPs, and condition of the environment (Hamouda and Gomari 2006) and the composition of formation brine (Nooney et al. 2015, Alroudhan et al. 2016). Theoretically, the Derjaguin – Landau – Verwey – Overbeek (DLVO) theory can demonstrate the effect of physicochemical interactions on NPs behaviour. DLVO theory suggested that the interaction forces between particles and between the particle and the surface control NPs aggregation, deposition, adsorption, adhesion, and desorption (Chen et al. 2011). In this context, DLVO force is the algebraic summation of the attraction and repulsive forces. The attraction force is the van der Waals force and the repulsive force is the electrostatic force (Alroudhan et al. 2016). In addition, in case of NPs adsorption, more forces can be considered within DLVO theory including hydrophilic and lipophilic forces (Guzmán et al. 2011), repulsive steric forces (Nugroho et al. 2013), and magnetic forces (He et al. 2012).

To-date, a limited number of studies have demonstrated the interactions between NPs and solid surfaces. Furthermore, all the previous studies were conducted at ambient condition ignoring the potential impacts of subsurface severe condition on the

adsorption scenarios of silica NPs. Moreover, all previous studies have used NPs concentration in the effluent as an indication for NPs adsorption or retention in the porous media. Lecoanet et al. (2004), for example, have assessed the transport of NPs in an artificially designed porous media. They reported that NPs display broadly diverse mobility behaviour. Further, surface-modified NPs (hydrophobic) exhibited maximum mobility. Rodriguez Pin et al. (2009) investigated the withholding of silica NPs after injection into sedimentary rocks. They have reported breakthroughs of effluent NP referring to significant mobility in the porous media.

Despite studies concerning NPs behaviour on solid surfaces in the lab at ambient condition, challenges in using NPs in real fields are of high potential due to the complex reservoirs conditions such as heterogeneous formations, high pressure, temperature, and salinity (Al-Anssari et al. 2016). This study, thus, investigated the fundamental aggregation, adsorption, and desorption properties of bare and hybrid (silanized) silica NPs onto oil-wet and water-wet carbonate surfaces at different pressures, temperatures, and initial hydrophilicity of NPs. This series of operation conditions help to cover all the potential scenarios in the oil production industry. Dynamic light scattering (DLS), atomic force microscopy (AFM), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS) were used to investigate NP-carbonate surface interactions at the nanoscale. These methods can directly evaluate the interactions of NPs with solid surfaces and their molecular arrangement and order.

3.2 Experimental Plan

The study technique adopted in this chapter was principally based on the aim and objectives of the work. The qualitative style of the study (Figure 3-1) was primarily adopted for analysis of NPs adsorption in terms of surface roughness and surface morphology at reservoirs conditions in addition to the stability measurements of the nanofluids. The practical aspect of the work includes laboratory experiments that allowed the accomplishment of the objectives of the study and makes up for most of the work. The experimental study process is shown in chart 3-1.

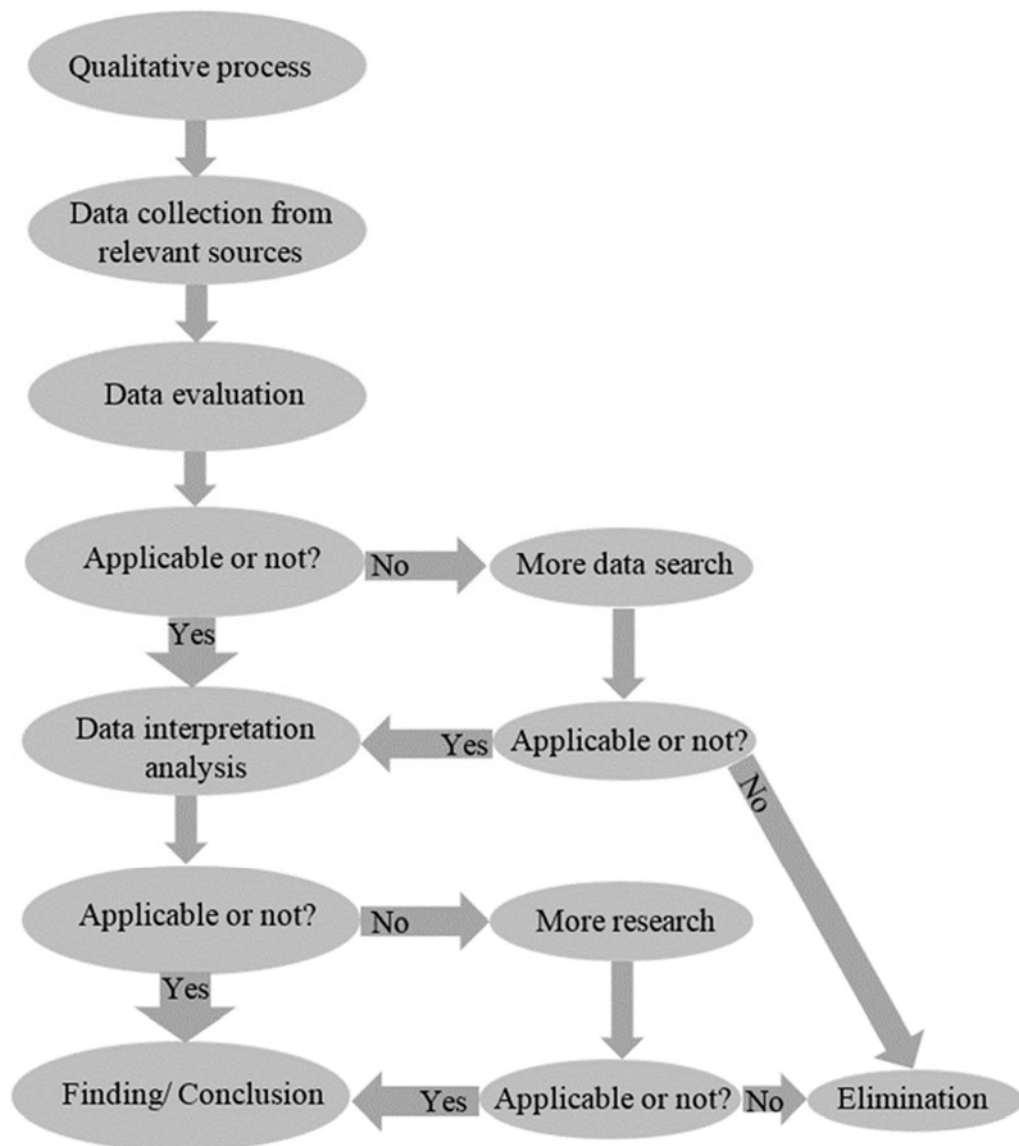


Figure 3-1: Flow chart of the study

3.3 Experimental Task Assessment

Experiments were systematically applied on carbonate surface at lab and reservoir conditions. The study was initiated with the choice of appropriate acid aging calcite samples to achieve oil-wet carbonate surfaces which are the status of carbonate reservoirs. Then, nanofluid formulations, surface treatment with NPs, and extensive series of AFM, zeta potential and particle size distribution measurement were conducted to evaluate the adsorption behaviour of NPs onto calcite surface at different reservoirs conditions including oil-wet, and water-wet calcite surfaces, ambient and high pressures, and ambient and high temperatures. The treatment with NPs was conducted via immersing of calcite off-cuts in diluted or concentrated nanofluids.

3.4 Materials

Hydrophilic silicon dioxide (SiO_2) NPs (5 – 10 nm powder, porous spherical, 99.5 wt% purity) supplied by Sigma Aldrich/ Australia was implemented in this study to formulate different nanofluids. NPs have been used as supplied (hydrophilic) or after treatment with silane components in the silanization process which produces hybrid (hydrophilic) NPs. Each type of NPs (hydrophilic and hydrophobic) were dispersed separately in base fluid (DI water, brine, or surfactant) to formulate different nanofluids. The bulk density of silica NPs are ranging between 2200 – 2600 kg/m^3 and the molecular mass is 60.08 g/mole .

DI-water (conductivity = 0.02 mS/cm) freshly supplied by David Gray was used as a cleaning agent and mainly to prepare different formulations such as brine, or directly as the base fluid for NPs in some nanodispersions. In this context, to simulate all potential conditions in subsurface formations, brine at different concentrations were formulated via dissolving of sodium chloride ($\text{NaCl} \geq 99.5$ mol%, supplied by Sigma Aldrich/ Australia) in water using magnetic stirrer for 30 minutes

3-aminopropyl triethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$; (Figure 3-2), supplied by Sigma Aldrich where used to manipulate the initial hydrophobicity of hydrophilic silica (pure) NPs into a hydrophobic (hybrid) condition via silanization process (Grate

et al. 2012, London et al. 2013). The density of this silane is 964 kg/m^3 and the molecular mass is 221.37 g/mole .

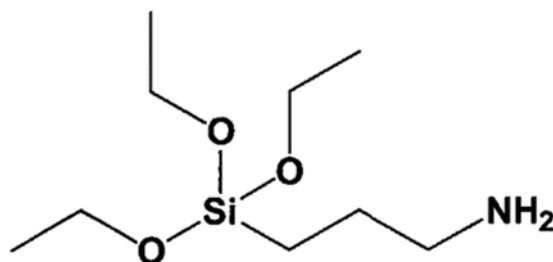


Figure 3-2 Chemical structure of (3-aminopropyl) Triethoxysilane

For adsorption measurements of NPs on carbonate surfaces at different initial wettability, calcite samples were used as a representative for carbonate reservoirs **Error! Reference source not found.** Further, to mimic all potential scenarios in oil reservoirs, some samples were aged with stearic acid to manipulate the initial surface wettability.

Stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ (weight solid; $\geq 98.5\%$ purity, long-chain (C18, number of carbon atoms = 18, Figure 3-3) supplied by Sigma Aldrich was used to prepare a 0.01 M stearic acid in decane solution which was used to alter the wettability of the original calcite surface to oil-wet (Hansen et al. 2000, Morse and Arvidson 2002, Shi et al. 2010, Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017, Ali et al. 2019).

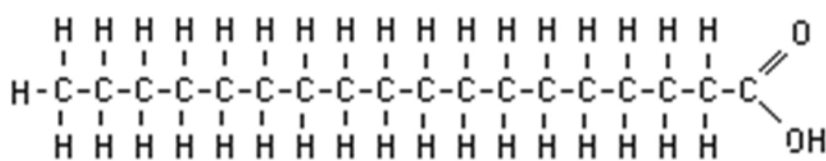


Figure 3-3 Stearic acid structural formula.

Decane (n-decane ($\text{C}_{10}\text{H}_{22}$), colourless liquid purity $\geq 99.9 \text{ mol}\%$ from Rowe Scientific) was used to prepare 0.01M stearic acid. The boiling point of n-decane is 574.1K and the molecular mass is 142.28 g/mol .

Carbon dioxide CO₂ food grad (99.9 mol% (liquid phase) from BOC, gas code-082) was injected to increase the pressure in the nano-treatment cell when it is required according to the experiment design.

Methanol (> 99.9mol%, from Rowe Scientific), n-hexane (> 95mol %, from Sigma-Aldrich), and acetone and were used as cleaning agents. Typically, such chemicals were used to clean the solid surfaces before each experiment.

Ultrapure nitrogen (N₂ colorless, non-reactive gas at purity 99.99 mol %) from BOC/Australia was used as a drying agent during surface cleaning steps. Nitrogen gas was used as a cleaner alternative to the compressed air for drying to prevent any potential contaminations that may extremely impact the liability of surface property investigations.

3.5 Instruments and measurements devices

Ultrasonic homogenizer (300 VT Ultrasonic Homogenizer/ BIOLOGICS) was used to separate NPs in different base fluids. The sonicator composed of two main parts including the generation part and the transducer part linked with each other by a power cord. The generation section comprises a control port with all indicators and regulators that govern the sonication energy (time and power). The transducer part, on the other hand, transforms the electric power to ultrasonic waves via solid titanium tip. The two parts of the sonicator can be compacted together or separated in a way allows the reduction of sound pollution via keeping the transducer part in a soundproof box. Mechanistically, the sonicator uses sound waves to disperse and suspend solid particles (i.e. fine and nanoparticles) in a liquid phase. In this context, the time and power of the sonication process are limited by several factors including the type, concentration and surface properties of NPs as well as the composition (i.e. salinity) of the liquid phase (Al-Anssari et al. 2016). A magnetic stirrer, 1500 RPM, made by Across International was utilized to mix NaCl with DI-water during the preparation of brine.

Surface preparation steps and particularly surface cleaning is an essential step in surface property measurements. Consequently, the plasma model Yocto, made by diener plasma-surface-technology, was used to clean and activate the solid surfaces. Mainly, plasma treatment can minimize contamination on calcite surface before

treatment with stearic acid or nanofluid and before surface measurements via an atomic force microscope (AFM). The plasma unit composed of the generator part (frequency: 100 kHz, power 30W), and vacuum pump (suction power: 0.75 m³/h). Typically, the programmed working period is 4 minutes. However, in the case of extensive contamination, the plasma treatment steps should be repeated more than once.

Four digits-electronic balance model BTA-623, made by PHOENIX Instruments was used in this study Figure 3-9. The high accuracy of this 4-digit device allows the accurate formulation of dilute nanofluids at small volume samples. For example, formulating of 20 ml 0.001 wt% nanofluid requires the weighing of 0.0002g of NPs to be dispersed in the base fluid. Formulating of such small sample help to minimize the waste and keep dealing with freshly formulated nanofluids at the desired concentration. In addition to NPs, the balance was used to weigh NaCl during brine formulation and to exactly weigh the calcite samples to use the accurate calcite to nanofluid weight ratio (i.e. 1/5 calcite mass/nanofluid mass).

The vacuum drying oven model VO-16020 made by Across International which connected to a vacuum pump model TW-1A made by Across International were used in this study for drying, and high-temperature-aging during calcite modification with stearic acid. The heating section of the vacuum drying oven stainless-steel chamber and two metal grids to place the solid samples or liquid containers on. The VDO unit can be used for heating purposes only or for vacuum only or for vacuum heading together according to procedure requirements.

