Role of Sulphates and Chloride Ions in Improved Oil Recovery in a Hybrid Smart-Low Salinity Flooding Technique

By

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Abstract

The growing demand for energy to cater for the growing world population has forced the exploitation and utilisation of existing hydrocarbon resources. Oil and gas are deemed the most conventional and common sources of energy, formed as a result of degradation of fossils deeply buried in underground. Utilising oil and gas require their extraction from their “traps” termed reservoirs. Their production is possible through the natural energy (in form of pressure) which forces the resources to the surface. The oil production from the well will eventually decline steadily due to pressure depletion associated with it and production will be halted. Studies have shown that almost 300 billion barrels of oil remain untapped to this day. This has forced the innovation and investigation of efficient recovery methods to recovery additional oil, and to reduce the residual oil saturation from the reservoirs. There are several methods employed for enhanced oil recovery (EOR). The choice of each method is peculiar to its application, ranging from demographic to economical vices. However, a method of EOR that shows a potential in terms of versatility and wide scale applicability is Low salinity flooding, which is characterised by many mechanisms including fine migration, electrical double layer expansion, multivalent ionic exchange, and micro dispersion. Despite much research on theses mechanisms, sulphate ions facilitate the fine migration at low concentration, while presence of chloride promotes micro dispersion. This study for the first time utilised a combined engineered water of sulphate and chlorides ions to understand its suitability for sandstone reservoir of Wara field, which has undergone successfully secondary recovery, with low salinity EOR being a candidate option for the tertiary recovery.

Low salinity flooding as a method of enhanced oil recovery has been proven to provide the additional oil recovery from the reservoirs. It is cheaper and more efficient method compared to the cheapest conventional EOR technique (CO_2 flooding). This study aims to investigate the feasibility of using low salinity flooding using engineering smart water through laboratory experiments on different real sandstone core samples obtained from the reservoir. A mineralogical analysis to obtain the rock composition, particularly clay types, was carried out using a combination of EDX, XRD, and SEM techniques. This will help to establish the fluid rock interaction in the subsequent analysis. Furthermore, a core flooding process was carried out, at reservoir conditions of 1600 psig and 40 °C, to investigate the effect of salinity variation and composition on the displacement efficiency and also to evaluate the dominant displacement mechanism of the process for this application at these conditions.

From the mineralogical analysis, Kaolinite clay was present in the core samples from the characterisation techniques aforementioned. This is an important finding as, stated in a number of literatures; it is a type of clay that is susceptible to the effects of low salinity by being a non-swelling clay which is responsible for some of the proposed low salinity displacement mechanisms. This is the first step which will provide information on the low salinity water formulation in order to have compatibility with the formation of interest and also an efficient medium through which additional oil recovery will be realised. Additionally, the results from the core flooding process indicated that the displacement by sulphate-based salts yielded the best recovery factors compared to the chloride-based brines. This is as a result of the interaction between the rock surface and the anionic components of the injected low salinity brine. A proposed mechanism showcased the role of ionic brine components in the wettability alteration associated with improved oil recovery. Furthermore, IFT reduction was also realised and contributed to the substantial recovery by the SO_4 brine. another noteworthy finding is the conformance effect which will affect the displacement front and impeded vertical sweep across the pay zone during EOR.

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Declaration

I, Athari Ghazi Alotaibi, declare that this dissertation report is my original work, and has not been submitted elsewhere for any award. Any section, part or phrasing that has been used or copied from other literature or documents copied has been clearly referenced at the point of use as well as in the reference section of the thesis work.

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List of Publications

1. Al-Otaibi. A, Abbas A.J and Nasr G.G (2018), Low salinity flooding: effect of salt composition on displacement efficiency, Salford postgraduate research conference, media city UK.

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Chapter 1: Introduction

1.1 Overview

The growing energy needs from different sources, including fossils and non-fossils types motivated by the low carbon future, are becoming more pronounced in the current decade [1-3]. This further encourages the use of secondary and tertiary mechanisms of oil recovery to harness oil after pressure decline during primary production, on the other hand developing other technologies for non-fossil fuel energy sources, such as renewables [4, 5] and hydrogen [6, 7]. Despite the high carbon footprints of the fossil fuels, gradual cost-effectiveness of integrated carbon capture and storage has provided another avenue to continue the sustainability of the oil industry over many decades to come, hence this study is considering a tertiary oil recovery using low salinity as a tertiary oil recovery mechanism.

Primary oil recovery is motivated by the high pressure of the oil reservoir but, with age, declining reservoir pressure necessitates the injection of reservoir-related fluids, such as water or gas - called secondary oil recovery. Furthermore, significant untapped oil reserves, despite secondary recovery, have identified the potential of using non-reservoir related fluids such as carbon dioxide, polymer, surfactants, bio-surfactants and low salinity water among others, are considered as tertiary oil recovery Despite the variety of technical and commercial successes of enhanced oil recovery (EOR), each technique requires fundamental factors to be suitable for economic recovery. Among the techniques, availability of the injecting fluid locally is considered paramount to large-scale EOR applications [8-11]. Availability of seawater in the Middle East region, has been a significant factor that favours the large-scale low salinity EOR. The reservoir formation types typically found in conventional oil fields globally are carbonates and sandstones reservoirs [12-14], with up to 60% of the global oil found in carbonate reservoirs [15], which is characterised as oil-wet as a result of a positively-charged surface of typically pH 8 to 9 [16] caused by brine in strong electrostatic attraction with negatively-charged oil particles charged by carboxylic groups, stearate and fatty acids [17, 18]. Hence, a significant study in the use of low salinity EOR was in the carbonate reservoirs. On the other hand, reservoirs, such as the Wara field in Kuwait, which has had extensive secondary recovery stimulation over the years, and which is considered to be the central field for this Study and is also located near the sea, has been identified as a sandstone reservoir [19]. This calls for deployment of specific theories to the application of low salinity in sandstone reservoirs, rather than in the commonest carbonate reservoirs [14, 20-22].

In spite of the bias nature of this Study to sandstone reservoirs due to access to key resources and reservoir data, understanding the mechanistic theories of low salinity EOR in carbonate reservoirs could help in understanding the challenge and design principles of this Study. Among the many mechanisms that were postulated and verified by researchers, such as the desorption of the polar organic charged ions on the carbonate surface regarded as multivalent ionic exchange [23], the anhydrite dissolution model was considered, which was further expanded by the electrical double-layer effect [24] and electrostatic bond linkage, which are all as results of rock-oil interactions. Two other models in carbonate reservoirs highlight the fluid-fluid interactions, i.e. surface charge alteration/EDL expansion and viscoelastic/snap-off effect [25]. Despite the abundant evidence provided by these mechanisms, they are heavily limited to carbonate reservoirs and also considered significant proportions of multivalent ions, such as Ca^{2+}, Mg^{2+}, and $(SO_4)^{2-}$. Hence a high abundance of seawater characterised by Cl^- could provide a huge potential for altering electrostatic interactions in sandstone reservoirs [26]. The models development according to the year of development has been shown in Figure 1.1.

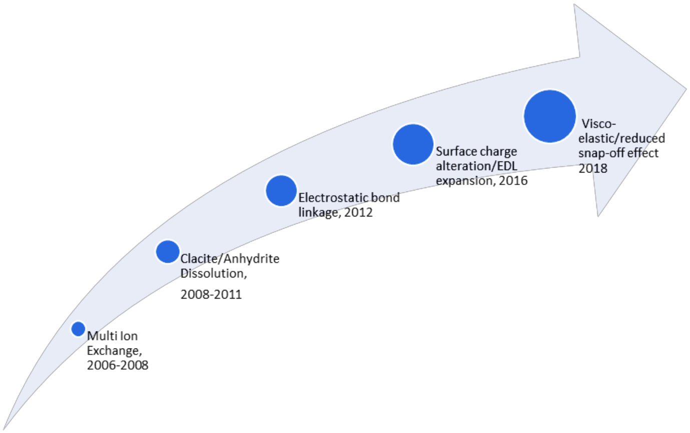


Figure 1.1: Low Salinity Mechanisms in Carbonate Reservoirs Modified [27]

Whereas the sandstone reservoirs employ a different mechanism due to varying composition and ionic interactions, including the Fines Migration mechanism, which hypothesised a salinity level of 5000ppm and below for its optimum occurrence for improved oil recovery [28], understanding the Fines Migration model in sandstone reservoirs integrated with high chloride ions concentration could provide a way forward to match a mechanism for a combined Fines Migration model and Micro Dispersion model. Again, a previous investigation of the Fines Migration model adopted a synthetic core sample with specified compositions, hence this Study employed the use of Wara sandstone samples. Figure 1.2 provides the technological development by age of low salinity mechanisms in sandstone reservoirs.

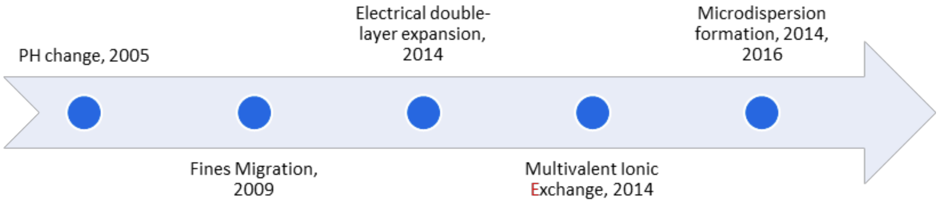


Figure 1.2: Low Salinity Mechanisms in Sandstone Reservoirs [27]

There are commonalities in the electrical double-layer expansion, multivalent ionic exchange and micro dispersion models, both for carbonate and sandstone reservoirs, although PH change has been considered as an important parameter that alters wettability in sandstone reservoirs [26].

1.2 Context of Low Salinity in the Wara Field

The Greater Burgan oilfield is regarded as the world's largest sandstone oilfield, which consists of the Wara field, Mauddud (Limestone), Upper Burgan (Sand), Lower Burgan (Sand 2), and Middle Burgan (Sand), first discovered in 1938 [29]. This field is located in South-Eastern Kuwait and has an area of 800km^2. Although Wara was discovered in 1948 it only came into production later and is characterised with high heterogeneity, which made it complex to study in field scale applications without detailed laboratory and analytical data. These complications were further pronounced by its subdivision into seven (7) different layers in terms of petrophysical properties and interpretation. Furthermore, the seven layers were grouped into three (3) zones based on depositional data of the environment. Due to the complex Wara reservoir heterogeneity and lack of pressure support for secondary recovery, most fields of Wara remained out of production. Later, Wara production was brought about through a massive secondary recovery project called the Wara Pressure Maintenance Project (WPMP).

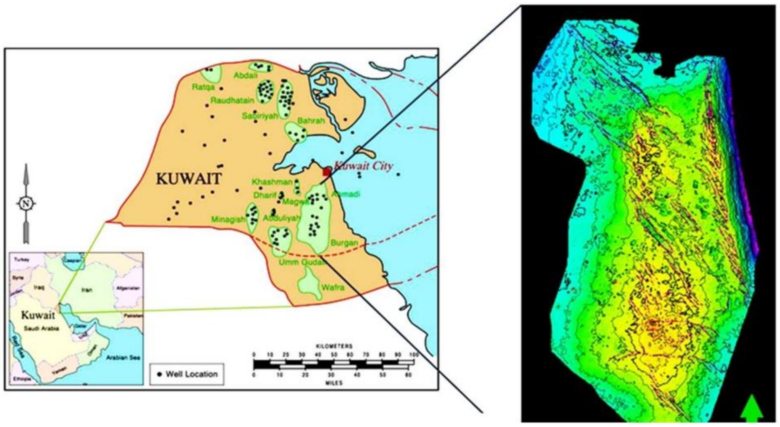


Figure 1.3: Map of Kuwait Indicating Wara Fields [30]

As secondary oil recovery is not usually sustainable [13, 31, 32], it is therefore a novel approach to further understand the potential of low salinity injection in Wara and any other field with similar complex heterogeneity, considering abundant seawater near to the Burgan field.

1.3 Problem Statement

Despite two decades of active and sequenced research in low salinity water flooding as far back as 2008, when Austad [23], who investigated multivalent ion exchange of Ca^{2+}, Mg^{2+} and $(SO_4)^{2-}$ in carbonate reservoirs as a consequence of desorption of the polarised organic group when interacted, it created subsequent changes in the surface chemistry. Although this study went further to investigate other factors, such as the dissolution of calcite and anhydrite, expansion of the double-layer electric and the electrostatic interactions, its efficacy in carbonate reservoirs is considered well understood when compared to sandstone reservoirs, which are still not well understood [11, 32]. This was caused by multiple factors, among which is whether or not rock-fluid (sandstone-oil) were investigated in most studies [33, 34], while others considered fluid-fluid interactions alone [35-37]. This Study considered both the rock-fluid interactions as well as the fluid-fluid interactions jointly to further understand the wettability alteration. Another indication from the literature is that a combination of $(SO_4)^{2-}$ and Cl^- were not mostly investigated due to the high electronegativity of the chlorides, although this could be viewed under the conditions but, altering the conditions that ensure temperature and pressure that are out of precipitation range could be a novel insight into the literature and practical applications leading to possible precipitation [20, 38]. This Study therefore employed the use of smart engineered water injected as a combination of $(SO_4)^{2-}$ and Cl^- , which is expected to supersede the previous combination due to higher electronegativity of the chloride combination; hence a potential improvement is sought through this Study to further understand their role in smart water EOR.

1.4 Research Contribution

(a) Provide understanding of the effect of complex sandstone reservoir heterogeneity in relation to smart water injection containing sulphate and chlorides ions.
(b) Highlight conditions that could allow chloride injection into sandstone reservoirs without precipitations.
(c) Identify the potential mechanism of improved oil recovery in heterogeneous reservoirs by injecting sulphate and chloride ions.

1.5 Research Aim and Objectives

The aim of this Study is to understand the relationship between heterogeneous sandstone reservoirs and improved oil recovery using hybrid low salinity smart water containing sulphate and chloride ions.

The key research objectives used to achieve the aim of the research are:

i. To understand the mineralogical composition of the heterogeneous core samples from sandstone reservoirs for potential low salinity EOR.
ii. To formulate engineered smart water that could potentially alter wettability of such heterogeneous reservoirs.
iii. To identify the displacement mechanism (rock-fluid) interaction of such heterogeneous reservoirs using the engineered smart water.
iv. Understand fluid-fluid interactions using interfacial tension (IFT) variables in the oil-smart water for heterogeneous reservoirs.
v. To assess the scale-off factors to be considered in the application of the findings from this study for the Wara fields.

1.6 Thesis Structure

The Thesis will be structured to compose of the following Chapters:

- *Chapter 1 – Introduction:* this Chapter provides an overview of different techniques employed for tertiary oil recovery, with an emphasis on low salinity smart water EOR due to its economic benefits considering the location of seawater near the field of application. It also provides the context of different mechanisms for the wettability alteration of carbonate and of sandstone reservoirs. For sandstone reservoirs, heterogeneity and chloride, and sulphate anions were further developed to understand the mechanism of such EOR and its practical applications in the Wara field. The Wara field's background, characteristics and potential for such applications were further discussed, followed by the aims, objectives and Chapter arrangement.
- *Chapter 2 – Literature Review:* this Chapter provides an insight into the fundamentals of rock-fluid and fluid-fluid interactions in enhanced oil recovery, with an emphasis on the chemistry and their types in carbonate and in sandstone reservoirs. Further arguments were provided into the context and need for further study in this area of complex heterogeneity of sandstone reservoirs and, in addition, where chloride, sulphate ions could provide certain potentiality in enhancing oil recovery.
- *Chapter 3 – Research Methodology and Materials:* this Chapter provides the rationale and justifications of the research methods and materials that were carefully selected to ensure the objectives were adequately completed.
- *Chapter 4 – Experimental Design and Equipment:* this Chapter provides the design of the experiments in this Study, with emphasis on the different techniques available and deployed to ensure appropriate data are gathered and analysed to provide key outputs data in understanding the heterogeneity of sandstone reservoirs and how engineered smart water has provided adequate wettability alterations for low salinity EOR.
- *Chapter 5 – Results and Discussions:* this Chapter presents the sequence of results obtained from each of the interlinked analyses that were conducted, which was further analysed and discussed with key outputs that matched the objectives of the Study.
- *Chapter 6 – Conclusion and Recommendations:* this Chapter provides the leading conclusions and way forward from this Study. The key academic and practical industry synergy in which laboratory scale data can be scaled-up to serve as a starting point for the application in the Wara field is also identified.