The high-pressure/high-temperature setup (Figure), was used to allow the treatment of calcite samples with nanofluid to take place at reservoirs condition; including high pressure, high temperature, and salinity. This setup consists mainly of a stainless-steel cell designed to work under harsh conditions similar to reservoir conditions. For increasing the temperature of the treatment-cell to the designed degree, a fiberglass-sheathed heating tape with a power density 0.013 watt/mm², made by THERMOCOAX was used. The exceptional flexibility of the product allowed the total pending of the heading tape around the stainless-steel cell.

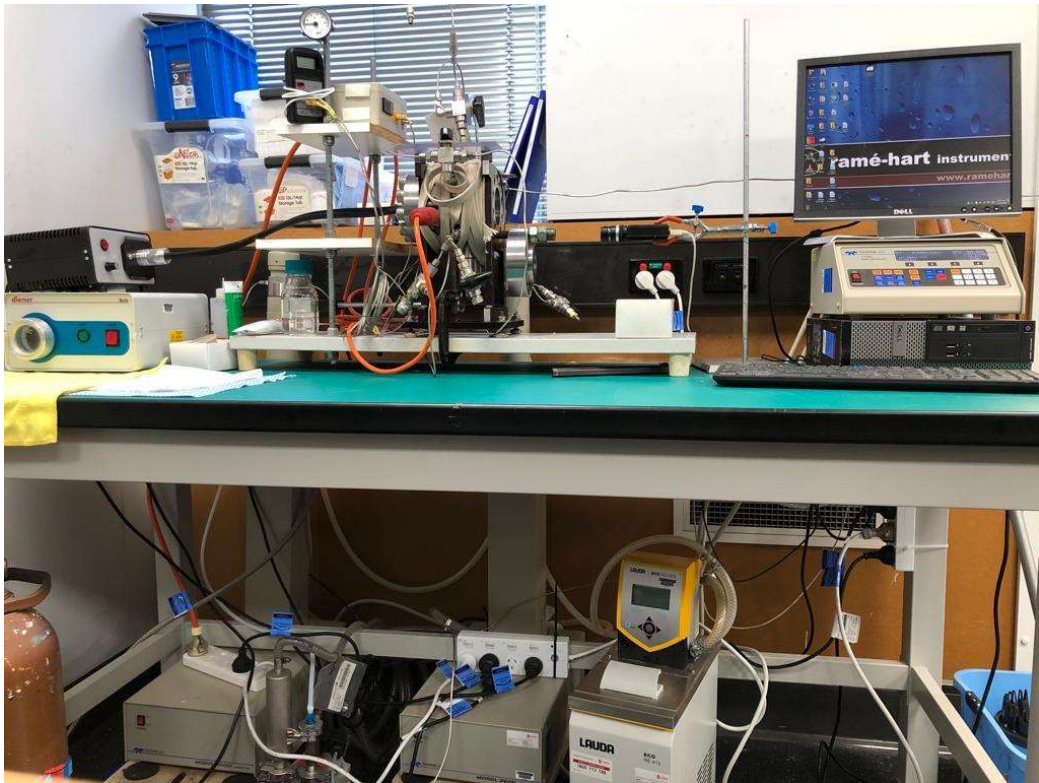


Figure 3-4 photographs of the high pressure/high-temperature setup.

Further, the temperature increase was controlled by digital thermal controller model TTM-002, TOHO which connected to a thermocouple model SA1XL, Omega was used. Eventually, to increase the pressure inside the treatment -cell to the desired pressure, Two high precision syringe pumps were used in this system with pressure accuracy 0.1% FS (Figure 3-4).

Experimentally, the pressure of the treatment-cell was increased by pumping CO₂ gas via the high precision syringe pump model 500D made by TELEDYNE. Then after stabilization of pressure and temperature inside the treatment-cell, the nanofluid was injected via an accumulator to immerse the calcite sample inside the treatment-cell by using the second-high precision syringe pump model 260D which also made by TELEDYNE. Before that, to avoid the potential interaction between calcite sample, nanofluid, and the CO₂ gas inside the treatment-cell, the CO₂ was equilibrated with the nanofluid before being injected into the treatment-cell. A high-pressure high-temperature equilibrator was used for this purpose and the equilibration state was indicated via observation pH rate of change (Sarmadivaleh et al. 2015).

The dynamic light scattering (DLS) and the zeta sizer features are compacted in the same device Nano ZS made by Malvern Instrument, UK. The Nano ZS is a high performance two angle particle and a molecular size analyzer. The DLS of the device allows the detection of aggregates and measurements of small or dilute samples. The main limitation of DLS is the sensitivity to light. Typically, the DLS is a laser-based technique that measures the particle size and particle size distribution for a sample placed in the measurement cell by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light. Thus, opaque samples with low transparency cannot give accurate results. In this context, Brownian motion is the backbone for particle size measurements by DLS. Brownian motion is defined as the movement of particles due to the random collision with the molecules of the liquid that surrounds the particles and due to the collisions between the adjacent particles. The key to Brownian motion for DLS measurement is the relationship between movement speed and size of the particle. Naturally, small particles move quickly and large particles move slowly. The relation between the particle size and particle speed due to Brownian motion is explained by the Stokes-Einstein equation (Eq. 3-1). This equation assumes the colloid particles are all spheres.

$$D = \frac{RT}{N_A * 6\pi * \eta * r} \quad \text{Equation 3-1}$$

where D is the diffusion coefficient (limits by the particle speed via Brownian motion). R is the gas constant, T is temperature, N_A is the Avogadro number, η is the solvent viscosity, and r is the hydrodynamic radius.

The theory of DLS measurements is based on the scattering of light passing through the colloid solution. Mechanistically, if a small particle is illuminated by a light source such as a laser source, the particle will scatter the light in all directions. As the particles move in all directions, the constructive and destructive phase addition of the scattered light will result in fluctuation of scattering light intensity. The DLS system measures the rate of the intensity fluctuation and then uses this value to measure the size of the particle.

The zeta potential of a colloid dispersion is a direct indicator of dispersion stability. Characteristically, higher (\pm) zeta potentials predict a more stable dispersion. A zeta-sizer model nano ZS made by Malvern Instrument is used in this study to measure zeta potential. Typically, the measurement is based on the response of charged particles to

an applied electric field. Experimentally, zeta potential measurement is conducted by introducing a small amount of colloid dispersion or emulsion to the sample container (measuring cell) and put in the cell into the device. The device software will automatically measure the accurate electric field strength, adjusts the reference beam intensity to ensure the optimal signal to noise ratio, collects and analyzes the data, and presents the results on the monitor of the computer.

Atomic force microscope (AFM) model DSE 95-200, Semilab was used to examine the changes in surface morphology after different steps of treatment with different fluids. The atomic force microscope is a laser-based technique. Describing the prob (cantilever with an attached bead of the defined radius (r), the components detecting the cantilever deflection (laser beam, photodiode) and the sample.

Studying the adsorption of NPs into solid surfaces require the use of microscopic devices to prob the adsorption, desorption, and precipitation behaviour of NPs into a solid surface in contact with nanofluid. To achieve this, scanning electron microscope (SEM) model 40EsB FIBSEM made by Zeiss Neon was used to 3D-analysis of silica NPs adsorption on calcite surface. In general, since calcite is a non-conductive substrate, the sample was coated with a platinum layer for more reliable results. The device is a double beam focussed ion beam SEM (FIBSEM) that armed with a field emission gun as well as liquid metal Ga^+ ion source.

Analyzing the surface elements at different stages of treatment is an essential measurement to understand the adsorption-desorption trend after being conducted or treated with different fluids. To achieve this, energy dispersive microscopy (EDS) model Oxford X-act SSD x-ray detector with Inca and Aztec software was used to analyze the surface elements of calcite surface before and after being treated with different fluids.

3.5.1 Modification of NPs hydrophobicity via silanization

Hydrophobicity of NPs is an essential factor influencing NPs adsorption on a solid surface. Consequently, the adsorption behaviour of both hydrophilic and hydrophobic

silica NPs was investigated. The hydrophobicity of NPs can be modified by changing the surface coating chemicals. To accomplish this, surface modification of silica NPs was performed by silanization, which is the reaction of solid surface with silane (Figure 3-). In general, chemical reaction with silane agent is a practical method to change the hydrophobicity of silica to more hydrophobic condition (Grate et al. 2012, London et al. 2013, Rostamzadeh et al. 2014).

Experimentally, 1 g silica NPs was dispersed in 50 mL ethanol via a sonicator (300 VT Ultrasonic Homogenizer/ BIOLOGICS) for 300 seconds to formulate NPs suspension. Moreover, a pre-hydrolyzed solution also formulated via dissolution of 0.7336 g (3-aminopropyl) triethoxysilane into a solution of 14.82 mL ethanol and 0.18 g H₂O (Al-Anssari, Barifceni, et al. 2018). The amount of silane, ethanol, and water was controlled by the number of hydroxyl groups moles that situated on 1 g of silica NPs (Ma et al. 2007, He et al. 2013). In this context, each (3-aminopropyl) triethoxysilane molecule requires three molecules of water for complete hydrolysis (Rostamzadeh et al. 2014). Drops of concentrated hydrochloric acid (HCl) were used to maintain the acidity of the modification solution (London et al. 2013) at pH below the isoelectric point of silica nanoparticles which is around 1 – 2 (Bhatti et al. 2014). The silanization formulation was mixed magnetically for 20 min and pipetted to the NPs suspension, and then obtained mixture was magnetically stirred for another 24 h, at ambient condition. Eventually, treated NPs were centrifuged and impregnated with ethanol for 1 day to remove the reversibly absorbed silane compounds and headed 70°C for 24 h for drying to produce dry hydrophobic (hybrid) NPs.

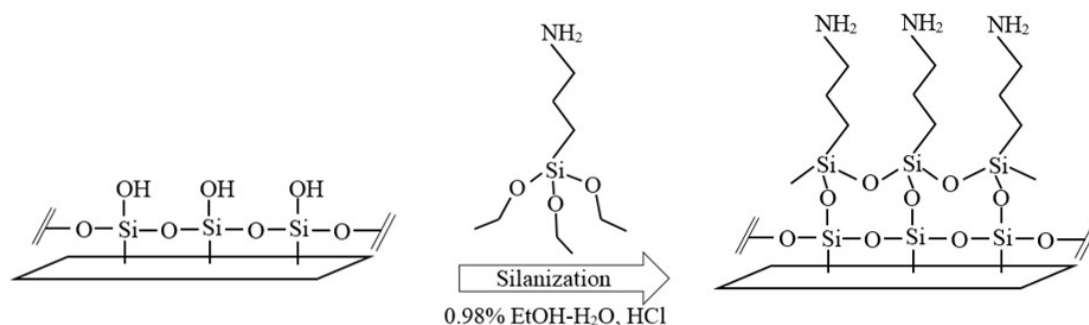


Figure 3-5 Attachment of (3-aminopropyl) triethoxysilane to silica nanoparticle surfaces (London et al. 2013).

3.5.2 Formulation of equilibrated brine and nanofluids

The equilibrium between aqueous phase, carbonate, and CO₂ is essential to avoid the dramatic dissolution of calcite and the subsequent changes in surface charge and morphology during nano-treatment (Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017). In addition, the formation brine is naturally at equilibrium with calcite and CO₂ inside carbonate reservoirs (Stumm and Morgan 1995).

Different salt concentrations were dissolved in DI water using magnetic stirrer (1500 RPM, Across International) to formulate brine at varied salinity. These different brines were used as a base-fluid for the nanofluid. On the other hand, nanosuspensions were prepared via sonication of silica NPs in brine using ultrasonic homogenizer (Al-Anssari, Barifcani, et al. 2018). Different weights of dry SiO₂ hydrophilic (bare) or hydrophobic (hybrid) NPs (0.002, 0.004, 0.01, 0.014, 0.02 g) were dispersed in 20 ml of brine at various salinity (0 – 5 wt% NaCl) to formulate nanodispersions at various NP loads (0.01, 0.02, 0.05, 0.07, 0.10 wt% SiO₂). Each suspension was sonicated for 120 seconds to assure a suitable homogeneity. Note that once meet water, NPs tends to rapidly aggregate due to the high surface energy (Metin et al. 2011, Metin, Bonnacaze, et al. 2012). Effective mixing is the only way to break down these aggregates and leave the NPs individually suspended. Also, to avoid the potential dissolution of calcite surface during nano-treatment, CO₂, calcite, and nanodispersion were all equilibrated in a mixing reactor (

Figure 3-). In this context, the nanosuspension was mixed with carbon dioxide and off-cuts of calcite in the equilibrators at the prescribed pressure and temperature for each experiment for 1 hour (Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017). Characteristically, equilibrium is established when no more CO₂ dissolves in the nanofluid (El-Maghraby et al. 2012) which was indicated by constant pH.

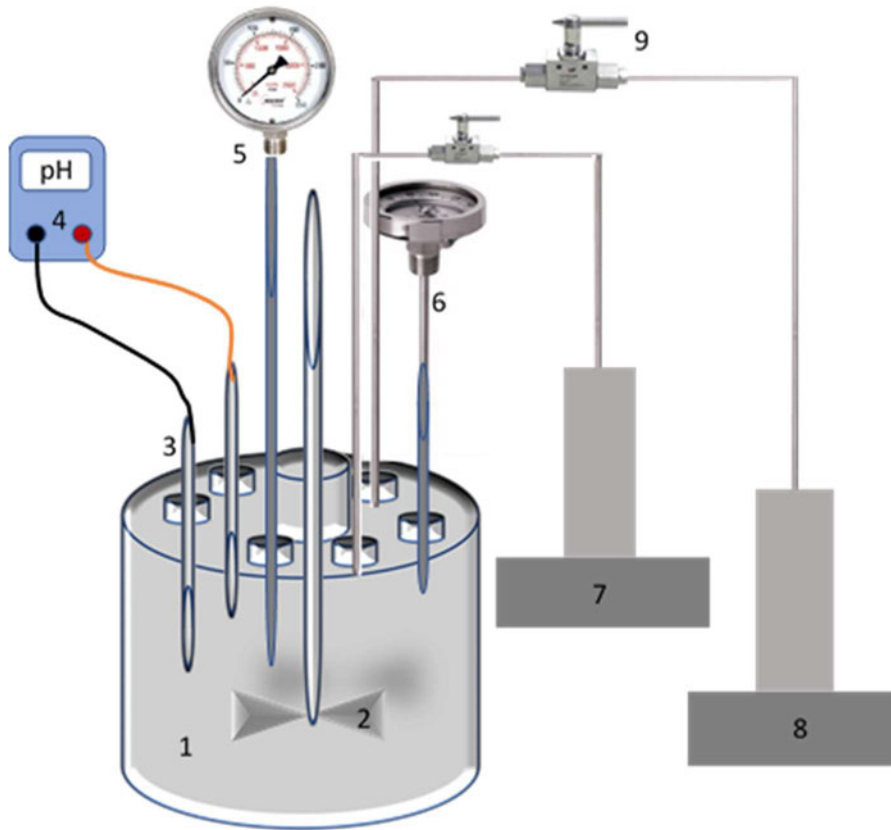


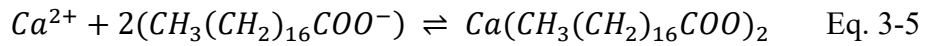
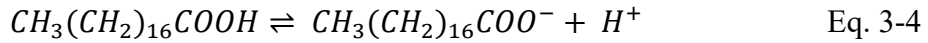
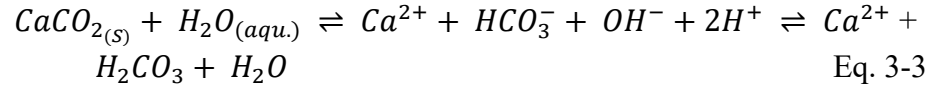
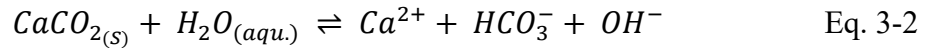
Figure 3-6 Schematic of the high pressure-high temperature equilibrator: (1) equilibration vessel, (2) the agitator, (3) pH electrode, (4) pH meter, (5) pressure gauge, (6) thermometer, (7) brine or nanofluid pump, (8) CO₂ pump, (9) valve.