Chapter 2: Literature Review

2.1 Overview

This Chapter first discusses the fundamentals of oil recovery ranging from primary, secondary, and tertiary methods, in which low salinity was identified as a potential means, based on its suitability to the formation, and gives access to sea and economic benefits from the related literature. The Chapter was then followed by an in-depth critical analysis of the different mechanisms of low salinity EOR from literature, with emphasis on their limitations in sandstone reservoirs, which promoted engineering of a hybrid water system that could potentially provide improved recovery for sandstone reservoirs. The Chapter further highlights the wettability alteration in relation to existing and potential smart water flooding, alongside interfacial tension phenomena, and its significance and changes to smart hybrid water in comparison with other mechanisms. The Chapter concludes with the identified gap(s) that this study has provided sufficient contribution and potential application in the Wara field, Kuwait.

2.2 Enhanced Oil Recovery (EOR)

Flow of oil from the reservoir to the surface is often driven by the energy of the flowing reservoir fluids, which can either be originally associated with the fluid by virtue of the original reservoir pressure or can result from the injection of a relevant fluid that provides the required flowing pressure. In this regard, reservoir engineers often monitor the reservoir production history to identify such energy, leading to the classification of the production scheme as either primary, secondary or tertiary oil recovery.

Primary, secondary and tertiary (enhanced) oil recoveries are usually expressions used in the oil industry to describe the recovery of hydrocarbon resources according to the method of extraction from the reservoir or the period at which this extraction or production was done. Primary oil recovery is described as the oil production through the naturally-inducing drive mechanism from the reservoir without the addition of external energy from fluids injection processes i.e. water or gas injections. More often, the natural drive mechanism is comparatively an inefficient process due to limited recovery of the 10-15% of the Original Oil in Place [11] resulting in poor recovery in the overall recovery of the oil from the reservoir. This inefficiency of the natural drive mechanism has led to devising a supplementary source of drive mechanism in the form of artificial induction which, in common practice, are gas injection and water injection as the basic methods to revitalise the reservoir for the purpose of improved production and recovery; this is considered as secondary [11, 39, 40].

Secondary oil recovery describes the additional resource recovery as a result of the common practice of gas and water injection preceding the primary recovery. Basically, it is employed to maintain the reservoir energy (pressure) as soon as primary recovery approaches low production rates, or sometimes can be done concurrently with primary recovery depending on the characteristics of the reservoir [9]. The most common method of secondary recovery is water injection [15]. However, before undertaking any method of secondary recovery process, it should be clear and concise that the natural drive mechanism is poor and inefficient in meeting targeted production. If this is not taken into account, there will be a high possibility of wasting the huge capital invested into the secondary recovery process [11, 41, 42].

Tertiary oil recovery, or enhanced oil recovery (EOR) is the additional recovery after the primary and secondary recovery techniques have been exhausted to their economic limits. There are several methods of enhanced oil recovery (EOR) with applications such as chemical, thermal and other conventional oil recovery types. EOR techniques are applied widely in most oil and gas reservoirs in the world to harness and recover residual hydrocarbon resources after primary production and even after pressure maintenance techniques such as gas injection and water injection. The overall concept of the three categories of recovery is depicted. Enhanced oil recovery (EOR) includes injecting a certain fluid into the oil reservoir, which increases the recovery factor, rather than the recovery factor, which is attained from just maintaining the pressure by water or by gas injection. For light oils, these processes comprise injection of miscible gas, injection of water alternating gas (WAG), flow diversion by polymer gels, the use of surfactants, and polymer flooding; for more viscous (the so called ‘heavy’) oils, those processes contain steam injection and air injection (leading to combustion in situ). Figure 2.1 has indicated the three (3) reservoir recovery regimes.

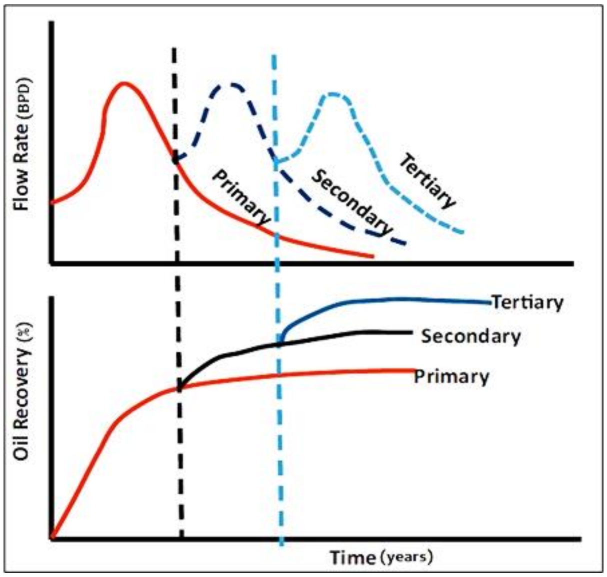


Figure 2.1: Oil Recovery Categories [43]

2.2.1 The Need for Enhanced Oil Recovery

Most oil companies today are trying to maximise the oil recovery factor (RF) from the majority of oilfields, as well as trying to increase the economic oil production rate [11, 29, 44], due to the significant difficulty in discovering new oilfields, the high demand for oil and the shortage of oil supplies. The enclosure where the oil resource is situated poses another inherent problem due to its location i.e. remote or inaccessible areas and containing basins. Many of the sedimentary basins that could already have oil, have been explored and new discoveries are likely to be rare [34]. Those basins that remain unexplored are in inaccessible and globally-sensitive areas around the world (e.g. the Antarctic or the Arctic). Although there are enormous volumes of the unconventional hydrocarbons, for example the oil shales, viscous oils, gas hydrates and shale gas, a number of technologies for using these resources may be energy-intensive or, up until now, not ready to be applied on a large scale [11].

The average recovery factor from the mature oilfields around the world is approximately between 20% and 40% [45]. This contrasts from gas fields where a typical recovery factor is between 80% and 90%. The existing proven oil reserves at the current oil production rate will last nearly 54 years as stated by Muggeridge et al. [45]. This is perhaps as good as it has ever been. Improving the oil recovery to by that amount which is usual for the oil and gas fields can be up to more than twice the time of the oil available or instead allow for increased the oil production rates [46]. This would deliver more time for a gradually energy-hungry world to try to develop an alternative energy source from other technologies. The techniques of enhanced oil recovery (EOR) could considerably extend the world oil reserves once the oil prices are high enough to make the EOR techniques economical. Given an extensive agreement that we are at a period of supply limitations, the operators can at last plan with the assumption that oil prices are likely to remain competitively high although the current pandemic has diminished these due to travel restrictions and online activities [47]. This, together with the understanding that huge new fields are becoming progressively difficult to find, is creating conditions for extensive deployment of EOR.

Oil and/or gas were extracted by applying pressure within the reservoir, which effects the oil or gas flow through an interconnected pore to all production wells. In many oilfields, pressure is maintained by injecting another fluid into reservoirs through the injection wells. The oil is displaced by water and the water occupies the space of the pores that was originally occupied by oil in the reservoir. Conversely, in gas fields, production is initiated simply by decreasing the pressure through the use of compressors at the production well. The gas in the reservoir then expands as long as the pressure drops and therefore flows into the production well [48], Considering this Study is however related to oil recovery, mechanisms of EOR were reviewed in the next Section.

2.2.2 Mechanisms of Enhanced Oil Recovery

Enhanced oil recovery (EOR) has been used interchangeably with improved oil recovery (IOR). Where these terms are all channelled to a specific definition, they are however not exactly the same. IOR is a term that generally implies improving the recovery of oil through whatever means i.e. operational practices, horizontal wells, and enhancing horizontal and vertical sweep efficiencies [25, 49, 50]. EOR, however, is more of a specific concept and can generally be considered as a sub-set of IOR as it tends to enhance oil recovery by reducing oil saturation way below the residual oil saturation [51]. The focal point of EOR varies widely with different oil types, ranging from light, intermediate and heavy oils. A depiction of the fluid saturations and the targets of EOR for generic light and heavy oil reservoirs is shown in Figure 2.2.

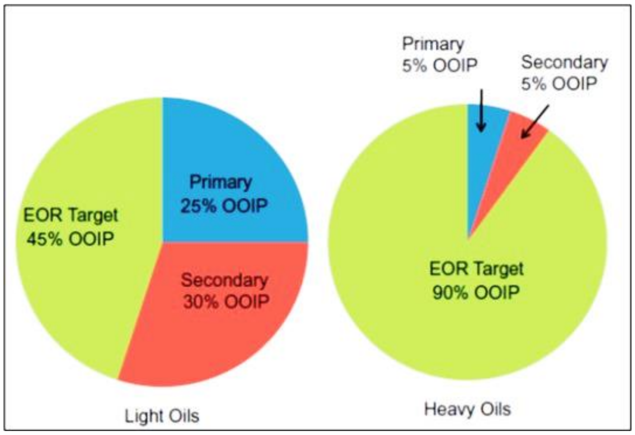


Figure 2.2: Focal Point for Different Oil Systems [52]

As seen in Figure 2.2, EOR is adopted in accordance with the conditions on site. For light oil reservoirs, the tertiary technique is applicable after the exploitation of the secondary recovery process to its economic limit i.e. approximately 45% original oil in place (OOIP) [43]. However, heavy oil reservoirs and oil sands' primary recovery is substantially poor due to the high viscosity of the oil resources, and the majority of the oil production stems from EOR processes.

The degree of mobilisation and the reduction of the residual oil saturation (S_{or}) by an EOR technique is dependent on two major dynamics [53];

- Mobility ratio (M)

and

- Capillary number (Nc).

Mobility ratio is defined as the ratio of mobility of the displacing fluid to the mobility of the displaced fluid expressed mathematically in Equation 2.1 [41, 43, 45, 52, 54, 55]:

$$M = \frac{\lambda_{\text{displacing}}}{\lambda_{\text{displaced}}} = \frac{(\frac{k}{\mu})_{\text{displacing}}}{(\frac{k_o}{\mu_o})_{\text{displaced}}} \tag{2.1}$$

where k is the effective permeability of the fluids (md), λ is mobility, and μ is fluid viscosity (cP). This mechanism affects the microscopic and macroscopic displacement efficiencies of EOR. When $M < 1$, the condition is considered favourable because it indicates that the displaced fluid flows more readily than does the displacing fluid. The reverse is the case when $M > 1$ i.e. an unfavourable condition where the displacing fluid flows more easily than the displaced fluid. This unfavourable condition causes many density-related issues like viscous fingering or channelling, thereby bypassing the residual oil in the reservoir. Improvements in the EOR mobility ratio can be achieved by altering the viscosity of the displacing fluid e.g., using additives like polymers.

Another essential concept in understanding the EOR process mechanism is the capillary number. It is defined as the ratio of viscous forces to the interfacial tension (IFT) forces. It is expressed in Equation 2.2 [43]:

$$N_c = \frac{\text{Viscous forces}}{\text{IFT}} = \frac{v\mu}{\sigma} = \left(\frac{k_o}{\phi\sigma}\right)\left(\frac{\Delta p}{L}\right) \tag{2.2}$$

where μ is the displacing fluid viscosity, σ is the interfacial tension between the displacing and displaced fluids, k_o is effective permeability of the displaced fluid, v is Darcy velocity, ϕ is medium porosity, and Δp/L is the pressure gradient. A plot of the ratio of residual oil saturation after EOR to the residual oil saturation before EOR vs capillary number is shown in Figure 2.3 and is a representation of the capillary number. It shows that reduction in residual saturation increases with the capillary number.

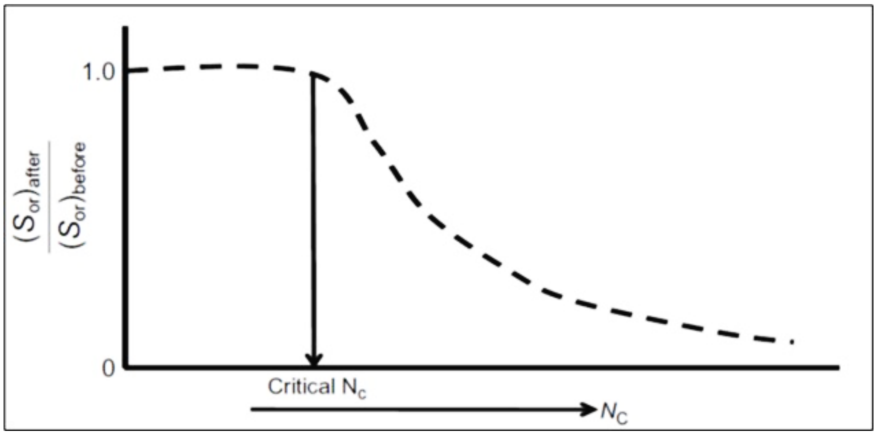


Figure 2.3: Effect of Capillary Number on Residual Oil Saturation [52]

So, in essence, increasing the capillary number tends to decrease residual oil saturation, hence improving oil recovery. This can be achieved, from the expression, by:

- Decreasing the interfacial tension between the fluids
- Increasing the pressure gradient

and

- Increasing the displacing fluid viscosity

Of all these factors mentioned above, decreasing the interfacial tension between the displaced and displacing fluids is the most practical approach to increasing the capillary number in order to reduce the residual oil saturation [42, 56, 57], hence this Study investigated the IFT of the reservoir samples from the Wara field. From Figure 2.3, it is shown that the capillary number has to exceed the critical capillary number to initiate mobility of the residual oil saturation.

2.3 Methods of Enhanced Oil Recovery

All enhanced oil recovery methods are designed in such a way to increase the capillary number by altering one or more of the parameters in Equation (2.2). Generally, EOR techniques can be broadly categorised as shown in Table 2.1 [12]:

Table 2.1: Enhanced Recovery Methods [52]

Chemical (Section 2.2.3.1)	• Polymer flooding • Alkaline flooding • Surfactant flooding • Alkaline-surfactant polymer (ASP) • Micellar
Miscible (Section 2.2.3.2)	• CO_2 injection • N_2 and flue gas injection • Rich gas injection • Lean gas injection • Water alternating gas (WAG) injection
Thermal (Section 2.2.3.3)	• Steam injection (steam flooding, cyclic steam simulation and steam assisted gravity drainage (SAGD)) • In situ combustion (wet combustion, forward combustion and reverse combustion)
Others (Section 2.2.3.4)	• Microbial enhanced oil recovery (MEOR) • Low salinity flooding • Foam • Acoustics • Electromagnetic

2.3.1 Chemical Methods

Chemical flooding tends to increase the injection water viscosity and to improve the mobility ratio and sweep efficiency of the EOR process. It involves the blending of water by the addition of chemicals to increase the viscosity whilst lowering the interfacial tension of the displacing and displaced fluids, thereby increasing the oil recovery [58]. This is actualised by increasing the overall sweep efficiency i.e. areal, vertical and displacement efficiencies. It is, simply, in essence, the modification of the waterflooding technique. However, the addition of specific chemicals is peculiar to the desired application.

For any secondary and tertiary oil recovery methods, the ultimate recovery is the combination of the products of individual efficiency factors expressed as:

$$\mathrm{Rf} = (\varepsilon_A \varepsilon_V)\varepsilon_D \quad \text{or} \quad \mathrm{Rf} = \varepsilon_{vol}\varepsilon_D \tag{2.3}$$

where, ε_A is the areal sweep efficiency, ε_V is the vertical efficiency, and ε_D is the displacement efficiency.

The areal sweep efficiency is the fraction of the area of the pattern of interest that is swept by the fluid displacing the in situ fluid (displaced). There are factors responsible for determining the areal sweep and are listed as follows [11, 31, 36]:

- Volume of injected fluids
- The pattern nature
- Areal heterogeneity
- Fluid mobilities

The fraction of the vertical section of the area of interest (payzone) in contact with the displacing fluid is the vertical sweep efficiency. The vertical sweep efficiency is chiefly a dependent on [59]:

- Volume of displacing fluid injected
- Level of gravity segregation
- Vertical heterogeneity
- Fluid mobilities

It is worth noting that the product of areal sweep efficiency and vertical sweep efficiency is termed as volumetric sweep efficiency, and it highlights the overall fractions of the pattern of the flooding process that are contacted by the displacing fluid injected.

On the other hand, displacement efficiency is the fraction of movable oil that has been displaced from the swept zone at any given time. Only when the residual oil saturation is zero will the displacement efficiency be 100% [37]. As stated in Section 2.2.1, chemical enhanced oil recovery tends to increase the capillary number to mobilise residual oil in lieu of the mechanism of EOR and/or decrease the mobility ratio for better vertical and areal sweep efficiencies.

Chemical oil recovery methods include: polymer flooding, alkaline flooding, surfactant flooding, alkaline-surfactant-polymer (ASP), and micellar.

These chemical methods involve the chemical mixing with water to form the displacing fluid for EOR. Therefore, these methods require the reservoir conditions and characteristics that work best for water injection. A discussion on the types of the chemical enhanced oil recovery processes will be presented in the subsequent Section.

2.3.1.1 Polymer Flooding

Enhanced oil recovery methods are usually geared to improve the displacement efficiency by reducing the residual oil saturation. Polymer flooding, however, is designed to improve the sweep efficiency by decreasing the mobility ratio [60, 61]. As stated previously, a mobility ratio of a magnitude of 1 or less is considered favourable and indicates that displacing fluid cannot travel faster than the displaced fluid.

$$M = \frac{k_w \mu_o}{k_o \mu_w} \tag{2.4}$$

When M equals 20, it means that the ability of the displacing fluid (injected water) flows 20 times lower than that of displaced fluid (oil). From Equation 2.4, the value of M can be made favourable by adopting any of the following processes:

- Increasing effective oil permeability (k_o)
- Decreasing effective water permeability (k_w)
- Decreasing oil viscosity (μ_o)
- Increasing water viscosity (μ_w)

Not much can be done to alter the flow characteristics of the oil in the reservoir using chemical methods. Polymers are added to water to increase the viscosity of the water and reduce the effective permeability to water, thereby reducing the mobility ratio of the process [11]. Polymer flooding is regarded as an improved and revised water flooding process for EOR, since the polymer alone does not recover the residual oil trapped in the reservoir pore spaces or isolated by formation water. In essence, polymer flooding can recover additional oil, over that which was obtained from ordinary water flooding, through a significant improvement in the sweep efficiency by increasing the reservoir volume that is contacted [40]. An aqueous solution of water-soluble polymers is able to reduce the mobility of the displacing water in the reservoir, hence improving the flood efficiency. Largely, partially-hydrolysed polyacrylamides (HPAM) and xanthan gum (GXG) are used as the additives in a polymer flood. They tend to reduce the mobility of the injected water by:

- Increasing the viscosity of the injected phase
- Reducing the effective permeability of the formation to water (as a result of retention of polymer molecules in the pore spaces of the reservoir rock). However, the oil permeability remains unaffected by this.

Polymer displacement mechanism

Polymer flooding can significantly produce a substantial recovery of residual oil compared to the ordinary water flooding process. Polymer flooding can be carried out by injecting slugs of polymer solution (~25 to 50% of reservoir pore volume) followed by water slugs to drive the polymer slug and the oil bank develops towards the production tubing [27, 62]. The follow-up water and the polymer slug mobility ratio are unfavourable, therefore, the follow up water tends to finger through polymer slug and slowly dilutes the slug. To minimise this unfavourable mobility ratio between the follow-up water and polymer slug, a buffer zone of fresh water containing polymer with a decreasing concentration of polymer (taper) separates the follow up water, and polymer slug is affected as shown in Figure 2.4. The grading on the buffer zone is designed in such a way as to balance the concentration of the injected fluids i.e. the viscosity of the leading edge of the buffer zone is the same as the viscosity of the polymer slug, and the viscosity of the follow-up water equals the viscosity of the trailing edge of the buffer zone.

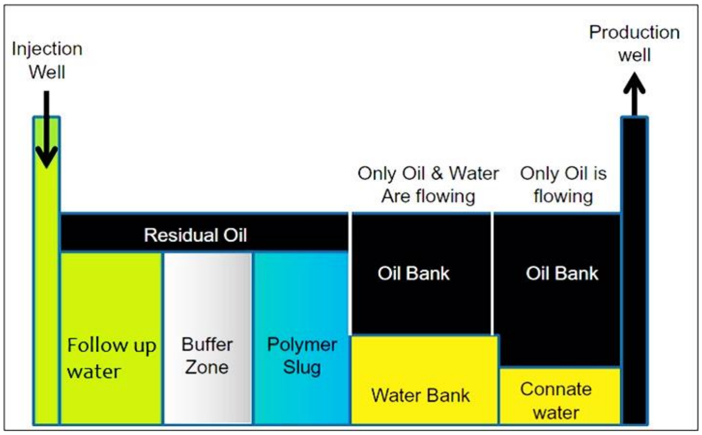


Figure 2.4: Schematic of Polymer Enhanced Oil Recovery [43]

2.3.1.2 Alkaline Flooding

Alkaline flooding, also known as caustic EOR, works by creating or forming surfactants in situ; these surfactants in turn lower the interfacial tension between oil and injected fluids. Some of the alkaline reagents used for the injection process include: sodium carbonates, sodium hydroxide or sodium silicates [21, 63]. These alkaline reagents react with the organic acids contained in certain crude oils to produce surfactants in the reservoir. The surfactants may also react with the reservoir rock favourably for wettability alteration purposes and to aid the displacement.

Furthermore, caustic, or alkaline, flooding has been used for a wide range of reservoirs containing light to intermediate oils, which could potentially match those in the Wara field, although their economics is not favourable [64]. The choice of alkaline flooding is highly-dependent on the targeted crude oil type [42]. Those having significant number of organic acids are more desirable. However, this sub method of EOR is most applicable in light to intermediate crude oil reservoirs because the mobility ratio is favourable. Alkaline flooding has a number of limitations. These include [64]:

- Cost of injection reagents
- Not suitable for carbonate reservoirs
- Scale formation and deposition in producers
- Temperature effects on the injected chemicals
- Reservoir heterogeneity to sensitivity

2.3.1.3 Surfactant Flooding

Surfactants, or surfacing acting agents, are chemicals that have the ability to reduce the surface tension of their solutions to a noticeable level to promote the mobility of the residual oil through displacement processes when it comes in contact with it.

These surfactants have amphiphilic (hydrophilic and oleophilic parts) molecules. One end of this molecule is attracted to water (hydrophilic) and the other one is attracted to oil (oleophilic). It is this peculiar phenomenon that enables them to partly dissolve in water and oil, thereby forming a miscible mixture. Sulfonate is one of the most common surfactants used in the oil and gas industry. It is a complex chemical agent sourced from hydrocarbons, with a molecular weight of up to 550lbm/mol [43, 65]. Surfactant slug injection is a stepwise process and consists of the following sequence:

- Pre-flush of water having low salinity
- Surfactant slug in colloidal solution
- Polymer as mobility buffer
- Water as driving fluid.

The objective of the pre-flush is to recondition the reservoir by injecting brine prior to the surfactant slug injection. This injection of brine is aimed at lowering the salinity of the formation water and the hardness of the formation water so as to avoid altering or annulling the surfactant interfacial property.

The range of the volume of surfactant slug is between 5-15% pore volumes for field applications, especially when the concentration of the surfactant is high. However, for chemicals in a lower concentration, the slug size is usually larger and, sometimes, as much as 50% pore volumes. From laboratory experiments and investigations, the minimum size of the slug needs to be 5% pore volume in order to achieve effective oil recovery.

The mobility buffer displaces the surfactant slug with varying polymer concentrations between the drive water and the surfactant slug, which prevents the rapid slug deterioration from the trailing end of the surfactant slug to the leading edge. The design and injection of the mobility buffer solution is an important process of all the chemical flooding techniques in that it tends to minimise and maintain the chemical slug size required for an economical and efficient recovery method.

Figure 2.5 demonstrates the chemical slug injection mechanism when employed as a secondary recovery technique. The surfactant slug will displace the oil in a miscible manner and form an oil bank, where the remaining oil and water are flowing together simultaneously. Here, the production wells will continue to produce at a decline rate from the start of production until water breakthrough from the water bank. However, an increase in the water and oil production rate indicates the response of the field to the surfactant slug (or any other chemical EOR technique).

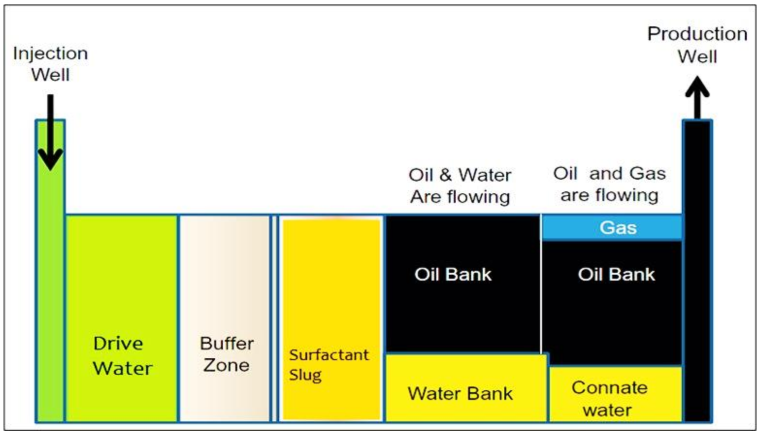


Figure 2.5: Schematic of Surfactant Flooding [43]

Figure 2.6 depicts a schematic of the general chemical EOR flooding technique as a tertiary recovery process. It signifies that the initial water flood has displaced the oil and has reduced it to the residual immobile saturation. Water is the only fluid produced until the water-oil bank reaches the producing well. One of the major causes for concern, however, is the problem of handling the produced water.

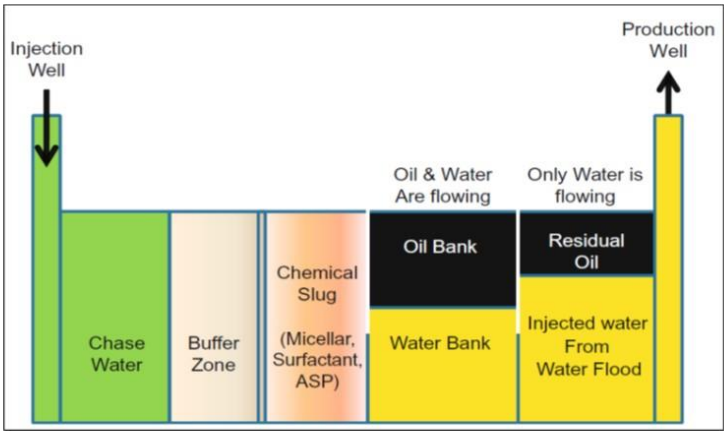


Figure 2.6: Schematic of ASP, Micellar and Surfactant Flooding [43]

There are certain limitations associated with surfactant slug flooding:

i. Injection materials are expensive
ii. Likely reaction between polymer and surfactant
iii. Temperature effects on chemicals
iv. Limited use in rock types
v. Applicable to only light oil reservoirs
vi. Ineffective in heterogeneous rocks
vii. Limited operating conditions

2.3.1.4 Alkaline-Surfactant-Polymer (ASP)

The alkaline-surfactant-polymer (ASP) chemical EOR technique is based on the same mechanism as other chemical EOR processes. It is designed to mobilise the residual oil in the reservoir. However, combines the mobility control chemicals with interfacial tension reducing chemicals to increase additional oil recovery and to improve displacement efficiency. It relies on the reduction of the expensive surfactant use by 20-70% by the addition of cheaper alkali as one of the chief additives of the injected slug of ASP [43, 52, 66]. Alkali, naturally, form surfactants in situ when it reacts with the naturally-occurring organic acids present in certain crude oil types. This phenomenon generally helps to significantly reduce the cost associated with the use of commercial surfactants by providing a cheaper alternative. The use of alkali has the following additional benefits:

- It alters the wettability of the reservoir rock to a more water-wet condition
- It reduces the polymer and surfactant adsorption on reservoir rock

The two most common alkaline reagents employed for ASP flooding are sodium carbonate (Na_2CO_3), commonly known as soda ash, and sodium hydroxide (NaOH), commonly known as caustic soda. In all chemical EOR techniques, there are merits and demerits of using them for additional oil recovery, ranging from environmental factors to economic stands. The advantage of the ASP solution preceded by polymer buffer is that it provides a high unit displacement of miscible floods and high areal sweep efficiency through better mobility control. The only difference between water flooding and ASP during field operation is the addition of chemical mix and filtration equipment.

The disadvantages and limitations of ASP flooding applications are quite pronounced and are a call for concern. Firstly, the high expenditure in the acquisition and use of chemicals for ASP application is daunting. It is dependent on the slug size, the parameters on which the income is based and on the initial oil saturation prior to the injection and volume recovered, which is really difficult to evaluate. Secondly, the ASP is used in depleted water flood oil reservoirs and only water will be produced for a long period of time (sometimes up to 2 years) [52]. This produced water will be analysed to see if it will be suitable for reinjection and, once the quality falls short of the intended use, it needs to be disposed of. Some of the salts will precipitate in the production well and scales will be formed and restrict production as the process is not well suited for carbonate oil reservoirs. Thirdly, the chemicals used are sensitive to temperature change and there is a degradation of the chemicals at higher temperatures. Lastly, the ASP reagents used are potentially hazardous to the environment. If, during the recovery process, the chemicals drain into the adjacent or adjoining water bodies, contamination of the environment is imminent.

2.3.1.5 Micellar

Also referred to as microemulsions, micellar is composed of an array of chemicals to form a suitable surfactant slug for EOR. It comprises of five main components: (i) electrolyte, (ii) hydrocarbon, (iii) surfactant, (iv) alcohol (co-surfactant), and (v) water. As one of the problems encountered by the any chemical flooding technique is the adsorption of the chemical reagent on the surface of the reservoir rock, the addition of alcohol, which is a co-surfactant, to the slug solution minimises the surfactant adsorption onto the reservoir rock. The electrolyte added, usually ammonium sulphate or sodium chloride, adjusts and controls the viscosity of the micellar solution as it contacts the formation water.

2.3.1.6 Application of Chemical Flooding

Chemical water flooding is applicable to many reservoirs that have undergone a successful water flooding. Generally, applications of chemical flooding are as follows:

- They have a limited applicability in carbonate reservoirs, or in reservoirs with brines containing calcium and magnesium ion, because chemical adsorption is high in these conditions, but is widely applicable in sandstone formations.
- They are best applied to reservoirs with intermediate crude oils. In low gravity crude oils, the high viscosity associated will require increasing the viscosity of the injection slug by the addition of more chemicals to attain a favourable mobility ratio resulting in incurring higher cost, hence it will be uneconomical.
- A chemical EOR technique is applicable, both for secondary and for tertiary recovery processes.