3.5.3 Preparation of carbonate surface

Surface cleaning processes are fundamental in surface treatment investigations since any remaining contaminants can impact the surface charges (Ma et al. 2013) and consequently the adsorption scenario of NPs. Thus, calcite samples were washed with equilibrated water to remove any carbonate dust on the surface. Subsequently, the samples were dried for 60 min at 90 °C and then exposed to air plasma for 10 min (using a Diemer Yocto instrument) to remove any potential organic contaminants (Iglauer et al. 2014).

3.5.4 Modification of original calcite with stearic acid

To simulate all the potential scenarios inside oil reservoirs including oil-wet and water-wet rocks, some calcite samples were treated with stearic acid to achieve oil-wet substrates. This helps in the study of the adsorption phenomena of NPs on both water-wet (hydrophilic) and oil-wet (hydrophobic) carbonate formations. Here, the cleaned calcite samples were first submerged for 30 min in 2 wt% equilibrated NaCl brine at pH = 4 to support the later adsorption of acid on calcite surface. Typically, ionization of carboxylic acid groups and the availability of positive sites on the carbonate surface are controlled by the pH and ionic strength of the aqueous phase (Eqs. 3-2, 3-3, 3-4, and 3-5) (Hoeiland et al. 2001). Subsequently, the samples were dried with ultra-pure nitrogen to remove the excess brine from the surface and eventually immersed in 0.01M steric acid at ambient conditions for 7 days. Mechanistically, carboxylate molecules from stearic acid solution are adsorbed on the positive sites of the calcite surface.



3.5.5 Nano-treatment of carbonate surfaces

To investigate the adsorption behaviour of silica NPs on different calcite samples at reservoirs conditions, nano-treated samples were prepared by submerging of calcite substrate in a nanofluid at designed exposure time, temperature and pressure. To accomplish this, each clean calcite sample (original or modified with stearic acid) was vertically rested in the nano-treatment vessel. Equilibrated nanofluids were pumped directly from the equilibrators into the treatment vessel which maintained at the same temperature and pressure of the equilibrators using syringe pump (Teledyne D-260, pressure accuracy of 0.1% FS). A constant immersion ratio of 10g nanofluid for each 1g of calcite was used to achieve duplicated interaction environment between calcite and nanoparticles. Further, the pressure inside the equilibrators and the nano-treatment vessel was increased using a high precision syringe pump (Teledyne D-500, pressure accuracy of 0.1% FS) to the desired value (0.1, 10, 20 MPa). Also, a heating tape was used to maintain the temperature at the pre-designed values (296, 323, or 343 K).

3.5.6 Characterization of NPs stability and adsorption

Adsorption of NPs on a solid surface is key to the success of nanofluid in subsurface applications. Thus, adsorption characteristics and particularly the ratio between reversibly and irreversibly adsorbed NPs were investigated using several techniques including atomic force microscopy (AFM, instruments model DME 95-200, Semilab), scanning electron microscopy (SEM, Phenom XL, PHENOMWORLD), and energy dispersive X-ray spectroscopy (EDS, Phenom XL, PHENOMWORLD). The nano-treated surfaces were exposed to different solvents including DI water and brine in different tests. After each step, the substrate was dried with N₂ gas, then EDS, and AFM measurements applied to study the irreversibility of NPs adsorption. Before that, stability and aggregation behaviour of NPs in the liquid phase were investigated via particle size distribution (PSD) using dynamic light scattering (DLS, Zetasizer, ZS Malvern). DLS used in this study is a laser-based technique and is very sensitive to the opacity of the fluid. Subsequently, relatively dilute nanofluids (0.05 wt% SiO₂) were used to conduct this measurement.

3.6 Results and Discussion

NPs efficiency as EOR agent at reservoirs condition may be different from that evaluated at ambient conditions using pure rock samples (Al-Anssari, Arif, Wang, Barifcani, Lebedev, et al. 2018). In this context, reservoirs conditions including temperature, pressure, and salinity can impact rocks properties (Arif et al. 2019) and potentially NPs stability (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). Furthermore, rock heterogeneity can limit the mobility and distribution of NPs through the formation (Rahman et al. 2016, Arif et al. 2019). The presented and discussed data in this section provide the first insight into these potentials.

3.6.1 Stability-aggregation characterization of NPs

Characteristics of the formulated nanosuspensions including NPs zeta potential, suspensions acidity, and salinity can impact the stability and aggregation rate of NPs (Espinasse et al. 2007, Metin, Bonneau, et al. 2012, Mondragon et al. 2012). Thus, different nanofluid composed of 0.1 wt% bare or hybrid NPs dispersed in base fluids under constant acidity (pH = 6.25) was formulated. The stability was monitored visually (Fig.3-7) and by particle size distribution (PSD) measurement (Fig 5, and 6).

The surface of bare silica NPs is appreciably negatively charged owing to the dissociation of the surface silanol (SiOH) groups (Rostamzadeh et al. 2014). Although, the pH of the suspension was 6.25 ± 0.25 which is way above the isoelectric point of silica suspension (IEP of SiO₂ occurs at pH = 2 – 3) (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017), visual evaluation of bare silica nanofluid showed a dramatic precipitation and sedimentation after only 6 hours with total phase separation after less than 3 days even when the NPs were dispersed in DI-water(Figure 3-). Here, the instability of nanofluid was characterized by the clarity of the liquid phase (base fluid) rather than the sediment height considering the impact of water content in the precipitant on sediment height. Characteristically, the relatively high surface energy of NPs owing to the highest surface area to particle size ratio (Dugyala et al. 2016) is the main reason for the observed aggregation activities of NPs.

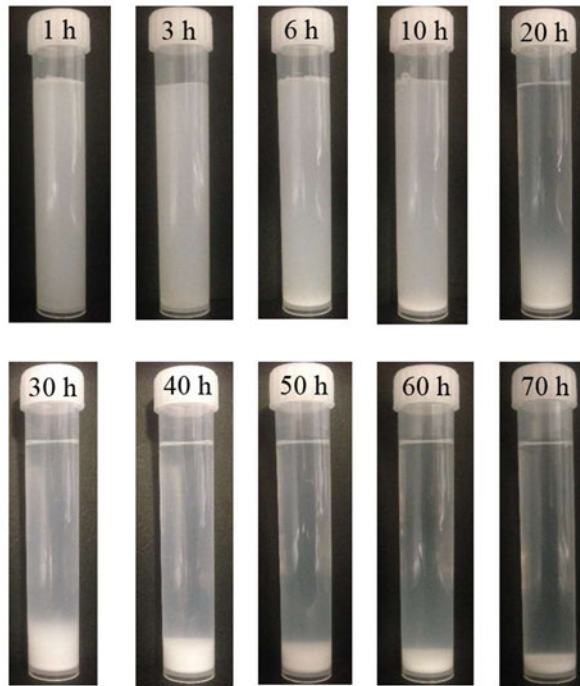


Figure 3-7 Photograph of the appearance of nano-suspensions (0.05 wt% bare SiO₂ dispersed in DI-water at pH = 6.25) at different times (h) after sonication process.

Average particle size (APS) measurements, based on particle size distribution (PSD) measurements were conducted on nanofluid samples. To assure an identical condition and thus measurements consistency, all samples were taken from the same point of nanofluid container, just below the top of the container. Samples were taken after different intervals from the end of sonication process. At these times, samples were taken from a point just below the upper surface of the nanofluid. PSD measurement on silica nanofluid reveals the formation of nanoaggregates directly after preparation of nanodispersion (Figure 3-8).

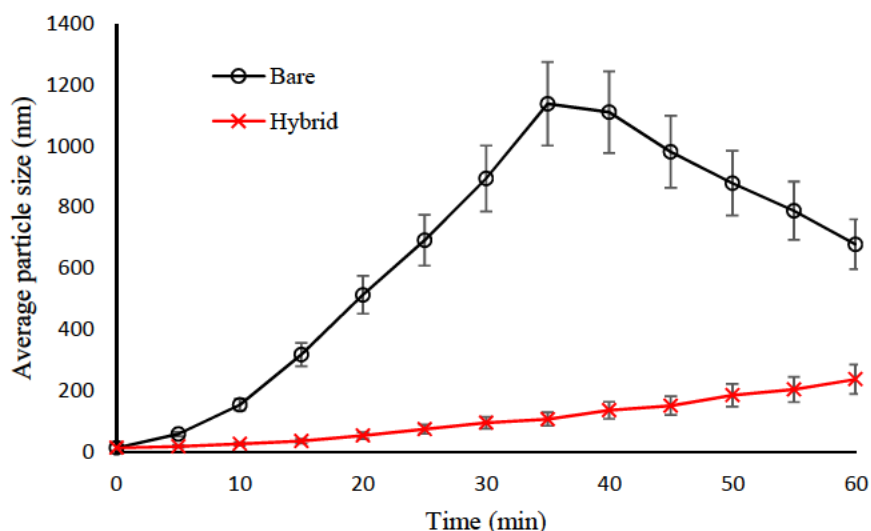


Figure 3-8 Average particle size (APS) measurements for both bare and hybrid silica nanoparticles dispersed in DI-water as a function of time.

Results showed that the PSD of bare NPs dramatically increased with time reaching a plateau (i.e. after 35 – 40 min from the end of sonication) then unexpectedly decreased with time. Different PSD trend, however, was observed for the hybrid silica nanofluid. Significantly smaller aggregates were formulated with time and continued to grow over the test period (60 min). Typically, the aggregation of NPs after sonication in the liquid phase was consistent with the reported data in the literature (Metin et al. 2011, Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). Nevertheless, the later decreased in APS was questionable. Further investigation was carried out to study this phenomenon. The APS was measured for each nanofluid using samples taken from six different points at a different depth of the nanofluid (Figure 3-). To achieve this, 6 duplicated tubes were filled with the exact same nanofluid. Then a syringe with a long nick needle was used to take samples from each tube from the desired height of the fluid. A similar approach has been conducted in our earlier work (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). This was to help measure aggregates size distribution in the nanofluid at different heights.

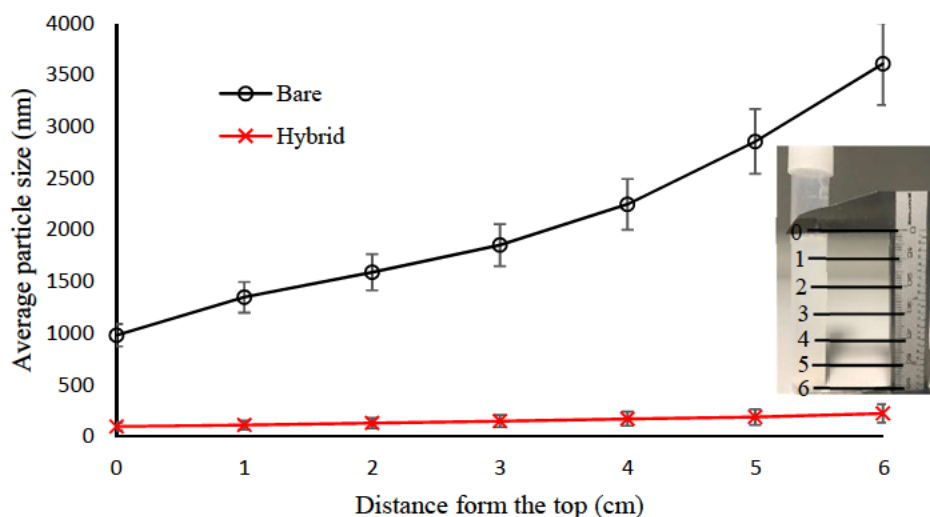


Figure 3-2 Average particle size (APS) measurements, for both bare and hybrid silica NPs, dispersed in DI-water as a function of distance from the top interface. Nanofluids were left for 45 min then samples were taken.

Figure 3-5 indicates that aggregates sizes of bare NPs were significantly bigger in the lower parts of the samples. The average size of these aggregates can reach very large sizes on the bottom side of the nanofluid (i.e. $\approx 3.7 \mu\text{m}$ in the bottom), which appears to be out of the nano-scale. The observations are consistent with those in the literature (Metin, Baran, et al. 2012, Mondragon et al. 2012). Considering the efficient sonication processes which most likely produces homogeneous nano-suspension, the variation of nano-aggregated size at different heights of the nanofluids is possibly related to the precipitation of larger aggregates from the top to the bottom side of the sample. Typically, the heavier weight of large aggregated promotes the precipitation of these aggregates. This explains the sudden reduction of aggregate size after 35 – 45 min (Fig. 3-5) due to the downward mobilization of heavier clusters to the bottom by the effect of gravity leaving the sprightly and swift (smaller) once on the top.

3.6.2 Reversible and irreversible adsorption of NPs

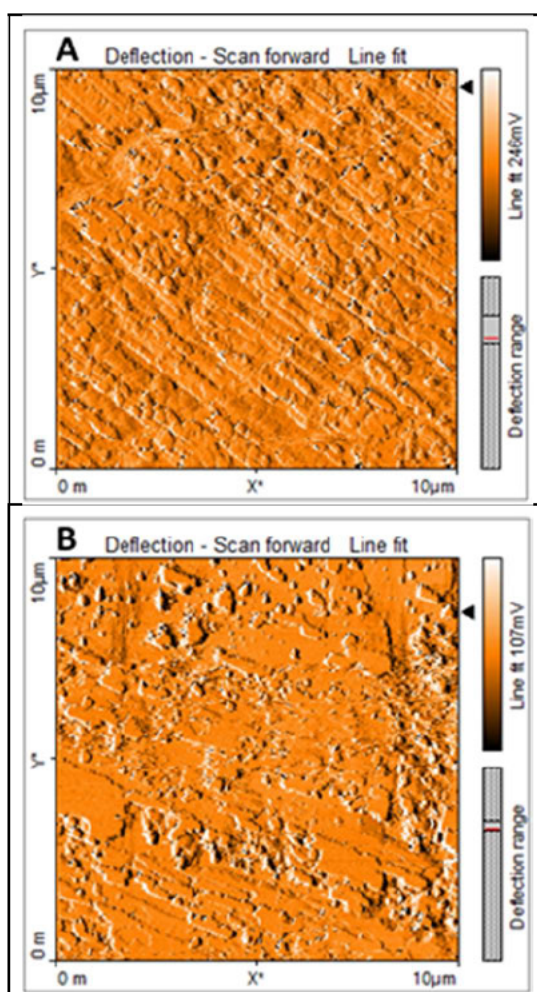
Adsorption and the potential desorption of NPs on a solid surface is a complicated phenomenon. Nano-treatment conditions including pressure and temperature have a direct impact on NPs settlement onto the solid surface and consequently the quality of

surface treatment. Thus, it is crucial to investigate the effect of treatment conditions on the adsorption-desorption behavior of NPs on the carbonate surface. To accomplish this, calcite samples were treated with the same nanofluid at different temperatures and pressures and the adsorption behavior was investigated by AFM, EDS measurements, and SEM images.

3.6.2.1 AFM measurement

Although the used calcite was smooth (18 – 54 nm), adsorption of nanoparticles may change the surface roughness and influence the morphology of the sample (Al-Ansari et al. 2016).

Figure 3-3 shows the dramatic effect of nano-treatment conditions on NPs adsorption and thus surface roughness of carbonate surfacers.



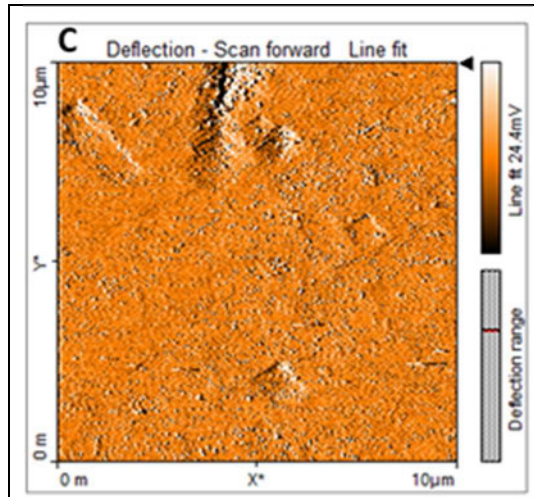


Figure 3-3 Atomic Force Microscopy of nano-treated calcite samples using bare NPs: A) at 70 °C and 0.1 MPa, B) 25 °C and 15 MPa, and C) using hybrid NPs at 25 °C and 15 MPa.

Immersing pure calcite sample in nanofluid at 70 °C and 0.1 MPa will raise the surface roughness to around 2490 nm (Figure 3-3, A). On the other hand, nano-treatment of the similar sample with identical nanofluid but at 25 °C and 15 MPa can only raise the surface roughness up to 396 nm. These results revealed a vital impact of nano-treatment operation condition on NPs adsorption and thus on the change in surface roughness (Figure 3-3, B). Also, hybrid NPs adsorption on calcite was examined (Figure 3-3, C). Thus, the effect of nano-treatment on surface morphology and roughness were addressed after each treatment step (Table 3-1) to understand the nature of NPs adsorption on carbonate surfaces.

Table 3-1 The surface roughness of pure and nano-treated carbonate surface with different nanoparticles at different treatment conditions.

Calcite surface condition	Nanoparticle type	Treatment pressure (MPa)	Treatment temperature (°C)	Nanofluid concentration (SiO ₂ wt%)	RMS* surface roughness (nm)
Pure calcite	-----	-----	-----	-----	42± 12
Oil-wet calcite	-----	-----	-----	-----	69± 15
Pure calcite	bare	0.1	23	0.1	450± 75
Pure calcite	hybrid	0.1	23	0.1	77± 15
Pure calcite	bare	0.1	50	0.1	1270± 125
Pure calcite	bare	0.1	70	0.1	2500± 175
Pure calcite	hybrid	0.1	70	0.1	250± 15
Oil-wet calcite	bare	0.1	70	0.1	2570± 180
Oil-wet calcite	hybrid	0.1	70	0.1	125± 15
Pure calcite	bare	15	23	0.1	313± 18

Pure calcite	bare	15	50	0.1	463± 22
Pure calcite	bare	15	70	0.1	604± 31
Pure calcite	bare	15	23	0.05	116± 15
Pure calcite	bare	15	50	0.05	178± 17
Pure calcite	bare	15	70	0.05	236± 21

*Root mean square, roughness measured by atomic force microscopy

Table 3-1 reports the statistics for the effect of NPs adsorption on calcite surface roughness. Although adsorption of bare NPs at ambient pressure can significantly increase carbonate surface roughness (Nwidee et al. 2017), treating the samples with nanofluid at high pressure showed insignificant influence on surface morphology. Further, nano-treatment with hybrid NPs has the minor influence of surface roughness indicating a uniform nano-coating of the carbonate surface. Mechanistically, the rapid aggregation of bare NPs and the subsequent accelerated precipitation of the formed aggregates leads to dramatic sedimentation of these nano or possibly micro-aggregates on solid surfaces (Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017, Nwidee et al. 2017). Mostly, these aggregates reversibly attached to the surface after precipitation by gravity effect (Al-Anssari, Nwidee, Ali, et al. 2017). On the other hand, the limited aggregation of hybrid NPs keeps these nanostructure suspended in the liquid phase. Subsequently, hybrid NPs can only reach the solid surface via a Brownian motion to adsorb irreversibly into the surface. This limited adsorption of hybrid NPs forms a uniform mono or double nano-layers (Metin, Baran, et al. 2012, Mondragon et al. 2012). This phenomenon was confirmed by the ultimately limited change in surface roughness after treatment with hybrid silica nanofluid.

The last three rows of Table 3-1 provide data about the sole effect of temperature on nano-treatment at reservoirs pressure (15 MPa), and low NPs concentration (0.05wt%). Keeping all other variables constant (Pure calcite, bare, 15 MPa, 0.05 wt% NPs), the increase in temperature from 23 °C to 70 °C results in surface roughness increase from 116 to 236 nm. This change in surface roughness is very limited referring to slight adsorption of NPs. On the other hand, at ambient pressure (0.1 MPa), and relatively high NPs concentration (0.1 wt%) the effect of temperature increase was more significant and surface roughness increased from 1270 to 2500 nm. This more significant changes in surface roughness at ambient pressure is mainly related to the dissolution of the carbonate surface (Hamouda and Gomari 2006, Alroudhan et al. 2016) rather than the adsorption of NPs.

3.6.2.2 EDS measurements

EDS results (Table 3-2) Provides data about adsorption of silica (Si) NPs after immersing with the same nanofluid (0.05 wt% bare or hybrid SiO₂) but at different pressure, temperature and initial surface wetness of calcite. Consistent with the outcomes of AFM measurements, regarding treatment with hybrid silica nanofluid, traces amount of Si was detected on all the tested points on carbonate sample. Note that, five different points were selected for EDS measurements at the tested surface of each sample and the average was calculated. Characteristically, the low measured Si ratio proves the absence of large aggregates and indicate the formation of thin NPs-layer. Experimentally, significantly higher Si ratios were detected after treatment with bare silica nanofluid with relatively high variation between different points. These high ratios result from the accumulation of large silica-aggregates (Zhang et al. 2015). In this case, most of the NPs are reversibly attached to each other and not adsorbed directly on carbonate surface (Al-Anssari et al. 2016).

EDS results also confirm the effect of pressure and temperature on NP adsorption. In this context, results show that the increase in temperature until 50°C has no significant effect on the adsorption of bare NPs. In this context, Hamouda and Gomari (2006) revealed that below 50°C, the carbonate surface entirely positively charges. However, with further increase in temperature (≤ 50 °C), the adsorption of such bare NPs decreases with temperature and reached a minimum value at 70°C (the highest tested temperature). Mechanistically, the change in surface charge of carbonate from positive to zero and then negative as temperature increased (Hamouda and Gomari 2006) is the main reason for this reduction in NPs adsorption with a potential desorption process of already attached NPs at this higher temperature range. In contrast, the adsorption of hybrid NPs increases with temperature on both oil-wet and water-wet carbonate surfaces. Basically, hybrid NP carries no surface charge (Rodriguez Pin et al. 2009) and the reduction of carbonate surface charge with temperature support the deposition of hybrid NPs.

Table 3-2 Chemical characterization of carbonate surfaces that treated with different nanofluids base on the average of five different points on each surface.

Calcite	nanoparticles	Temperature (°C)	Pressure (MPa)	Calcium % Ca	Carbon % C	Oxygen % O	Silicon % Si
Pure calcite	non	23	0.1	20.7	28.4	50.9	0
oil-wet calcite	bare	23	0.1	20.8	23.1	53.7	2.4
oil-wet calcite	bare	23	15	20.3	22.9	53.5	3.3
oil-wet calcite	hybrid	23	0.1	21.1	27.5	51.2	0.2
oil-wet calcite	hybrid	23	15	21.5	26.7	51.4	0.4
Pure calcite	bare	23	0.1	19.1	21.7	54.3	4.9
Pure calcite	bare	23	15	19.2	20.1	55.5	5.2
Pure calcite	hybrid	23	0.1	21.6	26.5	51.7	0.2
Pure calcite	hybrid	23	15	22.1	26.6	51.2	0.1
Pure calcite	bare	50	0.1	19.5	21.5	54.5	4.5
Pure calcite	hybrid	50	0.1	21.9	26.5	51.1	0.5
Pure calcite	bare	70	0.1	20.4	23.9	53.6	2.1
Pure calcite	hybrid	70	0.1	22.2	22.9	53.1	1.8
oil-wet calcite	hydrophilic	70	0.1	22.3	23.2	52.9	1.6
oil-wet calcite	hybrid	70	0.1	22.6	23.6	52.6	1.2

3.6.2.3 SEM images

NPs adsorption was evaluated with a scanning electron microscopy (SEM) and images showed the presence of silica clusters on both oil-wet and pure calcite surfaces (Figure 3-) when treated with bare silica nanodispersion at ambient and high pressure.

SEM images indicated a partial agglomeration of bare silica NPs into larger clusters confirming the APS results in Figure 3-, and Figure 3-. Moreover, the size of clusters decreases with pressure (Figure 3-11. A and B). Typically, the effect of CO₂-pressure on the pH of the nanofluid explains the formation of these larger clusters. Characteristically, the original pH of silica nanofluid was 6.25 which is far enough from the isoelectric point (IEP, pH = 2 – 3) of silica nanofluid (Al-Anssari, Wang, Barifcani, Lebedev, et al. 2017); however, the increase in CO₂-pressure brings the pH to a value close to the IEP leading to an accelerated agglomeration process between neighbouring NPs. Mechanistically, the low or zero repulsive force between particles at this low pH (e.g. at or near the isoelectric point IEP) increases the aggregation rate after each collision between particles (Nooney et al. 2015, Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). Consequently, the more and larger clusters will be

formed and electrochemically (irreversibly) adsorbed or gravitationally precipitated (reversibly) on carbonate surface.

Furthermore, immersing these nano-treated surfaces in DI-water at the same pressure led to smaller nano-silica cluster, which confirmed the degradation and detachment of nanoparticles from silica agglomerates and re-dispersing in the water phase due to the break of equilibrium condition.

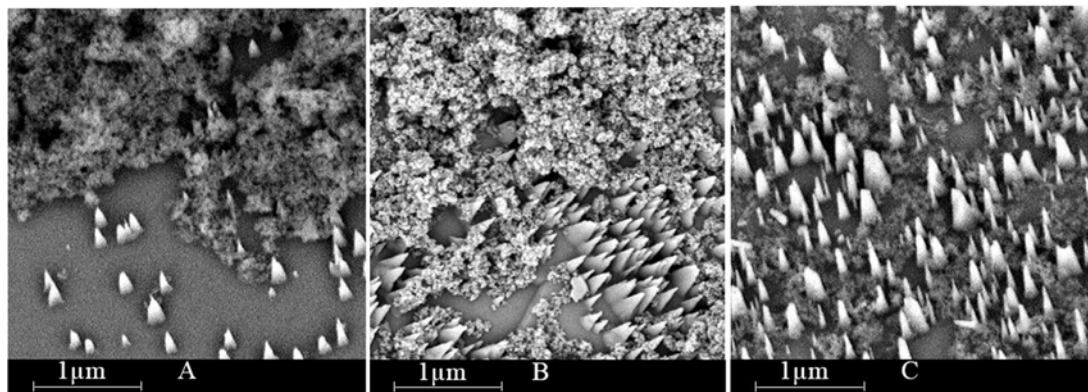


Figure 3-11 SEM images of nano-treated oil-wet carbonate surface: (A) hydrophilic NP at 0.1 MPa, (B) hydrophilic NP at 20 MPa, (C) nano-treated sample after immersing DI-water. The amorphous looking material is the nano-clusters and the small pyramid looking structures are the dissolved carbonate surface.