2.3.2 Miscible Flooding

Miscibility is achieved when multiple fluids wholly mix with one another and individual phases are indistinguishable. Water and oil are not miscible when they come into contact. They sparingly form a heterogeneous mixture that, on standing separate, split into two distinct phases. Crude oil and natural gas are also immiscible i.e. they do not mix wholly together to form a homogeneous mixture. In miscible flooding as an EOR technique, the reduction of the interfacial tension between the displaced and displacing fluid stems as the basis of miscible EOR. Other mechanisms include a decrease in oil viscosity and an increase in oil volume (swelling), which provides better sweep of the reservoir.

It is apparent from Equation 2.2 that reducing the interfacial tension between the displaced and displacing fluids will significantly increase the capillary number, meaning that the residual oil saturation can significantly be lowered. This is the chief principle of any miscible displacement process.

Miscible flooding entails the injection of gases into the reservoir at certain conditions to initiate miscibility between the injected gas and the in situ oil to improve mobility by increasing the volume of the reservoir fluids and pressuring the reservoir. This involves the injection of light to intermediate hydrocarbons, or CO_2, in most cases into the reservoir as displacing fluids. Since these gases act as solvents, they tend to reduce the interfacial tension between the now immiscible fluids and, as a result, improve the microscopic displacement of the residual oil, thereby enhancing recovery.

Miscibility between the injected solvent fluid and the in situ fluid occurs only when the reservoir pressure exceeds the minimum miscibility pressure (MMP), which is the lowest pressure for which a gas can develop miscibility through a multi contact process with a given reservoir oil at reservoir temperature. It is wholly a function of reservoir temperature and fluid composition.

For a miscible flooding process to be economically viable as an EOR technique, stringent conditions must be adhered to. These conditions can be summarised below:

- An abundant volume of injection gas solvent must be available at a cost-effective rate to favour the economic viability of the miscible project.
- The pressure required for the miscibility between the gas solvent and reservoir oil must be attainable for the process to work.
- Additional oil recovery must be enough substantially, and in terms of time taken, to compensate the project economics associated with the additional cost incurred.

There are two types of miscible displacement, namely contact miscible displacement and multi contact miscible displacement. Firstly, contact miscible displacement is that in which the injected fluid forms a homogeneous mixture when it contacts the in situ fluid in all ramifications. As for multi contact miscible flooding, the injected fluid and the in-situ reservoir oil are not first contact miscible, but miscibility could develop after multiple contacts.

2.3.2.1 CO_2 Injection

This type of miscible flooding comprises of injecting large quantities of CO_2 into the reservoir at high pressures to attain miscibility with the in situ oil in the reservoir. It plays a very important role in the incremental production in the EOR process in all non-thermal tertiary recovery techniques worldwide. The mechanisms of CO_2 miscible flooding are as follows:

i. Reduction of oil viscosity
ii. Swelling of oil
iii. Interfacial tension reduction at the miscible front
iv. Attainment of miscibility between injected solvent gas and in situ reservoir oil, which reduces the interfacial tension between the fluids when they contact each other.

The volume of CO_2 injected may be in excess of 15% pore volume. Normally, CO_2 is not miscible with crude oil[68], however it extracts the lighter components of the crude oil at high pressures. When the pressure is above the MMP, efficient displacement of the in situ crude oil from the reservoir occurs as miscibility will develop. In CO_2 miscible floods, the range of MMP is between 2200 to 3200psi under stated reservoir conditions and crude oil composition [67]. CO_2 has an advantage of extracting a wider range of components. Hence, miscible injection is most effective at a lower MMP and more reservoirs can be targeted for an EOR miscible technique. MMP is generally lower for high-gravity oils (> 40 API) and at a minimum reservoir depth of 2500ft [52]. However, miscibility is not achieved between injected CO_2 and in situ crude oil for low gravity oils (< 20 API) at shallow depths of 1800ft. Hence, recovery is poor due to immiscible displacement at that depth and crude oil characteristics. Here, the reservoir depth should be in excess of 4000ft to achieve miscibility.

As mentioned earlier, other mechanisms apart from miscibility that contribute to EOR are oil viscosity reduction, oil swelling and solvent extraction. CO_2 is readily soluble in crude oil at high pressures [12, 34], so swelling of the oil and viscosity reduction are noticed even before the complete miscibility is achieved. The oil and the CO_2 containing the light ends or components of the crude oil flow together as a result of the low interfacial tensions between the fluids at MMP or above it. The technique is not also without its limitations. They are summarised as follows:

i. CO_2 availability
ii. Corrosion in wells due to acidic gases
iii. Separation of oil from the CO_2 in the production effluent
iv. CO_2 requirement
v. Poor mobility control emanating from CO_2 low viscosity

2.3.2.2 Nitrogen and Flue Gas Flooding

Miscible EOR techniques based on the principle of injecting N_2 and flue gas recover oil by the vaporisation of the lighter components of crude oil at high pressure. Depending on the reservoir conditions and crude oil composition, the N_2 and flue gas injection technique can be either miscible or immiscible [9, 68]. The merits associated with this method of miscible displacement are summarised as follows:

- They can be used as chase or drive gas in gaseous miscible techniques
- The availability of injection gases
- The use of cheap non-hydrocarbon gases
- Miscibility achievement at high temperature

The limitations however are also stated as thus: (1) N_2 has lower viscosity than CO_2 resulting in adversely unfavourable mobility ratio; solubility in oil is poor; (2) considerably higher pressure is required for achieving miscibility with oil; (3) deeper reservoirs having light crude oil are candidates for N_2 and flue gas miscible EOR techniques; (4) viscous fingering is imminent and, as a consequence, large amounts of oil are bypassed [11]; (5) there are poor horizontal and vertical sweep efficiencies; (6) reservoirs with dips are preferred to avoid gravity segregation effects; (7) corrosion problems are experienced in wells when flue gas is used; and (8) separation of hydrocarbon gases in production stream or effluents.

2.3.2.3 Rich Gas Injection

This method is also based on the principle of injection gas and in situ oil miscibility as with any other miscible flood technique. Also called condensing gas drive, it entails the injection of a slug of 10 to 20% pore volume of natural gas enriched with ethane through hexane into the EOR candidate reservoir [69, 70]. The enriched hydrocarbon components from the injected gas are transferred to the in situ oil in the reservoir during the miscible flooding technique, and miscibility is attained between the displacing and displaced fluids. The miscible front, also referred to as the miscible bank or miscible zone, displaces the oil in the reservoir towards the production well [32, 71]. The cost associated with different flooding schemes has been an integral factor for selecting an appropriate injection, ensuring low cost during EOR.

2.3.2.4 Lean Gas Injection

Also referred to as the vaporising gas drive technique, it comprises the use of lean hydrocarbon gases, such as methane, as the injection fluid for the purpose of displacing the residual reservoir oil in an attempt to enhance the incremental recovery. In this method, the injected gas leads to the vaporisation of the light to intermediate components of the in situ oil to enact miscibility [69]. As lean hydrocarbon gas is injected into an oil reservoir, there is a drastic exchange of a variety of components between the injected and in situ fluids through multiple contacts with each other until miscibility is attained. Invariably, the miscible front forces the oil to the producing well. Rich and lean hydrocarbon gas injections for miscible flooding techniques are not also without their limitations: (i) the reservoir depth plays a very crucial role in this method as pressure increases with reservoir depth. Miscibility requires high pressure, therefore shallow reservoirs do not have the capacity to generate the pressures required for attainment of miscible conditions. Hence, the depth of the reservoir should support the use of this technique by providing the required MMP in order for the technique to be efficient; (ii) because of the large viscosity gradient between the injected hydrocarbon gases and the in situ oil, viscous fingering will be imminent during the flooding process. This will obviously affect the vertical and areal sweep efficiencies thereby bypassing large quantities of oil in the reservoir; (iii) the process may be appropriate in dipping formations where gravity is taken advantage of because of the unfavourable mobility ratio of the process, which can be prevalent in lowering the overall recovery of the process; and (iv) the process requires sacrificing large volumes of very expensive hydrocarbon gases that cannot be recovered later on [33, 64, 69].

2.3.2.5 Water Alternating Gas (WAG) Injection

The WAG technique is a process where a slug of rich hydrocarbon gas of about 5% pore volume is injected into the reservoir, followed by a lean gas. Water is injected with the drive gas in a water-alternating-gas fashion to improve the mobility ratio between the solvent slug and the drive gas. This process enhances the sweep efficiency and minimises the channelling of the gas. WAG is widely practiced in the CO_2 miscible flood technique [67, 72] In the CO_2-WAG technique, a CO_2 slug of about 20 to 50% pore volume is injected, followed by a slug of water, which tends to improve the mobility ratio between the injected fluids and in situ oil. It also enhances reservoir sweep efficiency. The schematic is depicted in Figure 2.7.

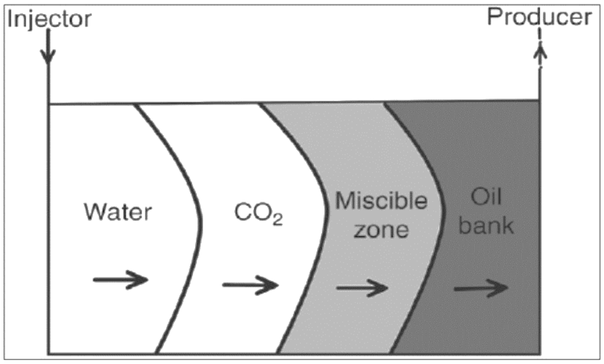


Figure 2.7: Schematic of CO_2-WAG Technique [52]

This method of oil recovery capitalises on the viscosity reduction of heavy crude oil when thermal energy is applied. The viscosity of the heavy oil reduces to a point where it becomes mobile and can flow into the well with ease from the reservoir for production. Viscosity is sensitive to temperature. It is not uncommon for a low gravity oil of about 13° API to have a very high viscosity of 2000cP at, say, a reservoir temperature of 100°F [67, 72-74]. The high viscosity can be reduced to 10cP when the oil is heated from 100 to 300°F, either by injecting hot fluids into the reservoir or by thermal energy generation through the combustion of some part of the oil in the reservoir [43]. This method is categorised broadly into two types: steam injection and in situ combustion.

2.3.2.6 Steam Injection

Steam flooding is similar to water flooding in that it is a pattern drive. Just like water flooding, a suitable well pattern is selected, steam is injected into some in the same proximal surrounding wells, and oil is produced from the adjacent wells. The recovery performance from steam flooding is highly-dependent on reservoir characteristics, pattern size and the chosen flooding pattern [12, 75]. There are about four phases of development in a steam flooding project:

- Screening of the reservoir to be flooded
- Pilot tests
- Field scale implementation
- Reservoir management

The process entails the continuous injection of steam to form a steam zone around the injector, which continues to advance into the reservoir with the injection towards the adjacent producer well. In a typical steam injection process, the injected fluid is made up of 80% steam and 20% water [41, 43, 76]. Usually, the steam injection process is carried out in conjunction with the huff-and-puff process, i.e. another steam injection process that will be discussed next, where the process is carried out on producing wells, specifically when the oil is too viscous to flow into the well from the reservoir, thereby heating it up to initiate mobility. When the steam passes through the reservoir between the injector well and the producer well, a region of different temperatures and oil saturation is created. These regions could range from the steam zone around the injector well, where the temperature is highest, to the region where the reservoir has not been contacted by the steam [77]. This region contains the reservoir fluid system, which exists at the initial reservoir condition in terms of fluid saturations and original temperature but, due to the vaporisation of the lighter components in the crude oil, in turn reduces the viscosity and improves mobility. In steam flooding, oil is recovered through a number of mechanisms (see Figure 2.8) combined to give its peculiar advantage over several other recovery systems.

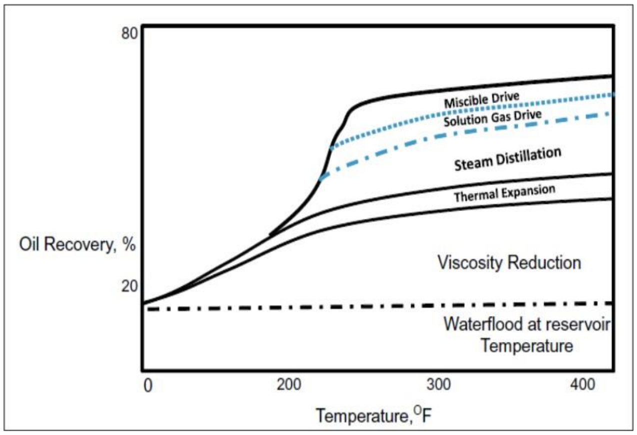


Figure 2.8: Steam Flooding Mechanisms Contribution to Oil Recovery [52]

Importantly, there are five drive mechanisms that have been thumbed as the main mechanisms of steam flooding:

- Solution gas drive
- Oil swelling and thermal expansion
- Viscosity reduction
- Steam distillation
- Miscible displacement

When temperature increases, the solution gas liberates from the bulk of the crude oil. This results in a proportional pressure decline gradient between the producer and injector with the expansion of the solution gas [77, 78]. This expansion provides the additional force or energy required to drive the oil into the producer. Oil expands with an increase in temperature, which, in turn, increases its saturation and makes it more mobile. The level of expansion depends on the oil composition. Thermal expansion is more effective in recovering light oils as a result of its ability to expand more rapidly than heavy oils and, as such, a thermal expansion mechanism is dependent on initial oil saturation, temperature of the heated zone and type of crude oil. Generally, recovery as a result of thermal expansion ranges between 5 to 10% [43].

Termed the most important driving mechanism for heavy oil recovery, viscosity reduction reduces the oil viscosity with increasing temperature. The overall result for increasing the temperature is improving the mobility ratio (M). Sweep and displacement efficiencies are improved with lower viscosity [32, 79]. When oil is displaced from the region of high temperature between the injector and the producer, to a lower temperature region, the oil viscosity, again, increases, hence the rate of advance flow of oil is considerably reduced. Conversely, a substantial volume of oil accumulates and forms an oil bank near the producer well. This bank is responsible for a considerable oil production rate in steam flooding of heavy oils.

Steam distillation is the primary mechanism in the steam zone between the injector and the producer. The distillation process entails the vaporisation of the lighter components of the crude oil to form a binary mixture of condensable hydrocarbons and steam mist [80]. This mixture will mix with the residual oil trapped by the oncoming hot condensate region superseding the steam zone [11]. A solvent bank will be created behind the hot condensate front. Essentially, residual oil saturation can be zero where the original crude oil has mixed with the distilled hydrocarbon condensate. An oil miscible drive is formed in the hot condensate zone when the solvent bank is generated by the steam zone and removes additional oil from the formation. The steam zone forms a miscible oil slug, which displaces oil it contacts with a 100% efficiency [43].

The main advantage of steam injection over other EOR techniques is that it can be applied to a wide range of reservoir types. Conversely, steam injection is also not without its limitations i.e reservoir depth and reservoir thickness.

2.3.2.7 Cyclic Steam Stimulation (CSS)

This is also known as “huff and puff” or “team soaking”, CSS consists of three major stages:

- The injection of steam
- Steam soaking
- Production

At the first stage, steam is injected into the well at a high injection rate for a period of one month [77]. At the end of the injection duration, the well is shut down for a few days. This is the steam soaking stage. This allows the oil to be heated in the area within the vicinity of the wellbore. The well then produces until the economic flowrate has been reached. This is the production stage of the CSS technique. The process cycle is then repeated. The frequency of the cycle is dependent on the stimulation response of the production after each cycle is completed. The process is quite effective in the first two cycles, after which the effect of the stimulation diminishes [12]. The steam soaking process improves the oil production rate significantly by the following means:

- Removal of accumulated wax deposits around the wellbore, thereby obtaining a favourable skin factor i.e. increasing the permeability
- Increasing the oil mobility and productivity by reducing the oil viscosity due to increase in temperature
- Thermal expansion of oil increase, which affects the relative permeability and oil saturations favourably.