3.7 Conclusions

Nanofluid is a dispersion of nanoparticles (NPs) in a base fluid. Nanofluid flooding is a potential approach for enhanced oil recovery (EOR). To give the first insight on NPs adsorption onto carbonate surface at the subsurface condition, a series of dynamic light scattering (DLS) studies were conducted, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) measurements. It was found that only a limited amount of hybrid (silanized) silica NPs could be adsorbed by oil-wet and water-wet calcite surface at ambient and reservoir conditions (Metin, Baran, et al. 2012, Mondragon et al. 2012). Also, the average particle size (APS) measurement, which based on particle size distribution measurement, showed a limited aggregation of hybrid NPs once dispersed in the liquid phase (Nooney et al. 2015, Al-Anssari, Arif, Wang, Barifcani, and Iglauer 2017). This stable behaviour of hybrid NPs supports the formation of a monolayer NP cluster on

the treated surfaces. In contrast, the dramatic agglomeration of bare silica NPs when dispersed in the base fluid result in large silica aggregates (Metin et al. 2011). Additionally, immersing the carbonate (calcite) sample in bare silica nanofluids result in precipitation of large silica clusters on the solid surface. This was proved by the significant increase in surface roughness (from 42 nm to 2500 nm) when measured using AFM. Most of bare NPs clusters, however, are reversibly adsorbed on calcite surface and easy to get detached when flushed with solvent (i.e. DI-water). It was also found that at high pressure, small nanoclusters were distributed more uniformly along the nano-treated substrate. Further, EDS measurements proved the presence of silica in all the tested points with narrow and adequate ratios. Nevertheless, at ambient pressure, significantly large silica clusters were separately distributed on the nano-treated surfaces with very wide differences in silica ratios (1.2 – 5.2 % Si). Moreover, although temperature values below 50°C showed no significant effect on nanoparticle adsorption, increasing the temperature above 55 °C decreases silica adsorption and thus the effect of nanofluid on surface wettability. Further, flushing the nano-treated surfaces with DI-water can lead to dramatic desorption of adsorbed bare NPs from the surface. We conclude that the attachment of NPs, after nanofluid injection into carbonate surface, are mostly reversible adsorption process.

Chapter 4 **Conclusion and Recommendations**

4.1 Conclusion

This study reported adsorption measurements of silica nanoparticles (NPs) with different initial hydrophilicity into oil-wet and water-wet carbonate surfaces at reservoirs conditions to represent more realistic subsurface scenarios. Carbonate oil reservoirs, even the mature ones, are naturally fractured oil-wet and mixed-wet which dramatically reduces the recovery rate of these reservoirs. Injection of nanofluids; dispersions of solid NPs in liquid phase, have drastic impact on the interfacial properties at the fluid/rock and fluid/fluid interfaces due to mobility, penetration, and adsorption of such NPs into the porous media. Accordingly, there is a direct effect of NPs (i.e. silica NPs) on hydrocarbon production during enhanced oil recovery (EOR) processes. Further, adsorption of NPs into fluid/rock interface, which is the topic that this study concentrated on, is key for such impact of NPs on the recovery rate.

The following deductions are drawn from this study:

1. SiO₂ NPs can be very efficient for chemical EOR applications even at reservoirs conditions including high pressure, temperature, and salinity.
2. Initial hydrophilicity of NPs (hydrophilic or hydrophobic) can dramatically impact the adsorption of such NPs into oil-wet and water-wet (pure) calcite surfaces.
3. Hydrophobic NPs (i.e. Hybrid NPs; SiO₂ NPs silanized with 3-aminopropyl triethoxysilane) only poorly adsorb into oil-wet and water-wet calcite surfaces at all studied conditions revealing lower potential of such hybrid NPs as a wettability alteration agent.
4. The average particle size (APS) data based on the particle size distribution (PSD) measurements of the dispersed NPs in the liquid phase (nano-colloidal) indicated very limited growing of hybrid NPs when dispersed in liquid phase revealing low aggregation rate and high stability. Such stable behaviour of hybrid NPs may support the formation of only monolayer of NP cluster on the treated surfaces leaving higher concentration of hybrid NPs freely suspended in the liquid phase. This phenomenon induces the potential of hybrid NPs as

interfacial tension reduction agent due to the effect of such NPs on the oil/water (fluid/fluid) interface rather than the fluid/rock interface.

5. The dramatic agglomeration of hydrophilic (bare) silica NPs; in contrast, when dispersed in the base fluid, result in large and heavy silica aggregates. Such heavy aggregates are easy to be precipitated into rock surfaces and this explain the significant adsorption of hydrophilic NPs onto oil-wet and water-wet calcite surfaces. Such phenomenon gives high potentials for hydrophilic NPs as wettability alteration agent in EOR processes.
6. At high pressure (15 MPa), small nano-clusters were distributed more uniformly along the nano-treated substrate. This was proved by SEM images and AFM measurements.
7. The total coverage of calcite surfaces via NPs priming was proved by EDS measurements at all treatment conditions. However, at ambient pressure, significantly large silica clusters were separately distributed on the nano-treated surfaces with very wide differences in silica ratios (1.2 – 5.2 % Si).
8. Increased temperature (above 50°C) reduces the adsorption rate on silica NPs into calcite surface. This is mainly due to the inversion of calcite surface charge from positive to negative charge at such temperatures. Thus, the charges difference between NPs and calcite surface is the prime mechanism for NPs adsorption into calcite surface.

4.2 Recommendations for Future Work

The data on the adsorption behaviour of NPs into porous media that available in the literature is very minimal, and almost all of it at pure surfaces (NPs, and solid surfaces), and ambient conditions (i.e. at atmospheric pressure, and no salinity). In the light of results discussed in this study, showing the greater influence of initial surfaces hydrophilicity, temperature, and salinity on the adsorption scenarios of NPs into carbonate rocks, a systematic study of the effect of various reservoirs rocks, pressure, and higher electrolyte concentrations (additional to Na, and Cl ions) on the adsorption behavior of different NPs at various initial hydrophilicity into various surfaces is needed. Thus, to achieve further insights for understanding of the adsorption behaviour

of NPs onto reservoirs rock at subsurface conditions, this study recommends bridges to the following gaps:

1. The current work applies to standard surfaces (i.e. pure calcite $\approx 99.9\%$ CaCO_3) while, even in carbonate reservoirs, rocks composition may be different making the applicability of the reported data limited.
2. The current data apply for carbonate reservoirs with a limited range of designed conditions (i.e. pressure of 0.1 and 15 MPa, temperature of 23, 50, 70 °C, salinity of 0, and 0.1 wt% NaCl) with NPs concentration of 0.05, and 0.1 wt% SiO_2). A field scale analysis at reservoirs conditions including wider range of pressure, temperature, and salinity may provide better insight.
3. Simulation model should account for the adsorption of NPs on rock/fluid interface.

APPENDIX A

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Author/Co-Authors	Conception and Design	Acquisition of Data and Method	Data Conditioning and Manipulation	Analysis and Statistical Method	Interpretation and Discussion	Final Approval	Total % contribution
Zain-Ul-Abedin Arain	90	80	85	80	80	80	82.5
Author Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Sarmad Al-Anssari	5	5	3	5	6	5	4.83
Co Author 1 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Muhammad Ali	0	3	2	2	2	0	1.50
Co Author 2 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Shoaib Memon	0	3	2	2	2	0	1.50
Co Author 3 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Masood Ahmed Bhatti	0	3	2	4	2	1	2.00
Co Author 4 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Christopher Lagat	0	3	2	2	2	4	2.17
Co Author 5 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							06/05/2020
Mohammad Sarmadivaleh	5	3	4	5	6	10	5.50
Co Author 6 Acknowledgment: I acknowledge that these represent my contribution to the above research output. Signed:							
Total %	100	100	100	100	100	100	100.00

REFERENCES

- Abdelfatah, Elsayed, Maysam Pournik, Bor-Jier Ben Shiau, and Jeffrey Harwell. 2017. "Modeling Coupled Transport, Aggregation, and In Situ Gelation of Nanoparticles in Porous Media." SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Jakarta, Indonesia, 2017/10/17/.
- Abhishek, Rockey, Aly A. Hamouda, and Ivan Murzin. 2018. "Adsorption of silica nanoparticles and its synergistic effect on fluid/rock interactions during low salinity flooding in sandstones." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 555:397-406. doi: <https://doi.org/10.1016/j.colsurfa.2018.07.019>.
- Afolabi, Richard O., and Esther O. Yusuf. 2018. "Nanotechnology and global energy demand: challenges and prospects for a paradigm shift in the oil and gas industry." *Journal of Petroleum Exploration and Production Technology*. doi: 10.1007/s13202-018-0538-0.
- Afolabi, Richard O., and Esther O. Yusuf. 2019. "Nanotechnology and global energy demand: challenges and prospects for a paradigm shift in the oil and gas industry." *Journal of Petroleum Exploration and Production Technology* 9 (2):1423-1441. doi: 10.1007/s13202-018-0538-0.
- Ahmadi, Mohammad Ali, and Seyed Reza Shadizadeh. 2012. "Adsorption of Novel Nonionic Surfactant and Particles Mixture in Carbonates: Enhanced Oil Recovery Implication." *Energy & Fuels* 26 (8):4655-4663. doi: 10.1021/ef300154h.
- Al-Anssari, Sarmad. 2018. "Application of Nanotechnology in Chemical Enhanced Oil Recovery and Carbon Storage." Ph.D. Thesis, Department of Chemical Engineering, Curtin University.
- Al-Anssari, Sarmad, Muhammad Arif, Shaobin Wang, Ahmed Barifcani, and Stefan Iglauer. 2017. "Stabilising nanofluids in saline environments." *Journal of Colloid and Interface Science* 508:222-229. doi: <https://doi.org/10.1016/j.jcis.2017.08.043>.
- Al-Anssari, Sarmad, Muhammad Arif, Shaobin Wang, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2017a. "CO₂ geo-storage capacity enhancement via nanofluid priming." *International Journal of Greenhouse Gas Control* 63:20-25. doi: 10.1016/j.ijggc.2017.04.015

- Al-Anssari, Sarmad, Muhammad Arif, Shaobin Wang, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2017b. "Wettability of nano-treated calcite/CO₂/brine systems: Implication for enhanced CO₂ storage potential." *International Journal of Greenhouse Gas Control* 66:97-105. doi: <https://doi.org/10.1016/j.ijggc.2017.09.008>.
- Al-Anssari, Sarmad, Muhammad Arif, Shaobin Wang, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2018. "Wettability of nanofluid-modified oil-wet calcite at reservoir conditions." *Fuel* 211:405-414. doi: <https://doi.org/10.1016/j.fuel.2017.08.111>.
- Al-Anssari, Sarmad, Muhammad Arif, Shaobin wang, Ahmed Barifcani, Lebedev Maxim, and Stefan Iglauer. 2018. "Wettability of nanofluid-modified oil-wet calcite at reservoir conditions." *Fuel* 211:405-414. doi: 10.1016/j.fuel.2017.08.111.
- Al-Anssari, Sarmad, Ahmed Barifcani, Alireza Keshavarz, and Stefan Iglauer. 2018. "Impact of nanoparticles on the CO₂-brine interfacial tension at high pressure and temperature." *Journal of Colloid and Interface Science* 532:136-142. doi: <https://doi.org/10.1016/j.jcis.2018.07.115>.
- Al-Anssari, Sarmad, Ahmed Barifcani, Shaobin Wang, Maxim Lebedev, and Stefan Iglauer. 2016. "Wettability alteration of oil-wet carbonate by silica nanofluid." *Journal of Colloid and Interface Science* 461:435-442. doi: <http://dx.doi.org/10.1016/j.jcis.2015.09.051>.
- Al-Anssari, Sarmad, Lezorgia N. Nwidee, Muhammad Ali, Jitendra S. Sangwai, Shaobin Wang, Ahmed Barifcani, and Stefan Iglauer. 2017. "Retention of Silica Nanoparticles in Limestone Porous Media." SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, 17-19 October, Jakarta, Indonesia, 2017/10/17/.
- Al-Anssari, Sarmad, Lezorgia N. Nwidee, Muhammad Arif, Shaobin Wang, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2017. "Wettability Alteration of Carbonate Rocks via Nanoparticle-Anionic Surfactant Flooding at Reservoirs Conditions." SPE Symposium: Production Enhancement and Cost Optimisation, 7-8 November, Kuala Lumpur, Malaysia, 2017/11/7/.
- Al-Anssari, Sarmad, Shaobin Wang, Ahmed Barifcani, and Stefan Iglauer. 2017. "Oil-water interfacial tensions of silica nanoparticle-surfactant formulations." *Tenside Surfactants Detergents* 54 (4):334-341. doi: <https://doi.org/10.3139/113.110511>.
- Al-Anssari, Sarmad, Shaobin Wang, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2017. "Effect of temperature and SiO₂

- nanoparticle size on wettability alteration of oil-wet calcite." *Fuel* 206:34-42. doi: 10.1016/j.fuel.2017.05.077.
- Al-Manasir, Nodar, Anna-Lena Kjøniksen, and Bo Nyström. 2009. "Preparation and characterization of cross-linked polymeric nanoparticles for enhanced oil recovery applications." *Journal of Applied Polymer Science* 113 (3):1916-1924. doi: 10.1002/app.30176.
- Al-Khdheawi, Vialle Stephanie, Barifceni Ahmed, Sarmadivaleh Mohammad, Zhang Yihuai, and Iglauer Stefan. 2018. "Impact of salinity on CO₂ containment security in highly heterogeneous reservoirs." *Greenhouse Gases: Science and Technology* 8 (1):93-105. doi: doi:10.1002/ghg.1723.
- Ali, Muhammad, Sarmad Al-Ansari, Muhammad Arif, Ahmed Barifceni, Mohammad Sarmadivaleh, Linda Stalker, Maxim Lebedev, and Stefan Iglauer. 2019. "Organic acid concentration thresholds for ageing of carbonate minerals: Implications for CO₂ trapping/storage." *Journal of colloid and interface science* 534:88-94.
- Alroudhan, A., J. Vinogradov, and M. D. Jackson. 2016. "Zeta potential of intact natural limestone: Impact of potential-determining ions Ca, Mg and SO₄." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 493:83-98. doi: <http://dx.doi.org/10.1016/j.colsurfa.2015.11.068>.
- Amedi, Hamidreza, and Mohammad-Ali Ahmadi. 2016. "Experimental investigation the effect of nanoparticles on the oil-water relative permeability." *The European Physical Journal Plus* 131 (5):125. doi: 10.1140/epjp/i2016-16125-4.
- Amraei, A., Zahra Fakhroueian, and Alireza Bahramian. 2013. "Influence of New SiO₂ Nanofluids on Surface Wettability and Interfacial Tension Behaviour between Oil-Water Interface in EOR Processes." *Journal of Nano Research* 26:1-8. doi: <http://dx.doi.org/10.4028/www.scientific.net/JNanoR.26.1>.
- Anderson, William G. 1987. "Wettability literature survey part 5: the effects of wettability on relative permeability." *Journal of Petroleum Technology* 39 (11):1,453-1,468.
- Anderson, William G. 1986. "Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability." *Journal of Petroleum Technology* 38 (10):1125-1144. doi: 10.2118/13932-PA.
- Arif, Muhammad, Sidqi A. Abu-Khamsin, and Stefan Iglauer. 2019. "Wettability of rock/CO₂/brine and rock/oil/CO₂-enriched-brine systems:Critical parametric analysis and future outlook."

- Advances in Colloid and Interface Science* 268:91-113. doi: <https://doi.org/10.1016/j.cis.2019.03.009>.
- Arif, Muhammad, Ahmed Z. Al-Yaseri, Ahmed Barifcani, Maxim Lebedev, and Stefan Iglauer. 2016. "Impact of pressure and temperature on CO₂-brine-mica contact angles and CO₂-brine interfacial tension: Implications for carbon geo-sequestration." *Journal of Colloid and Interface Science* 462:208-215. doi: <http://dx.doi.org/10.1016/j.jcis.2015.09.076>.
- Bashir Abdullahi, Mohammed, Kourosch Rajaei, Radzuan Junin, and Ali Esfandyari Bayat. 2019. "Appraising the impact of metal-oxide nanoparticles on rheological properties of HPAM in different electrolyte solutions for enhanced oil recovery." *Journal of Petroleum Science and Engineering* 172:1057-1068. doi: <https://doi.org/10.1016/j.petrol.2018.09.013>.
- Bayat, AliEsfandyari, Radzuan Junin, FarshadDaraei Ghadikolaei, and Ali Piroozian. 2014. "Transport and aggregation of Al₂O₃ nanoparticles through saturated limestone under high ionic strength conditions: measurements and mechanisms." *Journal of Nanoparticle Research* 16 (12):1-12. doi: 10.1007/s11051-014-2747-x.
- Bayat, AliEsfandyari, Radzuan Junin, Rahmat Mohsin, Mehrdad Hokmabadi, and Shahaboddin Shamshirband. 2015. "Influence of clay particles on Al₂O₃ and TiO₂ nanoparticles transport and retention through limestone porous media: measurements and mechanisms." *Journal of Nanoparticle Research* 17 (5):1-14. doi: 10.1007/s11051-015-3031-4.
- Bayat, Esfandyari Ali, Radzuan Junin, Ariffin Samsuri, Ali Piroozian, and Mehrdad Hokmabadi. 2014. "Impact of Metal Oxide Nanoparticles on Enhanced Oil Recovery from Limestone Media at Several Temperatures." *Energy & Fuels* 28 (10):6255-6266. doi: 10.1021/ef5013616.
- Bera, Achinta, T. Kumar, Keka Ojha, and Ajay Mandal. 2013. "Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies." *Applied Surface Science* 284:87-99. doi: <http://dx.doi.org/10.1016/j.apsusc.2013.07.029>.
- Bera, Achinta, Ajay Mandal, and B. B. Guha. 2014. "Synergistic Effect of Surfactant and Salt Mixture on Interfacial Tension Reduction between Crude Oil and Water in Enhanced Oil Recovery." *Journal of Chemical & Engineering Data* 59 (1):89-96. doi: 10.1021/je400850c.
- Bhatti, Qaisar Abbas, Musa Kaleem Baloch, Simona Schwarz, and Gudrun Petzold. 2014. "Effect of Various Parameters on the

- Stability of Silica Dispersions." *Journal of Solution Chemistry* 43 (11):1916-1928. doi: 10.1007/s10953-014-0260-6.
- Biswal, Nihar Ranjan, Naveen Rangera, and Jayant K. Singh. 2016. "Effect of Different Surfactants on the Interfacial Behavior of the n-Hexane–Water System in the Presence of Silica Nanoparticles." *The Journal of Physical Chemistry B* 120 (29):7265-7274. doi: 10.1021/acs.jpcc.6b03763.
- Chen, Gexin, Xuyang Liu, and Chunming Su. 2011. "Transport and Retention of TiO₂ Rutile Nanoparticles in Saturated Porous Media under Low-Ionic-Strength Conditions: Measurements and Mechanisms." *Langmuir* 27 (9):5393-5402. doi: 10.1021/la200251v.
- Cheraghian, Goshtasp. 2016. "Effect of nano titanium dioxide on heavy oil recovery during polymer flooding." *Petroleum Science and Technology* 34 (7):633-641. doi: 10.1080/10916466.2016.1156125.
- Cheraghian, Goshtasp, and Luky Hendraningrat. 2016. "A review on applications of nanotechnology in the enhanced oil recovery part B: effects of nanoparticles on flooding." *International Nano Letters* 6 (1):1-10. doi: <http://dx.doi.org/10.1007/s40089-015-0170-7>.
- Dastvareh, Behnam, and Jalel Azaiez. 2017. "Instabilities of nanofluid flow displacements in porous media." *Physics of Fluids* 29 (4):044101. doi: 10.1063/1.4978890.
- Dehghan Monfared, A., M. H. Ghazanfari, M. Jamialahmadi, and A. Helalizadeh. 2015. "Adsorption of silica nanoparticles onto calcite: Equilibrium, kinetic, thermodynamic and DLVO analysis." *Chemical Engineering Journal* 281:334-344. doi: <https://doi.org/10.1016/j.cej.2015.06.104>.
- Ding, Baodong, Guicai Zhang, Jijiang Ge, and Xiaoling Liu. 2010. "Research on Mechanisms of Alkaline Flooding for Heavy Oil." *Energy & Fuels* 24 (12):6346-6352. doi: 10.1021/ef100849u.
- Druetta, P., and F. Picchioni. 2019. "Polymer and nanoparticles flooding as a new method for Enhanced Oil Recovery." *Journal of Petroleum Science and Engineering* 177:479-495. doi: <https://doi.org/10.1016/j.petrol.2019.02.070>.
- Dugyala, Venkateshwar Rao, Jyothi Sri Muthukuru, Ethayaraja Mani, and Madivala G. Basavaraj. 2016. "Role of electrostatic interactions in the adsorption kinetics of nanoparticles at fluid–fluid interfaces." *Physical Chemistry Chemical Physics* 18 (7):5499-5508. doi: 10.1039/C5CP05959C.
- Ebrahim, Tangestani, Vafaie Sefti Mohsen, Shadman Mohammad Mahdi, Kazemi Tooseh Esmaeel, and Ahmadi Saeb. 2019.

- "Performance of low-salinity water flooding for enhanced oil recovery improved by SiO₂ nanoparticles." *Petroleum Science* 16 (2):357-365. doi: 10.1007/s12182-018-0295-1.
- Ehtesabi, Hamide, M. Mahdi Ahadian, Vahid Taghikhani, and M. Hossein Ghazanfari. 2014. "Enhanced Heavy Oil Recovery in Sandstone Cores Using TiO₂ Nanofluids." *Energy & Fuels* 28 (1):423-430. doi: 10.1021/ef401338c.
- El-Maghraby, R. M., C. H. Pentland, S. Iglauer, and M. J. Blunt. 2012. "A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements." *The Journal of Supercritical Fluids* 62:55-59. doi: <https://doi.org/10.1016/j.supflu.2011.11.002>.
- Esmaeilzadeh, Pouriya, Alireza Bahramian, and Zahra Fakhroueian. 2011. "Adsorption of Anionic, Cationic and Nonionic Surfactants on Carbonate Rock in Presence of ZrO₂ Nanoparticles." *Physics Procedia* 22:63-67. doi: <https://doi.org/10.1016/j.phpro.2011.11.009>.
- Esmaeilzadeh, Pouriya, Negahdar Hosseinpour, Alireza Bahramian, Zahra Fakhroueian, and Sharareh Arya. 2014. "Effect of ZrO₂ nanoparticles on the interfacial behavior of surfactant solutions at air–water and n-heptane–water interfaces." *Fluid Phase Equilibria* 361 (0):289-295. doi: <http://dx.doi.org/10.1016/j.fluid.2013.11.014>.
- Espinasse, Benjamin, Ernest M. Hotze, and Mark R. Wiesner. 2007. "Transport and Retention of Colloidal Aggregates of C₆₀ in Porous Media: Effects of Organic Macromolecules, Ionic Composition, and Preparation Method." *Environmental Science & Technology* 41 (21):7396-7402. doi: 10.1021/es0708767.
- Gao, Tao, Bjørn Petter Jelle, Linn Ingunn C. Sandberg, and Arild Gustavsen. 2013. "Monodisperse Hollow Silica Nanospheres for Nano Insulation Materials: Synthesis, Characterization, and Life Cycle Assessment." *ACS Applied Materials & Interfaces* 5 (3):761-767. doi: 10.1021/am302303b.
- Ghalemizade Elyaderani, Seyed M., Arezou Jafari, and Javad Razavinezhad. 2019. "Experimental Investigation of Mechanisms in Functionalized Multiwalled Carbon Nanotube Flooding for Enhancing the Recovery From Heavy-Oil Reservoirs." *SPE Journal Preprint (Preprint)*:14. doi: 10.2118/194499-PA.
- Giraldo, Lady J., Maria A. Giraldo, Sebastian Llanos, Gustavo Maya, Richard D. Zabala, Nashaat N. Nassar, Camilo A. Franco, Vladimir Alvarado, and Farid B. Cortés. 2017. "The effects of SiO₂ nanoparticles on the thermal stability and rheological behavior of hydrolyzed polyacrylamide based polymeric

- solutions." *Journal of Petroleum Science and Engineering* 159:841-852. doi: <https://doi.org/10.1016/j.petrol.2017.10.009>.
- Grate, Jay W., Karl J. Dehoff, Marvin G. Warner, Jonathan W. Pittman, Thomas W. Wietsma, Changyong Zhang, and Mart Oostrom. 2012. "Correlation of Oil–Water and Air–Water Contact Angles of Diverse Silanized Surfaces and Relationship to Fluid Interfacial Tensions." *Langmuir* 28 (18):7182-7188. doi: 10.1021/la204322k.
- Gupta, Robin, and Kishore Mohanty. 2010. "Temperature Effects on Surfactant-Aided Imbibition Into Fractured Carbonates." *SPE Journal* 25 (1):80-88. doi: 10.2118/110204-PA.
- Guz, I. A., A. A. Rodger, A. N. Guz, and J. J. Rushchitsky. 2007. "Developing the mechanical models for nanomaterials." *Composites Part A: Applied Science and Manufacturing* 38 (4):1234-1250. doi: <https://doi.org/10.1016/j.compositesa.2006.04.012>.
- Guzmán, Eduardo, Libero Liggieri, Eva Santini, Michele Ferrari, and Francesca Ravera. 2011. "Effect of Hydrophilic and Hydrophobic Nanoparticles on the Surface Pressure Response of DPPC Monolayers." *The Journal of Physical Chemistry C* 115 (44):21715-21722. doi: 10.1021/jp207713x.
- Hamouda, Aly Anis, and Rezaei Karam Ali Gomari. 2006. "Influence of Temperature on Wettability Alteration of Carbonate Reservoirs." SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA 22-26 April.
- Hansen, G., A. A. Hamouda, and R. Denoyel. 2000. "The effect of pressure on contact angles and wettability in the mica/water/n-decane system and the calcite+stearic acid/water/n-decane system." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 172 (1–3):7-16. doi: [http://dx.doi.org/10.1016/S0927-7757\(99\)00498-7](http://dx.doi.org/10.1016/S0927-7757(99)00498-7).
- He, Le, Mingsheng Wang, Jianping Ge, and Yadong Yin. 2012. "Magnetic Assembly Route to Colloidal Responsive Photonic Nanostructures." *Accounts of Chemical Research* 45 (9):1431-1440. doi: 10.1021/ar200276t.
- He, Wentao, Danhua Wu, Juan Li, Kai Zhang, Yushu Xiang, Lijuan Long, Shuhao Qin, Jie Yu, and Qin Zhang. 2013. "Surface modification of colloidal silica nanoparticles: Controlling the size and grafting process." *Bulletin of the Korean Chemical Society* 34 (9):2747-2752.
- Hendraningrat, Luky, Shidong Li, and Ole Torsæter. 2013. "A coreflood investigation of nanofluid enhanced oil recovery." *Journal of*

- Petroleum Science and Engineering* 111 (0):128-138. doi: <http://dx.doi.org/10.1016/j.petrol.2013.07.003>.
- Hendraningrat, Luky, and Ole Torsæter. 2015. "Metal oxide-based nanoparticles: revealing their potential to enhance oil recovery in different wettability systems." *Applied Nanoscience* 5 (2):181-199. doi: 10.1007/s13204-014-0305-6.
- Hernández Battez, A., R. González, J. L. Viesca, J. E. Fernández, J. M. Díaz Fernández, A. Machado, R. Chou, and J. Riba. 2008. "CuO, ZrO₂ and ZnO nanoparticles as antiwear additive in oil lubricants." *Wear* 265 (3-4):422-428. doi: citeulike-article-id:12672845
- 10.1016/j.wear.2007.11.013.
- Hoeiland, S., T. Barth, A. M. Blokhus, and A. Skauge. 2001. "The effect of crude oil acid fractions on wettability as studied by interfacial tension and contact angles." *Journal of Petroleum Science and Engineering* 30 (2):91-103. doi: [http://dx.doi.org/10.1016/S0920-4105\(01\)00106-1](http://dx.doi.org/10.1016/S0920-4105(01)00106-1).
- Höpfner, W. 1997. "Organic inhibitors of corrosion of metals. Von Yurii I. Kuznetsov. Wissenschaftliche Übersetzung A. D. Mercer
- Wissenschaftlicher Herausgeber J. G. N. Thomas, 283 Seiten, Plenum Press, New York und London 1996, \$ 95.00, IBN 0-306-45169-7." *Materials and Corrosion* 48 (6):399-399. doi: 10.1002/maco.19970480609.
- Iglauer, Stefan, Abdulsalam Salamah, Mohammad Sarmadivaleh, Keyu Liu, and Chi Phan. 2014. "Contamination of silica surfaces: Impact on water–CO₂–quartz and glass contact angle measurements." *International Journal of Greenhouse Gas Control* 22:325-328. doi: <https://doi.org/10.1016/j.ijggc.2014.01.006>.
- Johannesen, Else Birbeland, and Arne Graue. 2007. "Mobilization of Remaining Oil - Emphasis on Capillary Number and Wettability." International Oil Conference and Exhibition in Mexico, Veracruz, Mexico, 2007/1/1/.
- Ju, Binshan, Shugao Dai, Zhian Luan, Tiangao Zhu, Xiantao Su, and Xiaofeng Qiu. 2002. "A Study of Wettability and Permeability Change Caused by Adsorption of Nanometer Structured Polysilicon on the Surface of Porous Media." SPE Asia Pacific Oil and Gas Conference and Exhibition, Melbourne, Australia, 2002/1/1/.
- Ju, Binshan, and Tailiang Fan. 2009. "Experimental study and mathematical model of nanoparticle transport in porous media."