Many initial applications of huff and puff results in an increase in production substantially more than those predicted by the application of models. This is as a result of the well clean up and permeability improvement around the vicinity of the wellbore associated with the huff and puff method.

2.3.2.8 Steam-Assisted Gravity Drainage (SAGD)

SAGD is a thermal heavy oil recovery technique developed originally by Butler in 1991 [43]. The work postulated the use of steam injection with horizontal well technology to enhance the mobility of oil to a production well by the means of the forces of gravity [78]. The process employs a pair of parallel wells (horizontal) situated above and below the formation. Figure 2.9 and 2.10 show the schematic illustration of the SAGD procedure. The top well is the injector of the steam and the bottom well is the producer.

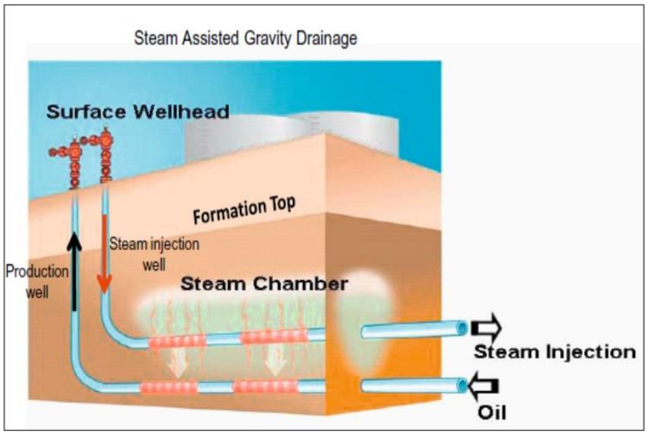


Figure 2.9: SAGD Concept [78]

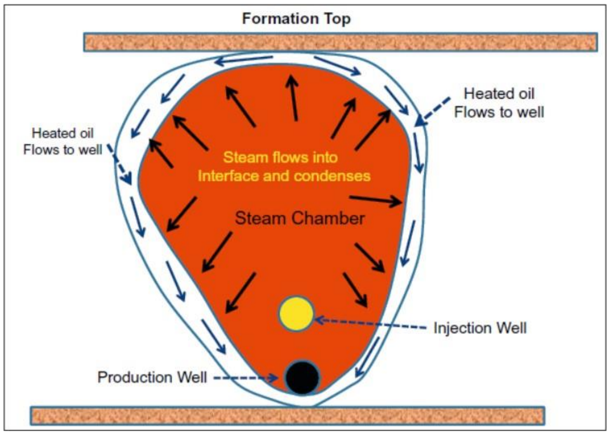


Figure 2.10: Transverse Section of a Formation Undergoing SAGD [52]

Initially, the heavy oil is cold and immobile. This calls for the establishment of a thermohydraulic communication between the pair of wells (injector and producer) through a preheating regime where steam is injected into both wells. This steam circulation is sustained for a period of time to reduce the heavy oil viscosity and enhance the mobility. Once this mobility has been enhanced, the steam injection is sustained in the upper well only. With the continuous injection of the steam into the upper well, the steam rises to the top of the formation forming a steam chamber that propagates horizontally and vertically. The steam injected will reach the steam chamber interface where it will heat the surrounding cold oil sands. The heated oil (with reduced viscosity) and condensate will drain by gravity and flow towards the horizontal well near the bottom of the reservoir in a counter-current flow to the rising steam from the top steam injection well. The fingering phenomenon associated with steam injection is however eliminated with SAGD because the oil and steam paths are separate. This also means that displacement will be slow.

2.3.3 In-Situ Combustion

Fire flooding is a distinctive EOR technique, where a portion of the oil in place is combusted to generate heat. The combustion is generated by oxidising the in situ oil and igniting it, and the fire in situ is sustained by a constant stream of air injection into a centrally-located injection well. A chemical reaction between the crude oil and the oxygen component of the injected air can generate heat even without combustion [10]. The duration of the oxidation process depends on the crude oil composition, and may be sufficient to develop temperatures that will ignite the oil in situ. If this is not feasible, there are other methods of ignition:

- Oxidisable chemicals in the injected air stream
- Preheating injection air
- Downhole electric heaters

There are different forms of in situ combustion processes, which will be discussed briefly in the following Sections.

2.3.3.1 Forward Combustion

The name "forward combustion" stems from the fact that the flame front is propagating in the same direction as the injected air. Figure 2.11 depicts the different regions and mechanisms formed in the oil reservoir when a forward combustion technique is applied.

The burned region is where the primary combustion occurs. This region may contain residual amounts of unburned organic material and is filled with air. It is sometimes clean when complete combustion occurs, hence it will be free of coke deposits.

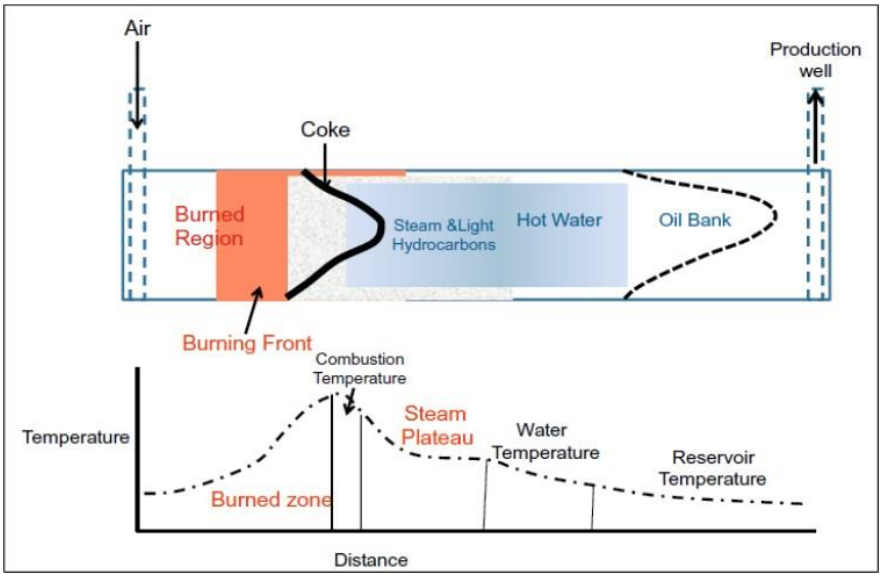


Figure 2.11: In Situ Combustion Temperature Zones [52]

The regions then propagate from the combustion front zone through the oil bank and to the production well. The temperature profile is also shown in Figure 2.11.

2.3.3.2 Reverse Combustion

The reverse combustion process has been suggested for applications in highly-viscous oils contained in a reservoir. This process is first started as a forward combustion by injecting air into a well that will later become the producer. After initiating the ignition and combusting a little portion of the in situ oil in the oil sands, the well is produced and air is then injected through another adjacent well. The air injection in the adjacent well then displaces the oil towards the now producer well, passing through the zone heated initially as the combustion front, and now travels in the opposite direction of the air injection [81]. However, there is a high possibility that spontaneous ignition of the air around the injector may occur. If this happens, the injection is stopped and the process then switches to forward combustion.

2.3.3.3 Wet Combustion

Forward combustion tends to be inefficient due to the poor heat carrying capacity of air. Only about 20% of the heat generated during the forward combustion process is carried ahead of the combustion front that is most beneficial to enhanced recovery technique. 80% of the heat is lost in the combustion zone to the base and cap rocks of the zone of interest [43]. It is essential, however, to utilise this lost heat. This gave birth to several variations of the lost heat utilisation during in situ combustion. Water may be injected alternatively or simultaneously with air for a better heat distribution. In the burned region, superheated steam is injected, which flows through the flame and heats the reservoir ahead [81]. This process is referred to as combination of forwards combustion and water process (COFCAW). When the superheated steam mixed with air reaches the combustion front, oxygen alone is utilised for the combustion process, after which the superheated steam mixes with flue gas (products of combustion) and the nitrogen component of the injected air, and displaces the oil in front of the combustion front in the combustion zone.

Utilised properly, COFCAW reduces the fuel needed, results in increased oil recovery and decreases air requirement for heating the reservoir. Consequently, injection of too much water can result in inefficiencies in flame front propagation, which undermines the entire technique. In situ combustion techniques have a tendency to sweep the upper part of the payzone, thereby making vertical sweep efficiency in very thick formations poor. A substantial amount of the heat generated in an in situ combustion process is not utilised and is lost to the cap rock and the oil-bearing strata. So, the feasibility of in situ combustion is highly dependent on the reservoir rock and formation generally.

The major limitations of in situ combustion process are as follows:

- The in situ combustion process could be rather complicated and suitability may well depend on a case-by-case basis;
- Combustion cannot be sustained if coke is not burned in sufficient quantities;
- However, excessive coke deposits lead to a slow progression of combustion front;
- Unfavourable mobility ratio; as the hot gases produced as a result of combustion are substantially more mobile than in situ heavy crude oil;
- Poor vertical sweep as it is more effective in the upper part of the formation, hence, relatively thick formations may not have satisfactory recovery;
- Environmental and operational issues related to the production of large amounts of flue gases, corrosion and other undesirable products.

2.3.4 Others

These are basically EOR methods and techniques borne from a combination of the aforementioned recovery processes discussed. They include the addition of materials, technology and processes to an existing or conventional EOR method. They are used in conjunction with a primary or base EOR technique to harness its potential and to annul some of its drawbacks to provide a better and more efficient recovery process.

2.3.4.1 Microbial Enhanced Oil Recovery (MEOR)

The concepts of using microorganisms to enhance oil recovery was proposed by Beckham in 1926 [82]. Beckham established that there was a high possibility of employing bacteria enzymes in additional oil recovery. The concept was largely dismissed in the United States because there was little interest in finding enhanced recovery methods at that time. Later, ZoBell in 1947 conducted a number of field trials and found that bacteria can release oil from reservoir rocks [83].

The technique involves the injection of microbes into the formation to enhance oil recovery. This injection stimulates the microflora (microscopic algae and fungi) in the reservoir, which will produce certain compounds that stimulate additional production of the residual oil. Injection of the microbes involves the formation of different gases in the reservoir (CH_4, CO_2, N_2), polymers, surfactants and enzymic breakdown of the crude oil molecules. Green and Willhite [41] and Zahid et al. [83] postulated that the basic effects or mechanisms that can be achieved by microbes are as follows:

- Gels production in situ for selective water shut offs
- Biosurfactants in situ production for surfactant flooding
- Acids production in situ for dissolving carbonate rocks
- CO_2 production in situ
- Long chain molecules degradation in situ for viscosity reduction
- Oil displacement by metabolites of inoculated bacteria grown in situ

In order to recover oil though MEOR, some nutrients must be introduced into the reservoir to stimulate the growth of the bacteria to enhance their performances as agents of EOR. Microbial processes can be divided into two categories of in situ and ex situ (surface) mechanisms [82, 83]. In the in situ mechanism, the generation of the desired by-products of the enzymic reactions, such as acids, gases, surfactants and polymers occur by the stimulation of the indigenous or nascent bacteria under appropriate reservoir conditions. The ex situ or surface mechanism, however, involves the selection and removal of the desired and undesired by-products, respectively, through microbial metabolic activity at the surface before the injection of the desired by-products for the purpose of EOR.

There are various beneficial metabolites produced by microorganisms in MEOR that enhance the ultimate recovery of oil from a reservoir [81]. These microbial by-products can significantly affect the reservoir physical properties, such as permeability, wettability and permeability, and can also alter the fluid properties and characteristics, including interfacial tension, viscosity, density etc [84]. By-products of microbial processes are generally classified into seven groups. These groups include biopolymers, bio surfactants, acids, gases, biomass, solvents and emulsifiers.

Biopolymers can alter the permeability and viscosity, which, in turn, alter the mobility ratio favourably. Bio surfactants have a specific impact on wettability alteration due to the potential to reduce the interfacial tension, emulsification and solubility. Acids have the drastic potential to dissolve different parts of the reservoir rock and, as a consequence, alter or improve the permeability and porosity of the medium and hence reduce the residual oil saturation. The gases produced as by-products of microbial processes tend to contribute to reservoir re-pressurisation, which leads to enhanced hydrocarbon recovery. The production of biomass within the reservoir plugs some of the pore spaces within the rock, which directs the flooded water towards the residual oil for displacement. Solvents act the same way as acids by dissolving certain parts of the oil-containing rock improving permeability and porosity. Emulsifiers produced can potentially initiate the emulsification of the remaining trapped oil in the reservoir, which aids in enhancing the displacement of the oil.

It is often stated that the technology is environmentally friendly and has some advantages over conventional EOR techniques, which makes them remarkable options in the oil and gas industries [82]. The advantages of MEOR technology include: being environmentally friendly and being cost-effective. For example: the applicability of MEOR is also applicable both to heavy and to light crude oils; is economically efficient; lowers the expenses and complexity of facilities set up; lowers injection costs of nutrients and microbes; enhances Microbial metabolic activities along with time, against other additives of EOR; is significantly efficient in sandstone and carbonate reservoir rocks; requires negligible energy consumption required for microbial metabolic activities; obtains better results because of the occurrence of multiple mechanisms simultaneously; and creates only low environmental pollution. These are also not without their demerits: aerobic bacteria activities may result in the corrosion of equipment; there are limited applications in offshore platforms in view of the requirement of much sugar as anaerobic bacteria activities; creates toxicity of microbes due to the existence of specific heavy metal ions; creates complexity of developing a comprehensive model to interpret all aspects of MEOR process; and shows tolerance limitation of microorganisms in regards to reservoir temperature and pressure. Comparatively, MEOR has the most prominent advantages in terms of lower cost and is more environmentally friendly [82-84].

2.3.4.2 Foam Flooding

Foam is a metastable dispersion of a rather large volume of gas in a continuous liquid phase, which constitutes a relatively small amount of foam [85]. Foams are formed when a gas contacts a liquid that contains a surfactant under mechanical agitation.

In oil and gas applications, foam has been employed to control gas mobility during injection techniques to mitigate the adverse effects of reservoir heterogeneity, low gas viscosity and gravity override. Other applications of foam include: stimulation by matrix acidising, hydraulic fracturing, near well bore production, water and gas shut-offs [55]. The concept of reducing the mobility due to the dispersed two-phase flow can be used in chemical flooding for realising mobility control during the displacement process. Simultaneous fluid flow in porous media can decrease the mobility of the injected chemicals and gases as in the case of SWAG and WAG [72]. Due to the presence of surfactants in the chemical slug, a simultaneous injection of gas and the chemical slug will result in the formation of foam. The gas therein will be coated with thin films of a material called lamella in the foam. The drag force and surface tension on each individual lamella permit it to slide along the walls of the pores, which induces a resistance to movement through the pore throats [55]. The resistance to swift movement results in the increase in gas-apparent viscosity and, hence, increases gas saturation. This increase in gas saturation will lead to a decrease in relative permeability and liquid saturation. Hence, foam formation decreases the chemical slug mobility and thus improves the mobility control of the flooding process. Liquid and gas injection rates are important factors that define the quality of the formed foam and also impact the technique's mobility reduction ability [71]. The stability of the foam in the slug or drive fluid determines the extent of the mobility reduction for surfactant solutions and gases. Gas and liquid mobilities are reduced, and the displacement efficiency of the technique will be improved if the foam is stable. Conversely, if the foam formed is unstable, the process will be utterly poor as a result of the smaller reduction in gas and liquid mobilities.