- Powder Technology* 192 (2):195-202. doi: <http://dx.doi.org/10.1016/j.powtec.2008.12.017>.
- Ju, Binshan, Tailiang Fan, and Mingxue Ma. 2006. "Enhanced oil recovery by flooding with hydrophilic nanoparticles." *China Particuology* 4 (1):41-46. doi: [http://dx.doi.org/10.1016/S1672-2515\(07\)60232-2](http://dx.doi.org/10.1016/S1672-2515(07)60232-2).
- Kamaei, Ehsan, Abbas Khaksar Manshad, Seyed Reza Shadizadeh, Jagar A Ali, and Alireza Keshavarz. 2019. "Comprehensive Investigation of the Effect of Henna Natural Surfactant on the Cementation Factor and Wettability Alteration." *Available at SSRN 3415206*.
- Karimi, Ali, Zahra Fakhroueian, Alireza Bahramian, Nahid Pour Khiabani, Jabar Babae Darabad, Reza Azin, and Sharareh Arya. 2012. "Wettability Alteration in Carbonates using Zirconium Oxide Nanofluids: EOR Implications." *Energy & Fuels* 26 (2):1028-1036. doi: 10.1021/ef201475u.
- Kazemzadeh, Yousef, S. Ehsan Eshraghi, Saeed Sourani, and Mahshid Reyhani. 2015. "An interface-analyzing technique to evaluate the heavy oil swelling in presence of nickel oxide nanoparticles." *Journal of Molecular Liquids* 211:553-559. doi: <https://doi.org/10.1016/j.molliq.2015.07.064>.
- Kazemzadeh, Yousef, Sanaz Shojaei, Masoud Riazi, and Mohammad Sharifi. 2018. "Review on application of nanoparticles for EOR purposes; a critical of the opportunities and challenges." *Chinese Journal of Chemical Engineering*.
- Kazemzadeh, Yousef, Sanaz Shojaei, Masoud Riazi, and Mohammad Sharifi. 2019. "Review on application of nanoparticles for EOR purposes: A critical review of the opportunities and challenges." *Chinese Journal of Chemical Engineering* 27 (2):237-246. doi: <https://doi.org/10.1016/j.cjche.2018.05.022>.
- Keshavarz, A., H. Vatanparast, M. Zargar, M. Mostafazadeh, and M. Haghghi. 2012. "An Experimental Investigation of Optimum Capillary Number on Vertical Immiscible Gas Injection in Iranian Carbonate and Sandstone Rocks." *Petroleum Science and Technology* 30 (13):1379-1391. doi: 10.1080/10916466.2010.506460.
- Ko, Saebom, and Chun Huh. 2019. "Use of nanoparticles for oil production applications." *Journal of Petroleum Science and Engineering* 172:97-114. doi: <https://doi.org/10.1016/j.petrol.2018.09.051>.
- Kobayashi, Motoyoshi, Frédéric Juillerat, Paolo Galletto, Paul Bowen, and Michal Borkovec. 2005. "Aggregation and Charging of

- Colloidal Silica Particles: Effect of Particle Size." *Langmuir* 21 (13):5761-5769. doi: 10.1021/la046829z.
- Kondiparty, Kirti, Alex Nikolov, Stanley Wu, and Darsh Wasan. 2011. "Wetting and Spreading of Nanofluids on Solid Surfaces Driven by the Structural Disjoining Pressure: Statics Analysis and Experiments." *Langmuir* 27 (7):3324-3335. doi: 10.1021/la104204b.
- Kumar, Narendra, and Ajay Mandal. 2018. "Oil-in-water nanoemulsion stabilized by polymeric surfactant: Characterization and properties evaluation for enhanced oil recovery." *European Polymer Journal* 109:265-276. doi: <https://doi.org/10.1016/j.eurpolymj.2018.09.058>.
- Lan, Qiang, Fei Yang, Shuiyan Zhang, Shangying Liu, Jian Xu, and Dejun Sun. 2007. "Synergistic effect of silica nanoparticle and cetyltrimethyl ammonium bromide on the stabilization of O/W emulsions." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 302 (1–3):126-135. doi: <http://dx.doi.org/10.1016/j.colsurfa.2007.02.010>.
- Lecoanet, H el ene F., Jean-Yves Bottero, and Mark R. Wiesner. 2004. "Laboratory Assessment of the Mobility of Nanomaterials in Porous Media." *Environmental Science & Technology* 38 (19):5164-5169. doi: 10.1021/es0352303.
- Li, Wei, Jian-hua Zhu, and Jian-hua Qi. 2007. "Application of nano-nickel catalyst in the viscosity reduction of Liaohe extra-heavy oil by aqua-thermolysis." *Journal of Fuel Chemistry and Technology* 35 (2):176-180. doi: [http://dx.doi.org/10.1016/S1872-5813\(07\)60016-4](http://dx.doi.org/10.1016/S1872-5813(07)60016-4).
- Li, Y. 2011. "Oil Recovery by Low Salinity Water Injection into a Reservoir: A New Study of Tertiary Oil Recovery Mechanism." *Transport in Porous Media* 90 (2):333-362. doi: 10.1007/s11242-011-9788-8.
- Liu, Qi, Zhonghao Sun, and J. Carlos Santamarina. 2019. "Transport and Adsorption of Silica Nanoparticles in Carbonate Reservoirs: A Sand Column Study." *Energy & Fuels* 33 (5):4009-4016. doi: 10.1021/acs.energyfuels.9b00057.
- London, Gabor, Gregory T. Carroll, and Ben L. Feringa. 2013. "Silanization of quartz, silicon and mica surfaces with light-driven molecular motors: construction of surface-bound photo-active nanolayers." *Organic & Biomolecular Chemistry* 11 (21):3477-3483. doi: 10.1039/C3OB40276B.
- Ma, Jian-Zhong, Jing Hu, and Zhi-Jie Zhang. 2007. "Polyacrylate/silica nanocomposite materials prepared by sol-gel process." *European*

- Polymer Journal* 43 (10):4169-4177. doi:
<http://dx.doi.org/10.1016/j.eurpolymj.2007.06.051>.
- Ma, Kun, Leyu Cui, Yezi Dong, Tianlong Wang, Chang Da, George J. Hirasaki, and Sibani Lisa Biswal. 2013. "Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials." *Journal of Colloid and Interface Science* 408:164-172. doi: <http://dx.doi.org/10.1016/j.jcis.2013.07.006>.
- Maerker, JM, and WW Gale. 1992. "Surfactant flood process design for Loudon." *SPE reservoir engineering* 7 (01):36-44.
- Mason, Geoffrey, and Norman R. Morrow. 2013. "Developments in spontaneous imbibition and possibilities for future work." *Journal of Petroleum Science and Engineering* 110 (0):268-293. doi: <http://dx.doi.org/10.1016/j.petrol.2013.08.018>.
- Maurya, Neetish Kumar, and Ajay Mandal. 2018. "Investigation of synergistic effect of nanoparticle and surfactant in macro emulsion based EOR application in oil reservoirs." *Chemical Engineering Research and Design* 132:370-384. doi: <https://doi.org/10.1016/j.cherd.2018.01.049>.
- Metin, Cigdem O., Jimmie R. Baran, and Quoc P. Nguyen. 2012. "Adsorption of surface functionalized silica nanoparticles onto mineral surfaces and decane/water interface." *Journal of Nanoparticle Research* 14 (11):1246. doi: 10.1007/s11051-012-1246-1.
- Metin, Cigdem O., Roger T. Bonnecaze, Larry W. Lake, Caetano R. Miranda, and Quoc P. Nguyen. 2012. "Aggregation kinetics and shear rheology of aqueous silica suspensions." *Applied Nanoscience* 4 (2):169-178. doi: 10.1007/s13204-012-0185-6.
- Metin, CigdemO, LarryW Lake, CaetanoR Miranda, and QuocP Nguyen. 2011. "Stability of aqueous silica nanoparticle dispersions." *Journal of Nanoparticle Research* 13 (2):839-850. doi: 10.1007/s11051-010-0085-1.
- Moghaddam, Nazari, Rasoul, Alireza Bahramian, Zahra Fakhroueian, Ali Karimi, and Sharareh Arya. 2015. "Comparative Study of Using Nanoparticles for Enhanced Oil Recovery: Wettability Alteration of Carbonate Rocks." *Energy & Fuels* 29 (4):2111-2119. doi: 10.1021/ef5024719.
- Mohan, K Krishna, and H Scott Fogler. 1997. "Effect of pH and layer charge on formation damage in porous media containing swelling clays." *Langmuir* 13 (10):2863-2872.
- Mondragon, Rosa, J. Enrique Julia, Antonio Barba, and Juan Carlos Jarque. 2012. "Characterization of silica–water nanofluids dispersed with an ultrasound probe: A study of their physical

- properties and stability." *Powder Technology* 224:138-146. doi: <http://dx.doi.org/10.1016/j.powtec.2012.02.043>.
- Morse, John W., and Rolf S. Arvidson. 2002. "The dissolution kinetics of major sedimentary carbonate minerals." *Earth-Science Reviews* 58 (1–2):51-84. doi: [http://dx.doi.org/10.1016/S0012-8252\(01\)00083-6](http://dx.doi.org/10.1016/S0012-8252(01)00083-6).
- Mungan, Necmettin. 1965. "Permeability reduction through changes in pH and salinity." *Journal of Petroleum Technology* 17 (12):1,449-1,453.
- Negin, Chegenizadeh, Saeedi Ali, and Quan Xie. 2016. "Application of nanotechnology for enhancing oil recovery – A review." *Petroleum* 2 (4):324-333. doi: <https://doi.org/10.1016/j.petlm.2016.10.002>.
- Nikolov, Alex, Kirti Kondiparty, and Darsh Wasan. 2010. "Nanoparticle Self-Structuring in a Nanofluid Film Spreading on a Solid Surface." *Langmuir* 26 (11):7665-7670. doi: 10.1021/la100928t.
- Nooney, Robert I., Angela White, Christy O'Mahony, Claire O'Connell, Susan M. Kelleher, Stephen Daniels, and Colette McDonagh. 2015. "Investigating the colloidal stability of fluorescent silica nanoparticles under isotonic conditions for biomedical applications." *Journal of Colloid and Interface Science* 456:50-58. doi: <http://dx.doi.org/10.1016/j.jcis.2015.05.051>.
- Nugroho, Robertus Wahyu N., Torbjörn Pettersson, Karin Odelius, Anders Höglund, and Ann-Christine Albertsson. 2013. "Force Interactions of Nonagglomerating Polylactide Particles Obtained through Covalent Surface Grafting with Hydrophilic Polymers." *Langmuir* 29 (28):8873-8881. doi: 10.1021/la401076m.
- Nwidee, Lezorgia N., Sarmad Al-Ansari, Ahmed Barifcani, Mohammad Sarmadivaleh, and Stefan Iglauer. 2016. "Nanofluids for Enhanced Oil Recovery Processes: Wettability Alteration Using Zirconium Oxide." Offshore Technology Conference Asia, Kuala Lumpur, Malaysia, 2016/3/22/.
- Nwidee, Lezorgia N., Sarmad Al-Ansari, Ahmed Barifcani, Mohammad Sarmadivaleh, Maxim Lebedev, and Stefan Iglauer. 2017. "Nanoparticles influence on wetting behaviour of fractured limestone formation." *Journal of Petroleum Science and Engineering* 149:782-788. doi: <http://dx.doi.org/10.1016/j.petrol.2016.11.017>.
- Nwidee, Lezorgia Nekabari. 2017. "Nanoparticles for Enhanced Oil Recovery Processes." Curtin University.
- Nwidee, Lezorgia Nekabari, Ahmed Barifcani, Maxim Lebedev, Mohammad Sarmadivaleh, and Stefan Iglauer. 2018. "A Realistic Look at Nanostructured Material as an Innovative Approach for

- Enhanced Oil Recovery Process Upgrading." In *Recent Insights in Petroleum Science and Engineering*. InTech.
- Ogolo, NA, OA Olafuyi, and MO Onyekonwu. 2012. "Enhanced oil recovery using nanoparticles." SPE Saudi Arabia section technical symposium and exhibition.
- Onyekonwu, Mike O., and Naomi A. Ogolo. 2010. "Investigating the Use of Nanoparticles in Enhancing Oil Recovery." Nigeria Annual International Conference and Exhibition, Tinapa - Calabar, Nigeria 2010/1/1/.
- Petosa, Adamo R., Deb P. Jaisi, Ivan R. Quevedo, Menachem Elimelech, and Nathalie Tufenkji. 2010. "Aggregation and Deposition of Engineered Nanomaterials in Aquatic Environments: Role of Physicochemical Interactions." *Environmental Science & Technology* 44 (17):6532-6549. doi: 10.1021/es100598h.
- Ponmani, Swaminathan, R. Nagarajan, and Jitendra S. Sangwai. 2015. "Effect of Nanofluids of CuO and ZnO in Polyethylene Glycol and Polyvinylpyrrolidone on the Thermal, Electrical, and Filtration-Loss Properties of Water-Based Drilling Fluids." *SPE Journal* 21 (2):405-415. doi: 10.2118/178919-PA.
- Rahman, Taufiq, Maxim Lebedev, Ahmed Barifceni, and Stefan Iglauer. 2016. "Residual trapping of supercritical CO₂ in oil-wet sandstone." *Journal of Colloid and Interface Science* 469:63-68. doi: <http://dx.doi.org/10.1016/j.jcis.2016.02.020>.
- Rankin, D. W. H. 2013. *Structural Methods in Molecular Inorganic Chemistry*. Edited by Norbert Mitzel and Carole Morrison, *Inorganic Chemistry*. Hoboken: Hoboken : Wiley.
- Ravera, Francesca, Michele Ferrari, Libero Liggieri, Giuseppe Loglio, Eva Santini, and Alessandra Zanobini. 2008. "Liquid–liquid interfacial properties of mixed nanoparticle–surfactant systems." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 323 (1–3):99-108. doi: <http://dx.doi.org/10.1016/j.colsurfa.2007.10.017>.
- Rellegadla, Sandeep, Himanshu K. Bairwa, Mankamna R. Kumari, Ganshyam Prajapat, Surendra Nimesh, Nidhi Pareek, Shikha Jain, and Akhil Agrawal. 2018. "An Effective Approach for Enhanced Oil Recovery Using Nickel Nanoparticles Assisted Polymer Flooding." *Energy & Fuels* 32 (11):11212-11221. doi: 10.1021/acs.energyfuels.8b02356.
- Rezaei Gomari, Sina, Yann Gorra Diallo Omar, Farida Amrouche, Meez Islam, and Donglai Xu. 2019. "New insights into application of nanoparticles for water-based enhanced oil recovery in carbonate reservoirs." *Colloids and Surfaces A: Physicochemical and*

- Engineering Aspects* 568:164-172. doi: <https://doi.org/10.1016/j.colsurfa.2019.01.037>.
- Rodrigue, Jean-Paul. 2020. *The Geography of Transport Systems*. 5th Edition ed: Taylor and Francis Group.
- Rodriguez Pin, Elena, Matthew Roberts, Haiyang Yu, Chun Huh, and Steven Lawrence Bryant. 2009. "Enhanced migration of surface-treated nanoparticles in sedimentary rocks." SPE annual technical conference and exhibition.
- Rostami, Peyman, Mohammad Sharifi, Babak Aminshahidy, and Jalal Fahimpour. 2019. "Enhanced oil recovery using silica nanoparticles in the presence of salts for wettability alteration." *Journal of Dispersion Science and Technology*:1-12. doi: 10.1080/01932691.2019.1583575.
- Rostami Ravari, Reza, Skule Strand, and Tor Austad. 2011. "Combined Surfactant-Enhanced Gravity Drainage (SEGD) of Oil and the Wettability Alteration in Carbonates: The Effect of Rock Permeability and Interfacial Tension (IFT)." *Energy & Fuels* 25 (5):2083-2088. doi: 10.1021/ef200085t.
- Rostamzadeh, Pardis, S. Mojtaba Mirabedini, and Masoud Esfandeh. 2014. "APS-silane modification of silica nanoparticles: effect of treatment's variables on the grafting content and colloidal stability of the nanoparticles." *Journal of Coatings Technology and Research* 11 (4):651-660. doi: 10.1007/s11998-014-9577-8.
- Roustaei, Abbas, and Hadi Bagherzadeh. 2014. "Experimental investigation of SiO₂ nanoparticles on enhanced oil recovery of carbonate reservoirs." *Journal of Petroleum Exploration and Production Technology*:1-7. doi: 10.1007/s13202-014-0120-3.
- Saleh, Navid, Hye-Jin Kim, Tanapon Phenrat, Krzysztof Matyjaszewski, Robert D. Tilton, and Gregory V. Lowry. 2008. "Ionic Strength and Composition Affect the Mobility of Surface-Modified Fe₀ Nanoparticles in Water-Saturated Sand Columns." *Environmental Science & Technology* 42 (9):3349-3355. doi: 10.1021/es071936b.
- Sarmadivaleh, Mohammad, Ahmed Z. Al-Yaseri, and Stefan Iglauer. 2015. "Influence of temperature and pressure on quartz–water–CO₂ contact angle and CO₂–water interfacial tension." *Journal of Colloid and Interface Science* 441 (0):59-64. doi: <http://dx.doi.org/10.1016/j.jcis.2014.11.010>.
- ShamsiJazeyi, Hadi, Clarence A. Miller, Michael S. Wong, James M. Tour, and Rafael Verduzco. 2014. "Polymer-coated nanoparticles for enhanced oil recovery." *Journal of Applied Polymer Science* 131 (15):1-13. doi: 10.1002/app.40576.

- Sharma, Gaurav, and Kishore Mohanty. 2013. "Wettability Alteration in High-Temperature and High-Salinity Carbonate Reservoirs." *SPE Journal* 18 (4):646-655. doi: 10.2118/147306-PA.
- Sharma, Tushar, G. Suresh Kumar, and Jitendra S. Sangwai. 2014. "Enhanced oil recovery using oil-in-water (o/w) emulsion stabilized by nanoparticle, surfactant and polymer in the presence of NaCl." *Geosystem Engineering* 17 (3):195-205. doi: 10.1080/12269328.2014.959622.
- Shen, Min, and Daniel E. Resasco. 2009. "Emulsions Stabilized by Carbon Nanotube–Silica Nanohybrids." *Langmuir* 25 (18):10843-10851. doi: 10.1021/la901380b.
- Sheng, James. 2013. *Enhanced oil recovery field case studies*: Gulf Professional Publishing.
- Shi, Xuetao, Roberto Rosa, and Andrea Lazzeri. 2010. "On the Coating of Precipitated Calcium Carbonate with Stearic Acid in Aqueous Medium." *Langmuir* 26 (11):8474-8482. doi: 10.1021/la904914h.
- Siddiqui, Shameem, and Aon A Khamees. 2004. "Dual-energy CT-scanning applications in rock characterization." SPE annual technical conference and exhibition.
- Stumm, Werner, and James J. Morgan. 1995. *Aquatic chemistry : chemical equilibria and rates in natural waters* 3rd ed. New York Wiley
- Suleimanov, B. A., F. S. Ismailov, and E. F. Veliyev. 2011. "Nanofluid for enhanced oil recovery." *Journal of Petroleum Science and Engineering* 78 (2):431-437. doi: <http://dx.doi.org/10.1016/j.petrol.2011.06.014>.
- Sun, Xiaofei, Yanyu Zhang, Guangpeng Chen, and Zhiyong Gai. 2017. "Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress." *Energies* 10 (3):345. doi: <http://dx.doi.org/10.3390/en10030345>.
- Tabellion, Jan, Johannes Zeiner, and Rolf Clasen. 2006. "Manufacturing of pure and doped silica and multicomponent glasses from SiO₂ nanoparticles by reactive electrophoretic deposition." *Journal of Materials Science* 41 (24):8173-8180. doi: 10.1007/s10853-006-0599-1.
- Tabrizy, V. Alipour, A. A. Hamouda, and R. Denoyel. 2011. "Influence of Magnesium and Sulfate Ions on Wettability Alteration of Calcite, Quartz, and Kaolinite: Surface Energy Analysis." *Energy & Fuels* 25 (4):1667-1680. doi: 10.1021/ef200039m.
- Thomas, S. 2008a. "Enhanced oil recovery-an overview." *Oil & Gas Science and Technology-Revue de l'IFP* 63 (1):9-19.
- Thomas, S. 2008b. "Enhanced Oil Recovery - An Overview." *Oil & Gas Science and Technology - Rev. IFP* 63 (1):9-19.

- Vatanparast, H., A. H. Alizadeh, A. Bahramian, and H. Bazdar. 2011. "Wettability Alteration of Low-permeable Carbonate Reservoir Rocks in Presence of Mixed Ionic Surfactants." *Petroleum Science and Technology* 29 (18):1873-1884. doi: 10.1080/10916461003610389.
- Wasan, Darsh, Alex Nikolov, and Kirti Kondiparty. 2011. "The wetting and spreading of nanofluids on solids: Role of the structural disjoining pressure." *Current Opinion in Colloid & Interface Science* 16 (4):344-349. doi: <http://dx.doi.org/10.1016/j.cocis.2011.02.001>.
- White, Eliot J, Oren C Baptist, and Carlon Sanford Land. 1964. Formation damage estimated from water sensitivity tests, Patrick Draw area, Wyoming. Bureau of Mines, Laramie, Wyo.(USA). Petroleum Research Center.
- Worthen, Andrew J., Lynn M. Foster, Jiannan Dong, Jonathan A. Bollinger, Adam H. Peterman, Lucinda E. Pastora, Steven L. Bryant, Thomas M. Truskett, Christopher W. Bielawski, and Keith P. Johnston. 2014. "Synergistic Formation and Stabilization of Oil-in-Water Emulsions by a Weakly Interacting Mixture of Zwitterionic Surfactant and Silica Nanoparticles." *Langmuir* 30 (4):984-994. doi: 10.1021/la404132p.
- Wu, Yongfu, Patrick J. Shuler, Mario Blanco, Yongchun Tang, and William A. Goddard. 2008. "An Experimental Study of Wetting Behavior and Surfactant EOR in Carbonates With Model Compounds." *SPE Journal* 13 (1):26-34. doi: 10.2118/99612-PA.
- Xu, Ke, Peixi Zhu, Tatiana Colon, Chun Huh, and Matthew Balhoff. 2016. "A Microfluidic Investigation of the Synergistic Effect of Nanoparticles and Surfactants in Macro-Emulsion-Based Enhanced Oil Recovery." *SPE Journal*. doi: 10.2118/179691-PA.
- Yarranton, Harvey W., Richard O. Baker, and Jerry Jensen. 2015. *Practical Reservoir Engineering and Characterization*. Saint Louis, UNITED STATES: Elsevier Science & Technology.
- Yousef, Ali A, Salah Al-Saleh, Abdulaziz Ubaid Al-Kaabi, and Mohammed Saleh Al-Jawfi. 2010. "Laboratory investigation of novel oil recovery method for carbonate reservoirs." Canadian Unconventional Resources and International Petroleum Conference.
- Yousefvand, H., and A. Jafari. 2015. "Enhanced Oil Recovery Using Polymer/nanosilica." *Procedia Materials Science* 11:565-570. doi: <https://doi.org/10.1016/j.mspro.2015.11.068>.
- Youssif, Magda I., Rehab M. El-Maghraby, Sayed M. Saleh, and Ahmed Elgibaly. 2018. "Silica nanofluid flooding for enhanced oil

- recovery in sandstone rocks." *Egyptian Journal of Petroleum* 27 (1):105-110. doi: <https://doi.org/10.1016/j.ejpe.2017.01.006>.
- Zallaghi, Mehdi, Riyaz Kharrat, and Abdolnabi Hashemi. 2018. "Improving the microscopic sweep efficiency of water flooding using silica nanoparticles." *Journal of Petroleum Exploration and Production Technology* 8 (1):259-269. doi: 10.1007/s13202-017-0347-x.
- Zargartalebi, Mohammad, Nasim Barati, and Riyaz Kharrat. 2014a. "Influences of hydrophilic and hydrophobic silica nanoparticles on anionic surfactant properties: Interfacial and adsorption behaviors." *Journal of Petroleum Science and Engineering* 119:36-43. doi: <http://dx.doi.org/10.1016/j.petrol.2014.04.010>.
- Zargartalebi, Mohammad, Nasim Barati, and Riyaz Kharrat. 2014b. "Influences of hydrophilic and hydrophobic silica nanoparticles on anionic surfactant properties: Interfacial and adsorption behaviors." *Journal of Petroleum Science and Engineering* 119 (0):36-43. doi: <http://dx.doi.org/10.1016/j.petrol.2014.04.010>.
- Zargartalebi, Mohammad, Riyaz Kharrat, and Nasim Barati. 2015. "Enhancement of surfactant flooding performance by the use of silica nanoparticles." *Fuel* 143 (0):21-27. doi: <http://dx.doi.org/10.1016/j.fuel.2014.11.040>.
- Zendehboudi, Sohrab, Mohammad Ali Ahmadi, Amin Reza Rajabzadeh, Nader Mahinpey, and Ioannis Chatzis. 2013. "Experimental study on adsorption of a new surfactant onto carbonate reservoir samples—application to EOR." *The Canadian Journal of Chemical Engineering* 91 (8):1439-1449. doi: 10.1002/cjce.21806.
- Zhang, Hua, Alex Nikolov, and Darsh Wasan. 2014. "Enhanced Oil Recovery (EOR) Using Nanoparticle Dispersions: Underlying Mechanism and Imbibition Experiments." *Energy & Fuels* 28 (5):3002-3009. doi: 10.1021/ef500272r.
- Zhang, Hua, T. S. Ramakrishnan, Alex Nikolov, and Darsh Wasan. 2016. "Enhanced Oil Recovery Driven by Nanofilm Structural Disjoining Pressure: Flooding Experiments and Microvisualization." *Energy & Fuels* 30 (4):2771-2779. doi: 10.1021/acs.energyfuels.6b00035.
- Zhang, Lingling, Yunhong Jiang, Yulong Ding, Malcolm Povey, and David York. 2007. "Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles (ZnO nanofluids)." *Journal of Nanoparticle Research* 9 (3):479-489. doi: 10.1007/s11051-006-9150-1.
- Zhang, Tiantian, Drew Davidson, Steven Lawrence Bryant, and Chun Huh. 2010. "Nanoparticle-Stabilized Emulsions for Applications

in Enhanced Oil Recovery." Improved Oil Recovery, Tulsa, Oklahoma, USA, 2010/4/22/.

Zhang, Tiantian, Michael J. Murphy, Haiyang Yu, Hitesh G. Bagaria, Ki Youl Yoon, Bethany M. Nielson, Christopher W. Bielawski, Keith P. Johnston, Chun Huh, and Steven L. Bryant. 2015.

"Investigation of Nanoparticle Adsorption During Transport in Porous Media." *SPE Journal*

20 (04):667-677. doi: 10.2118/166346-PA.

Zhong, Huiying, Qiuyuan Zang, Hongjun Yin, and Huifen Xia. 2018.

"Experimental Study on Medium Viscosity Oil Displacement Using Viscoelastic Polymer." *Geofluids* 2018.