Farzaneh and Sohrabi [55] stated that studies have been carried out on foam in porous media and must account for three flow regimes encountered in the field. First, bulk foam may be created as a result of the inertial flow at the surface facilities and even at the well. The second regime is as a result of the pressure gradient and flowrate at the near well bore region, which are usually high. The last regime occurs at the formation away from the injector, where the pressure gradient and flow rates are comparatively low. With these flow regimes, the flow behaviour will be different at each stage and, hence, the foam-forming mechanisms. They further presented that it is widely accepted that lamellae are created through three different mechanisms in a porous medium: i) leave-behind mechanism. This is the creation of stable liquid films or coatings in pore throats as gas flows through and invades the adjacent pore spaces through interconnected porosities. Often cited as a source of a weak foam-forming mechanism, the mechanism can generate a substantial number of lamellae; ii) the lamella division mechanism is the creation of two or more lamellae from a single one. When the mobilised lamella passes through a porous medium where one or more pore throats are devoid of other fluids, it either snaps or breaks several open throats; iii) snap-off mechanism: this mechanism is the lamella generation one. Lamellae are formed in gas-filled pore throats when the throat capillary pressure falls below the capillary entry pressure of the throat.

2.3.4.3 Acoustics Treatment

The use of acoustic treatment of productive wells has been proven to be effective for restoring the permeability of payzones damaged by scale deposits and mud penetration or invasion, and also for mobilising crude oil from reservoir rock [86].

Beresnev and Johnson [86] said that the first use of acoustics or ultrasound for enhanced oil recovery dates back to the 1950s and 1960s. Primarily, during water flooding or gas injection for the purpose of EOR, the use of ultrasound wave excitation in the payzone was prosed for cleaning oil containing formations, inducing additional fractures in the reservoir, and improving oil mobility.

Abramova et al. [87] also stated that the acoustical method of enhanced oil recovery is one of the most promising wave propagation methods. The effect of ultrasound on the reservoir and well, which improves enhanced oil production, is based on these aspects:

- Enhancement of the oil flow from the reservoir rock into the pumping pool
- Viscosity reduction of the oil to improve mobility

2.3.4.4 Electromagnetic Heating

The major challenges faced today in the oil and gas industry are those of primarily increasing or improving the hydrocarbon recovery from the reservoir [11, 31]. One of the most common recovery techniques is steam flooding, but its limitations, stemming from thin payzones, reservoirs at high depths, and reservoirs with low permeability and also reservoir heterogeneity, makes its application unfeasible [79]. An alternative to the steam injection technique is electromagnetic heating [79]. This technique involves the use of electromagnetic waves in microwaves and radio frequency regions. The electromagnetic waves transfer electrical energy to the resistive and dielectric material in the form of heat and reduce the viscosity of the oil, improving the mobility of the oil. Heating the reservoir using the electromagnetic technique can be achieved in two ways: high frequency i.e. radio waves and microwaves, and low frequency.

This method, as in all the other methods of enhanced oil recovery, is used in conjunction with conventional recovery processes. This can be seen in the works of Kashif et al. [88] who combined the electromagnetic technique with gas injection and reported an additional recovery of 45%.

2.3.4.5 Low Salinity

Water flooding has widely been practiced because of the availability of the sources of water and also due to it being a relatively cheaper method, among other practical merits of the process [89]. The potential of using low salinity injection water for the flooding process was not established till Morrow and his co-workers between 1990 and 1999 [89] observed from their laboratory experiments that additional recovery is dependent on the injection water composition. Their results show that higher oil recovery can be obtained when the injection water salinity is lower than the formation water salinity. There are different mechanisms proposed to explain the effect of low salinity injection with regards to additional oil recovery. Detailed discussion on low salinity flooding will be done in the next Chapter where the mechanisms and benefits will be wholly discussed.

2.4 Screening Criteria for EOR Methods

The criteria for selecting a specific EOR process are complex due to a large number of chemicals, geological, petro-physical and fluid properties (density and viscosity, which are dependent on temperature) and environmental properties that have to be considered for each case alone [54]. There are always important economical, practical and technological aspects that need to be addressed before deploying any EOR technologies in the field.

Taber et al. [90] have proposed the screening criteria for all enhanced oil recovery (EOR) methods. They gathered and examined data from all EOR projects worldwide and noted the optimum reservoir and fluid characteristics for successful recovery projects. Their proposed screening criteria are based largely on oil recovery mechanisms of the techniques and field trial results. From their examinations, they came to a conclusion that steam flooding is the most dominant EOR method, while the chemical flooding technique has been declining. Invariably, gels and polymers are being used for sweep improvement and water shut-off successfully. An increase in activity has been found with the use of the CO_2 miscible flooding technique only, perhaps due to the drive to mitigate greenhouse gases.

Since EOR involves the injection of materials into the reservoir, the choice of the injectants must be carefully made along with the overall technique that will recover the most oil from the reservoir, whilst still making profit and being kind to the environment [58]. The bulk of enhanced oil recovery processes that are used today were initially used at the time of relatively high oil prices. From experience, the best profits come from the EOR methods that permit a number of barrels of injected fluids at reservoir conditions that can be injected per barrel of additional oil produced [58]. This notion limits the main methods to either inexpensive gases or water. Polymer and micellar methods have had some technical successes, but have had apparently low economic successes.

Taber et al. [90] provided screening criteria for the major of recovery techniques aforementioned. They conveniently arranged and depicted these methods in terms of oil gravity as presented in Figure 2.12.

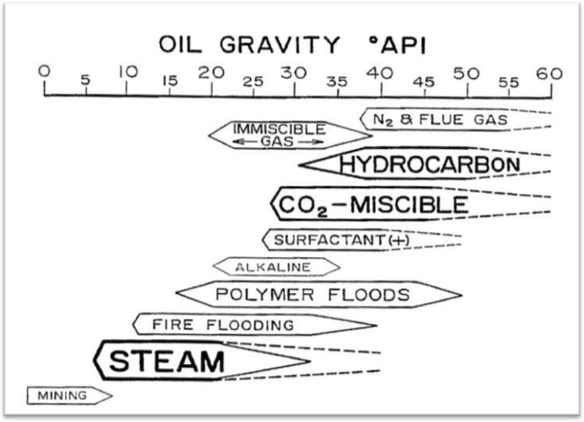


Figure 2.12: Oil Gravity Range of the Most Effective EOR Technique [152}

The general classification of the EOR methods is based on the mechanisms of displacement of the process/technique. These are:

- Solvent extraction or miscible type processes -
    - N2 and flue gas injection
    - Hydrocarbon gas injection

    - CO2 miscible flooding
- IFT reduction processes -
    - Polymer/Micellar flooding
    - ASP
- Viscosity reduction of oil/ viscosity increase of the driving fluid -
    - In situ combustion (fire flooding)
    - Steam flooding
    - SAGD
    - Polymer flooding

Tarek and Meehan [43] used the template of the EOR screening guidelines and presented them in this form below:

Table 2.2: EOR screening guidelines [43]

(A) Steam Flooding			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		
2	Oil gravity	8 – 25	
3	Viscosity	< 100000 cP	
4	Reservoir characteristics		
5	Net formation thickness (ft)	> 20	
6	Oil saturation (%)	> 40	
7	Permeability (md)	> 200	
8	Formation depth (ft)	< 5000	
(B) In-situ Composition			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		• Asphaltic component presence promotes coke deposition.
2	Oil gravity	1 – 27	
3	Viscosity	< 5000 cP	
4	Reservoir characteristics		
5	Net formation thickness (ft)	> 10	
6	Oil saturation (%)	> 50	
7	Permeability (mD)	> 50	
8	Formation depth (ft)	< 11500	
9	Formation temperature (°F)	> 100	
(C) CO_2 Miscible Flooding			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		• If injection rate can be maintained, permeability is not critical. It is applicable both in carbonate and in sandstone formation.
2	Oil gravity	> 22	
3	Viscosity	< 10 cP	
4	Reservoir characteristics		
5	Net formation thickness (ft)	Thin formation	
6	Oil saturation (%)	> 20	
7	Formation depth (ft)	> 2500	
(D) Hydrocarbon Miscible Flooding			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		

2	Oil gravity	> 23	• High percentage of light hydrocarbon required.
3	Viscosity	< 3 cP	
4	Reservoir characteristics		
5	Net formation thickness (ft)	Thin formation	• Ineffective in the presence of high permeability streaks or fractures.
6	Oil saturation (%)	> 20	
7	Formation depth (ft)	> 4000	
(E) Polymer – Micellar, ASP, Alkaline			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		• Light intermediate hydrocarbon components are desirable.
2	Oil gravity	> 20	
3	Viscosity	< 35 cP	
4	Reservoir characteristics		• Organic acids are required to create low interfacial tension.
5	Oil saturation (%)	> 35	
6	Formation depth (ft)	> 9000	
7	Formation temperature (°F)	< 200	• Formation thickness is not critical, preferably sandstone formations, adsorption problems with clays.
(F) Polymer			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		• Oil composition is not critical
2	Oil gravity	> 15	
3	Viscosity	10 – 100 cP	
4	Reservoir characteristics		
5	Net formation thickness	> 10	
6	Oil saturation	> 50	
7	Formation temperature	< 200	
8	Permeability (mD)	> 10	
9	Formation depth (ft)	> 9000	
(G) N_2 and Flue Gas Injection			
SN	**Type**	**Range**	**Comment(s)**
1	Oil properties		• Ineffective in high permeability streaks and in the presence of fractures, reservoirs temperature is not critical.
2	Oil gravity	> 35	
3	Viscosity	cp	
4	Reservoir characteristics	> 0.4	
5	Oil saturation	> 40	
6	Formation depth (ft)	> 6000	

EOR methods usually require substantial capital investment and are generally associated with a high level of risk. No single EOR technique is effective for all reservoirs [43].

2.5 Economics of EOR Techniques

Taber et al. [58] stated that the screening criteria are essential for precautionary assessment of many candidate reservoirs undergoing recovery projects before stringent economic evaluation and costly reservoir descriptions are done. They used the technical screening criteria of CO_2

flooding for the economic evaluation in terms of how much CO_2 is needed for the all the reservoirs they assessed. If only oil gravity and depth of the reservoirs are considered, they presented a purview that 80% of the world's oil reservoirs could be subjected for some form of CO_2 flooding technique.

Potential Oil price increase in the future could favour EOR projects because EOR projects are based on economics rather than on technical screening criteria alone [90]. They examined the impact of the prices of oil on the EOR projects. There is a trend of fewer EOR projects due to the drop in oil prices. Additional oil production from CO_2 flooding appears to be on the increase, even with the drop in oil production [58]. This is attributed to the environmental stand to dispose of large volumes of anthropogenic CO_2 in hydrocarbon reservoirs and deep saline aquifers [91] to avert global warming [90]. The potential of CO_2 flooding for a number of oilfields was evaluated by the screening criteria of depth and oil gravity, and has been published in literature [58]. A good percentage of the fields in each country that met the criteria of depth and oil gravity for CO_2 miscible and immiscible flooding was combined with the country's reserves of oil to estimate the additional oil recovery.

The impact of oil prices on EOR projects tends to have a significant effect on the choice of an EOR technique. Major EOR projects will be embarked upon only if they appear profitable and are dependent on the perception of future oil prices. Taber et al. [58] showed that the EOR production increases when the oil prices increase and falls when the oil prices decline. According to a National Petroleum Council report, reinforced by Taber et al. [58], lower oil prices since 1986 have reduced the EOR projects embarked upon and the actual additional recovery has been close to that predicted in the US, pegged at \$20/bbl. Additional recovery of oil from CO_2 injection has continuously increased and has now exceeded the prediction for the pegged oil price mentioned earlier.

2.6 Low Salinity Water Flooding

The practice of injecting low salinity water (LSW) has been widely adopted to reduce residual oil saturation and to improve oil recovery [89], due to the cheap and readily available sources of water. Its potential, however, was not recognised until the advent of the works of Morrow and co-workers [9, 14, 35, 68, 92] in which they observed in their laboratory experiments, that there was a dependence of oil recovery on the injected water composition. Conversely, the mechanisms of displacements through low salinity flooding have been a question for debate as we will see in Section 2.7, where a detailed depiction of works from literature have been extracted and presented.

2.6.1 Concept of Low Salinity Water Flooding

Low salinity water flooding is an emerging technique for enhanced-oil-recovery (EOR), where the salinity of injected waters is controlled to improve oil recovery [93-96]. It is an enhanced oil recovery method that uses water with a low concentration of dissolved salts as a flooding medium [89]. The sources of low salinity water are usually lakes, rivers or aquifers that are associated with meteoric water. Low salinity of water flooding has been widely practiced as an EOR technique and is relatively cheaper and is more environmentally friendly than other conventional recovery techniques [89, 97]. Around 15 years ago [89] it was observed that a higher oil recovery could be obtained when flooding a core with low salinity water in a core of high salinity initial water saturation, mimicking formation water. Such low salinity water flooding effects or benefits have drawn the attention of the oil industry since then [98]. In recent years, many researchers [99-106] have conducted laboratory core floods, and several companies have carried out field tests to ascertain the feasibility of low salinity flooding for improved oil recovery.

Although many of the results showed positive effects, some results showed that there was no benefit from using low salinity water to enhance oil recovery. Many mechanisms have been proposed by researchers, but there is no agreement on the dominant mechanism(s) of low salinity displacement [35, 100, 107-120].

2.6.2 Mechanisms of Low Salinity Water Flooding

There are several proposed mechanisms of low salinity displacement and a consensus as to which of the mechanisms is dominant is still lingering, common amongst which are wettability alteration, fines migrations and reduction in interfacial tension.

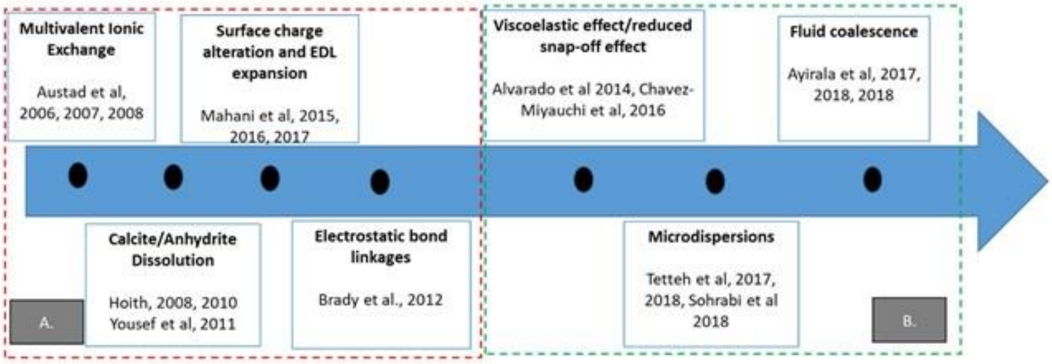


Figure 2.13: Progress in Low Salinity EOR [27]

Tang and Morrow [28] proposed the first LSW flooding mechanism, which was partial stripping of mixed water fines, and modified the wettability of the rock as shown in Figure 2.14 [104]. This proposal however was questioned by the works of Zhang et al. [49] and later by Abhishek et al. [33] when they observed that there was no sign or presence of clay components in the effluent stream during production.

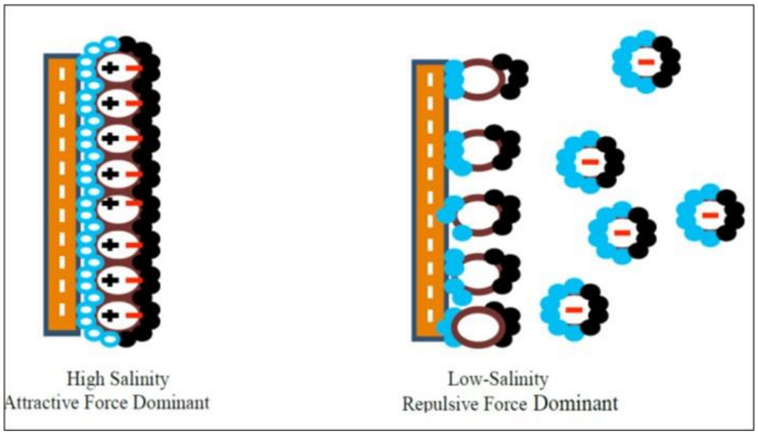


Figure 2.14: Depiction of Partial Stripping of Mixed-Water Fines Mechanism [104]

The second displacement mechanism for low salinity water flooding, suggested by McGuire et al. [99, 104], was interfacial tension (IFT) reduction as a result of an increase in the pH values. This was subsequently challenged and disputed by Lager et al. [121] who carried out an experiment that depicted that the additional oil recovery through low salinity flooding had a pH of less than 7 in brine [42, 92]. The third recovery mechanism proposed for low salinity displacement was based on the concept that negatively-charged oil is bridged to the clay minerals by multivalent cations [104]. Lager et al. [121] however, suggested multicomponent ion exchange (MIE), shown in Figure 2.15, which resulted in oil desorption due to the low electrolyte medium used for water flooding.

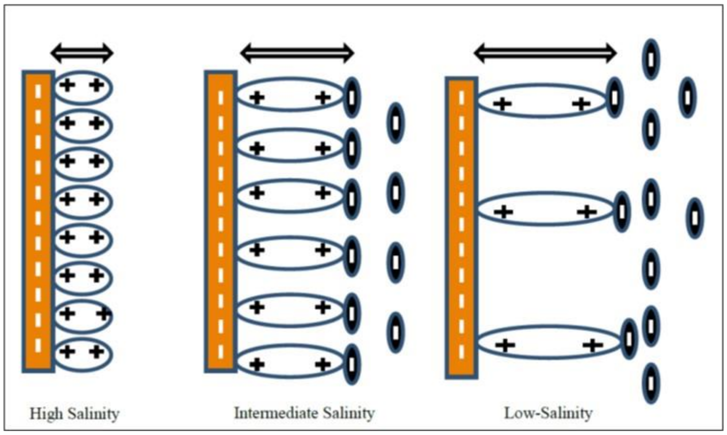


Figure 2.15: Multi-Ionic Exchange in Sandstone Reservoirs [104]

This was paramount especially for Mg^{2+} exchange, which was reaffirmed by measuring the magnesium content in the effluent produced from the flooding process. There has been a mixed disposition on this issue over the years, some of which agreed with the concept of multicomponent ion exchange [122]. Others disputed that cation stripping is not an essential factor for wettability alteration or modification [49, 92, 106, 123]. The fourth proposed low salinity flooding mechanisms suggested a relationship between the incremental oil recovery and the mineral clay content of the formation. This finding also had its foundation footing toppled as Cissokho [108] carried out an experiment and concluded that incremental oil recovery was substantially achieved through low salinity water flooding in clay-free cores.

A brief discussion on some of the proposed mechanisms will be presented as thoroughly researched by [89], who made a critical review of low salinity flooding, citing the principles on which they are based. He stated that there are 17 mechanisms proposed in the literature, some of which are not entirely valid for a low salinity water flooding technique. They are (1) fine migration, (2) emulsification, (3) mineral dissolution, (4) limited desorption of mixed wet particles, (5) reduced IFT and increased pH effects, (6) multicomponent ion exchange, (7) saponification, (8) salinity shock, (9) wettability alteration (more water-wet), (10) end effects, (11) surfactant-like behaviour, (12) double-layer effect, (13) particle stabilised interfaces, (14) salt-in effects, (15) wettability alteration (less water-wet), (16) osmotic pressure, and (17) viscosity ratio [89]. Notably, the most investigated mechanisms for low salinity flooding are almost always wettability alteration as well as interfacial tension reduction given the importance of the fluid rock interaction at reservoir conditions, which were depicted by a two step process as predicted by Zhang et al. [49].

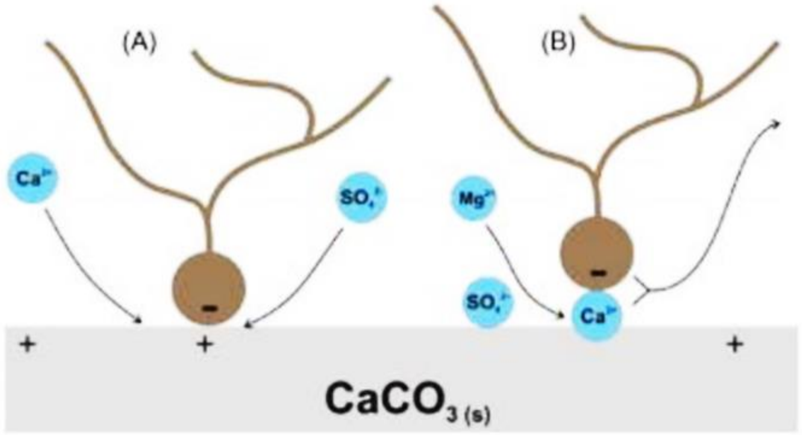


Figure 2.16: Multi-Ion Exchange Model[49]

Sheng [89] also stated that most of these mechanisms presented are related to one another, which cited an example with saponification, emulsification, and surfactant-like behaviour being related as they all increase the pH effect and reduce IFT. Furthermore, he gave another example with salinity shock and osmotic pressure, where he stated that they are directly related to salinity contrasts between the displacing water and initial water. The major low salinity displacement mechanisms will now be discussed with their working conditions and principles.

2.6.2.1 Fine Migration

Technically, clay tends to hydrate and then to increase in volume when contacting fresh water. That is, insufficient salts present in the freshwater cannot halt the clay swelling and hydration [89]. Sheng further explained that fine migration mechanism occurs if the critical flocculation concentration is greater than the ionic strength of the injected brine [89]. The critical flocculation concentration is highly-dependent on a comparative concentration of the divalent cations. Divalent cations reduce the repulsive force by reducing the Zeta potential [107, 115, 117]. Hence, this has been identified to stabilise the clay. The low saline water destabilises the clay and the silt in the rock formation [28, 124]. The clay and silt, during dispersion, flow along with the water. Water favourably flows along the high permeability zones and channels. The silt and clay dispersing in the water become stuck in the small pores within the pore channels.

The formation permeability thus decreases, and the water will be forced to take other flow routes [89]. Subsequently, the sweep efficiency will be better improved. Clay particles that are poorly cemented, such as illite and kaolinite, can come loose during the aqueous flow, especially when the flowing brines become fresher, that is, become less saline. Apart from the reactivity of the clays, fines migration is also aided by the physical nature of the clay.

Sheng [89] reported that clay swelling and dispersion with an increase in differential pressure resulted in incremental oil recovery. The permeability reduction was observed to be lowered when calcium ion was also present in a salt solution. Conversely, formation damage was practically eliminated when the composition of the solution was adjusted to give calcium surface coverage greater than a critical value of the 75%, or when the solution Ca^{2+} fraction is larger than 20 to 30% [89].

Based on their observations from their experiments, Tang and Morrow [28] also reach a conclusion that the fine migration (mainly kaolinite) increased oil recovery, and stated that: firstly, acidised and fired Berea core did not show any sensitivity to the salinity on oil recovery, while the untreated Berea sandstone core sample did. Secondly, for the clean untreated sandstones, the increase in the oil recovery when lowering the salinity was lower than that for the clay sands. Conversely, Lager et al. [121] concluded that there is no fines migration or important reduction in permeability observed during several low salinity core floodings at a series of reservoir conditions, even though these core floods all showed an increase in oil recovery. Zhang et al. [49] also reported that no clays were identified at the effluent stream. In their conducted experiments, Boussour et al. [108] stated that there was no low salinity effect except with the sand production. Furthermore, Sheng [89] concluded on fines migration by showcasing the important roles that the mechanisms play and how they are interlinked. That is: decrease in ion binding, osmotic effects, interfacial tension gradient, transient emulsion formation, interfacial viscosity, and oil viscosity resulting from gradients in the brine composition, also play a role in the oil mobilisation [49]. The formation of interfaces, particularly in the form of the clay stabilised lamellae, would enhance the potential of developing the capillary structure resulting in the large resistance to flow (viscosity) of the brine.

2.6.2.2 Limited Released of Mixed Wet Particles

This mechanism was proposed and explained by Tang and Morrow [28]. Initially, the crude oil coats fines that are situated at the pore walls. Reducing the salinity increases the tendency of the aqueous phase to strip the fine, which is as a result of the electrical double layer in the aqueous phase between the particles expanding. The stripped fines migrate and are aggregated so that the oil combines or coalesces. Consequently, limited removal of the mixed wet fines from the pore walls resulted in locally heterogeneous wetting conditions and, thus, the oil recovery is enhanced. This mechanism combines the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory, which is named after the individuals whose names appear in the name of the theory, and fine migration [89].

2.6.2.3 Increased pH and reduced IFT

Surfactant-like behaviour, emulsification and saponification are all related to reduced IFT and increased pH mechanisms [89]. Sheng [89] discussed them collectively, which he rightly did because of the similarities in principles. McGuire et al. [99] suggests that low salinity mechanisms could be caused by the increased pH and reduced IFT similar to flooding with alkaline. This increase in pH is caused by the exchange of hydrogen ions in water with the adsorbed sodium ions. Additionally, a small change in bulk pH can enact a substantial change in the zeta potential of a rock [95, 107, 125]. The organic materials will be desorbed from clay surfaces when pH increases. The pH of the solutions injected into the sandstone for all the experiments was about 6.5. The pH of the effluent, however, was found to be around 7.5 during the flowing of $CaCl_2$ salt, during NaCl salt was 8.6 and, with fresh water flow the pH was 8.3. The increase in pH is due to solubilisation of the trace amounts of the dissolvable minerals, like calcite. Sheng [89] reported other investigations that showed the dispersion of the clays was minimised at the lowest pH.

The exchange of ions between the adsorbed Na^+ and H^+ in solution in low salinity water flooding resulted in an increase of OH^- concentration in the bulk solution, that is, pH increase. The pH increase improved the release of the fines and that led to a substantial reduction in the formation permeability. When a pH greater than 11 is reached, a drastic and rapid decrease in the permeability was observed. However, in cases where the pH was observed to decrease, the interaction between the fluids and rock may have changed the polarity of the test fluids and the generic assumption will definitely change to accommodate this trend. More H^+ will be released into the effluents as opposed to the OH^- anions.

In many low salinity flooding cases, the pH was lower than 7 and, in some cases, the pH remained unchanged. Tetteh et al. [27] tried to explain why such low pH values work and suggested a hypothesis that there is a cation exchange followed by local increasing of pH close to clay surfaces. Zhang et al. [49] also reported that, after low salinity brine injection, small increases and decreases in the pH were observed. They further concluded that there was no apparent relationship between recovery and effluent pH.

In high pH cases, saponifiable components (usually organic acids) in the crude oil react to form a surfactant in situ that can lower the interfacial tension between water and oil. The created surfactant helps in forming water/oil or oil/water emulsions due to the low interfacial tension. The water sweep efficiency may be improved by these emulsions. Conversely, in a generic alkaline solution, the pH ranges between 11 and 13.

Some researchers argued that the interfacial tension during low salinity flooding is not very low. These values of IFT are substantially high to be considered in residual oil saturation reduction. From many field projects, it has been observed that the extent of additional oil recovery from alkaline flooding is not substantial [89]. From the analysis of the data that has been reported by Sheng [89] it can be observed that the improved oil recovery from water flooding was from 1-2% in many of the projects, and from 5–6% in very few projects. He further explained that, if the low salinity mechanism is related to the reduced IFT and increased in pH similar to the alkaline flooding, the additional oil recovery factor must be even lower than the result from an alkaline flooding.

Furthermore, as a result of the pH from the actual tests being lower than that which is paramount to achieve the emulsification or saponification and the fine migration or mobilisation, the pH mechanism similar to the alkaline flooding might not be feasible in low salinity water flooding. The pH values of the effluent may be unpredictable as it might decrease or increase depending on the other chemical reactions therein. Hence, the pH values cannot be used as a factor to ascertain or depict low salinity water flooding.

2.6.2.4 Multicomponent Ion Exchange (MIE)

The effect of multicomponent ion exchange (MIE), given the diverse affinities of the ions to the surface of the rock, is to have the divalent or multivalent cations such as Mg^{2+} and Ca^{2+} strongly adsorbed on or attached to the surfaces of the rock until the rock is wholly-saturated. Multivalent cations at the clay surfaces are attached to the polar compounds that appear in the oil phase (asphaltene and resin), creating the organometallic complexes and the supporting oil-wetness on the surface of the rock [15]. However, some of the organic polar compounds are adsorbed directly onto the mineral surfaces, where the most labile cations appear at the clay (mineral) surface and promote the oil wetness of the clay surface hence water is displaced.

When injecting low salinity brine, the multicomponent ion exchange will occur, thus removing the organometallic complexes and organic polar compounds from the surface, replacing them with the non-complex cations formed [89].

Lager et al. [121] carried out an experiment where their results matched the prediction from these postulates. In the first step in their experiment, the core sample from North Slope was prepared to enact the initial water saturation and was then aged in dead crude oil to simulate the local condition of a representative reservoir. The experiments of initial screening were conducted at a temperature of 25°C. Using a conventional high salinity water flooding, a recovery of 42% of OOIP was produced, and a tertiary low salinity water flooding produced a total recovery of 48% of OOIP (an additional 6% OOIP compared to the former method). A second set of experiments was conducted at a simulated reservoir temperature of 102°C. The conventional high salinity water flooding produced a recovery of a 35% of OOIP. The core was flushed with a brine containing only high salinity NaCl as the salt component until Mg^{2+} and Ca^{2+} was efficiently eluted from the pore surface. The initial water saturation was then re-established, and the sample was then also aged in the crude oil. A high salinity water flooding consisting of only NaCl also resulted in a recovery of 48% of OOIP. The tertiary low salinity water flooding was then conducted (again no Mg^{2+} andCa^{2+}), and no additional recovery was observed.

From their experiments, this order of events from Lager et al. [121], indicates that high salinity Mg^{2+} and Ca^{2+} containing connate brine resulted in the low recovery factors of 35% and 42%. Eliminating Mg^{2+} and Ca^{2+} from a rock surface prior to water flooding led to a greater recovery factor (48%) regardless of the salinity. They pointed out that there was no improvement in oil recovery observed when low salinity water was injected into the clastic reservoir while the mineral structure was well-preserved and intact.

Clearly, their suggested multicomponent ion exchange explicates why low salinity water flooding was not noticeable when the core was treated (acidising followed by firing). This is because the capacity of the cation exchange of the clay mineral was altered and destroyed during the treatment. This explains why low salinity water injection had little effect on the mineral oil, as stated by Tang and Morrow [28] and Zhang et al. [49] , given that no polar compounds appear to interact strongly with clay minerals. Additionally, Sheng [89] stated that another supporting result is that adding divalent (Ca^{2+}) in low salinity brine did not facilitate incremental oil recovery in Morrow's and Tang core flooding experiments. The suggested mechanism of MIE is also enhanced by the pore-scale model suggested by Sorbie and Collins [113].

Furthermore, Zhang et al. [49], reported that incremental recovery was achieved when salt concentration of the brine was switched from 8000ppm to 1500ppm, even with added divalent ions. The data reported by Sheng [89] showed the highest oil recovery was obtained when the initial formation brine contained 2% $CaCl_2$ flooded by a brine with 0.5% $CaCl_2$ and 4% of NaCl, and subsequently by 2% of $CaCl_2$. Sheng [89], however, explained that the MIE mechanism was not able to explain the experiments because more oil was recovered in lower initial water formation salinity, while the flooded water composition was the same.

An additional discussion about the cation ion exchange was made by Sheng [89], in that, he stated that, during the cation exchange capacity (CEC) and isotherm measurements, the effluent concentrations of magnesium and calcium in a steady state was observed to be marginally higher than the injected concentrations. As the injection concentrations decreased, these excess concentrations increased. When a NaCl-based brine was injected into the cores, the leftover magnesium and calcium concentrations were still noticed in the effluent.

Sheng [89] carried out an experiment where they injected fresh water in an aquifer with brackish water and observed that the concentration of and Mg^{2+} and Ca^{2+} in different reference wells were less than with injected water and connate water. Furthermore, Lager et al. [121] reported similar observations. In their core flooding experiments, the injected brine had an Mg^{2+} concentration of 55ppm, similar to connate brine, but the Cl^- concentration was less. There was a sharp decrease in Mg^{2+} in the effluent concentration at the onset of the experiment, which indicates that the rock matrix strongly adsorbed the Mg^{2+}.

A new equilibrium must be reached when the salinity of the injection water and the initial water brine are different. This equilibrium is thus governed by the law of mass action. Whether the cations had adsorbed or desorbed is not only determined by the composition of the injected brine, but also by the adsorbed concentrations [89].

2.6.2.5 Double Layer Effect

The double layer theory, or denoted as the DVLO theory, defines the force, through a liquid medium, between charged surfaces interacting with one another. It includes the effects of the electrostatic repulsion and the van der Waals force of attraction due to what is referred to as the double layer of counter ions [89]. The low salinity brine reduces the attraction between the clay particles by expanding the electric double layer therein [16, 17]. Partial release of the clay particles may depend on subtle interactions between rock/brine/oil systems that include the charge distributions of the individual platelets of clay particles (kaolinite). A number of studies were carried out using the Environmental Scanning Electron Microscope (ESEM), the Cryo Scanning Electron Microscopy (CSEM) and the (XPS) - X-ray Photoelectron Spectroscopy, and showed that there is attachment of crude oil to the kaolinite, as reported by Sheng [89]. Low salinity water renders the water film substantially stable due to the effect of the expanded double layer, causing the clay surfaces to be more water-wet and the oil to be more detached. The adsorption of divalent at the water/oil and sand/water interfaces, on the opposite site, changes from water-wet to oil-wet according to Sheng [89], Shakeel et al. [11]. They have also reported that, in the presence of sodium cation Na^+, the electrical charge present in the surface of the clay material (kaolinite) is a function of the pH of the solution and the surface carries negative charges. Many of the reported values from literatures have shown that edges of the kaolinite, when the pH is higher than 6-8, are negatively charged [89]. Consequently, between these interfaces there exists an electrostatic repulsion. There is an increase in the repulsion when low salinity brine is injected and, conversely, a decrease in this repulsion due to the surface charges screening, is observed when high salinity brines are injected. Through the same mechanism, as the electrostatic repulsion increases when the low salinity brine is injected, the stability of the water film between the brine/oil and clay particle/brine will be substantial [89]. The wetness state of the rock surface changes from oil- wet to more mixed-wet or more water-wet. Mixed-wet cores exhibit lower residual oil saturation than the strongly oil-wet or water-wet cores. The incremental oil recovery is greater. Nevertheless, Ayirala et al. [24] and Zhang et al. [49] had observed that water film was steadier at the high salinities in their experiments, varying with the above observations, or with the DLVO theory according to Sheng [89].

2.6.2.5 Salt-In Effects

The addition of salt to a solution can significantly reduce the solubility of any organic material in water, which is defined as the salting-out effect, and removing the salt from the water can also increase the solubility, which is rightly defined as the salting-in effect [126]. Consequently, a reduction in salinity below the critical ionic strength can augment the solubility of the organic material in water, improving the oil recovery. This mechanism alters wettability to more water-wet from the oil-wet conditions. The increase in the organic solubility in the aqueous phase is related to desorption of the oil from clay surfaces. Conversely, this mechanism cannot explain other phenomena like the salinity shock, the dependence of mineral composition, pH, etc [89].

2.6.3 Osmotic Pressure

An experiments study showed that the oil droplets performed as semi-permeable membranes i.e. oil droplets, could move under the osmotic pressure gradient. They suggested that such osmotic gradient transfers oil by expanding the trapped aqueous phase within the porous rock medium. In field cases they assumed that a new water pathway could be opened and oil could be relocated when low salinity water is injected into a reservoir. This is as a result of water being channelled away from the primary flow paths and into fewer conductive pore channels by diffusing through the oil [127]. They considered that a system in an oil-wet condition, with substantial oil saturation, high initial temperature and with a wide range of pore size distribution, should present an ideal case for osmosis to be feasible and effective. However, the need of existence of crude (polar) oil and clays cannot be explained by this mechanism [89].

2.6.4 Wettability Alteration

Sheng [89] stated that, at low salinity, brine films are more stable. This statement shows that the low salinity water will result in mixed wet cores, which is less water-wet [13]. The mixed-wet cores show low residual oil saturations or high oil recoveries more strongly than the oil-wet or water-wet cores. Nasralla et al. [120] also showed that low salinity water could reduce the contact angles. Yousef et al. [14] concluded from their experiments that low salinity water injection can change wettability in carbonate reservoir rocks to more water-wet.

Sheng [89] also suggested that, when pH is >9, the wettability changes from oil-wet to water-wet and, at a pH of <9, from water-wet to intermediate-wet, as depicted in Figure 2.17.

Alternatively, the wettability alterations or changes are possible in all pH ranges [92]. From literatures [89], in low salinity water flooding, the pH is likely to below 9. The chances are that the wettability changed from water-wet to mixed-wet or intermediate-wet. This phenomenon can explain why connate water is required for the establishment of the low salinity effect given the presence of the connate water, which makes the water-wettability possible. Dang et al. [128] proposed that wettability alteration is the most commonly suggested mechanism, and several mechanisms could be related to this mechanism. Alteration of the wettability can be the end result of the other mechanisms. This is a possible explanation of the low salinity effect on oil recovery [89].

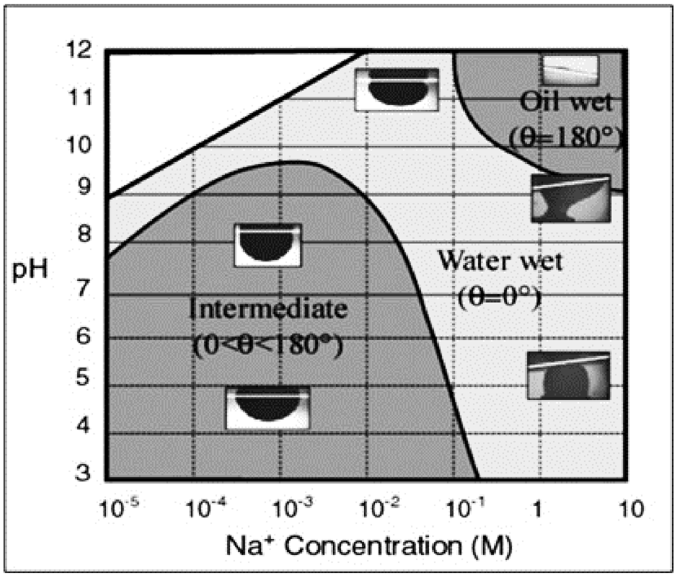


Figure 2.17: Schematic of Relationship Between Salinity, pH and Wettability [89]

Many mechanisms that are being referred to above are interrelated. For example, to mobilise fines, their availability must be in the form of an injection fluid. These fines may comprise released particles or may also comprise mineral dissolution. Thus, small ejection of those particles that are mixed-wet, and also a small ejection of mineral dissolution, is associated with fine migrations. The viscosity of low salinity solution due to mineral dissolution has high viscosity. Saponification, emulsification and surface-active oriented behaviours are linked with reduced IFT and increased pH effect. Osmotic pressure and salinity shock are directly linked with salinity variance between initial water and displacing water. The end effect shows up in the laboratory scale.

In all the discussions onthe mechanisms of low salinity, it can be noted that there does not exist any agreement with regards to primary mechanism for low salinity phenomenon. Various examples of data exist for every mechanism. This represents a challenging task to define the mechanisms of low salinity water flooding. As compared to other processes of chemical flooding, there is relatively higher recovery of oil with, for example, surfactant flooding [27, 34, 128]. This gives rise to a question whether or not low salinity water flooding is powerful. 1000 to 7000ppm of fresh water was injected in a reservoir in Daqing, of chemical EOR floods [89]. Sheng [89] also mentioned that there is 9% of enhanced oil recovery on average from a Chinese polymer flooding project.

It is worthy of mention that, in laboratory settings, injection of many pore volumes of low salinity water took place. That is not usually the case in actual field water flooding and, therefore, a higher magnitude of oil recovery cannot take place. Another important element is that low salinity water is usually used for chemical flooding. Having regard to the ratio of recovery of incremental oil from chemical flooding projects, a higher recovery of oil from low salinity water does not usually take place, but, since a low salinity effect is regarded positive and environmentally friendly, the research in this area is likely to continue. Among all the mechanisms mentioned, the most plausible one is wettability alteration as it can be employed to explain more observations from results of laboratory experiments and field trials.

Some advantages of low salinity flooding are as follows:

- Injection of low-salinity water (LSW) has widely been practiced because, among other practical advantages, sources of water are available and are relatively cheap.
- Low salinity water injection is very similar to conventional water flooding as it is simple to plan and deploy. There is no additional processing after production or additional chemicals required. The main additional cost is the need for desalination equipment (and is a limiting factor on existing platforms).
- At present, their deployment is controlled by operational constraints and economic factors. Research continues to try to reduce these constraints and factors, as well as to develop more effective and advanced recovery processes, but the challenge they face is to move these technologies more quickly from the laboratory to the field.
- With low salinity water flooding, there is no need for high capital cost, unlike with gas and chemical injection where large equipment and facilities are needed.
- Normal water injection results in reduced recovery.
- Low salinity water injection does not require complicated injection and production new facilities as do chemical or gas injection.
- The research on low salinity recovery mechanisms are not well established worldwide.
- EOR generally is a key subject in current business strategy to boost production and recovery; investors have a strong interest in applying low salinity water injection.
- Low salinity water flooding is considered friendly and environmentally friendly, and does not require too much facility investment.
- Water flooding consists of much lower cost investment compared to other EOR methods and is convenient to operate.
- There is less dependency on detailed characterisation of the rock of the reservoir, and the fluids are less complex to implement.

Referring to the concept of low salinity flooding, some laboratory observations were established for typical behaviour of the low salinity of water flooding, and could be summarised as thus: (1) As the injected salinity of brine was reduced, which is lower than the initial salinity of the brine in the core sample, more oil was produced. (2) When the brine salinity was reduced, a high-pressure drop was observed. These phenomena were explained by Tang and Morrow [28] as the reduction in permeability caused by fines migration. These phenomena have also been observed by Zhang [49] in their experimental works, and (3) When injecting water with low salinity, maximum pH value was about 9 or lower. A number of parametric sensitivity analyses were carried out in relation to the low salinity flooding technique. A summary of the sensitivity experiments was made by Sheng [89] and is summarised here in this work as follows.

2.6.4.1 Effect of Connate Water Saturation

In their experimental work, Tang and Morrow [28] observed that there was no substantial difference in the oil recovery from the flooding with high salinity water as in the one from a low salinity (that is 1% of the high salinity water) injection, when there was zero initial water saturation. Thus, to get the low salinity effect, connate water must exist [27, 128]. The presence of connate water plays an essential role in the mechanism by which the oil recovery can be affected by low salinity [28].

2.6.5 Crude Oil Presence

The presence of crude oil is a necessary condition for the effectiveness of low salinity and also for the injected water. A different effect was observed by Tang and Morrow [28] when they used refined oil instead of crude oil; with all other conditions kept the same, the salinity had no effect on the oil recovery [28]. For low salinity injection or flooding to be effective, there must be a working condition that must be satisfied. Some of these working conditions are summarised next.

2.7 Conditions for Low Salinity Water Injection

Working conditions necessary for the low salinity effects based on core flooding experiments are presented here as reported by Sheng [89].

2.7.1 Porous Medium

The low salinity effect has not received wide documentation for pure carbonates due to some effects in the sandstone rocks with dolomite crystal therein.

2.7.2 Presence of Clays

The presence of clays is important in the low salinity effect for incremental oil recovery and, depending on the clay type, plays an important role. Illites and kaolinites are clays that are non-swelling and which have the tendency to detach from the rock surface and migrate as the conditions are conducive for the release. Despite this ability, the number and types of clays are not well defined in any literature.

2.7.3 Presence of Polar Components in Crude Oil

The polar components in crude oil must be present to obtain the low salinity effect [28]. The polar components of crude oil, which are more likely to absorb reservoir minerals, are believed to be basic or acidic in nature. The acidic components are usually termed naphthenic acids, wherein the carboxylic groups are part of a large number of molecules that usually present in the asphaltene fraction and resins. There are also fatty acids that form a component present in the crude oil as reported by Sheng [89]. Those organic naphthenic acids had pK values around 4.9. Therefore, when pH is equal to the pK value, the concentration of the disassociated anionic and the non-disassociated acid is equal. Therefore, based on the characteristic related to condition, both the neutral form and protonated base of the acid are able to absorb negatively charged minerals into the reservoir, and relative adsorption characteristics surely depend on the pH.

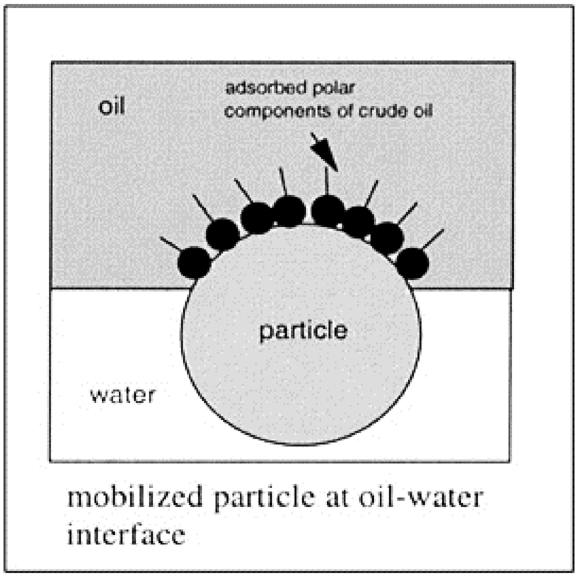


Figure 2.18: Adsorption of Polar Component from Crude Oil to Form Mixed Wet Fines [89]

2.7.4 Effect of the Salinity of Connate Water

In another experimental study the results found that the salinity of connate water was a vital factor affecting oil recovery. When the salinities of connate water were 0.3%, 3% and 20% NaCl, while the injection water salinity was 3% NaCl, the oil recovery was greater for lower connate brine salinities. They attributed this dependence to alteration of the wettability to mixed-wet conditions from water-wet conditions during the drainage process. Mixed-wet cores showed lower residual oil saturations than strongly water-wet or oil-wet cores, resulting in higher oil recovery being obtained with the lower salinity of connate water. This phenomenon was also supported by McGuire et al. [99]. However, the salinity of injection brine must be considerably lower than the preceding water salinity [49]. This effect is going to be reduced in the field scale because of the salinity buffering.

2.8 Wettability and Interfacial Tension Alteration in Low Salinity Flooding

Rock wettability is defined as the tendency of a fluid to adhere to the surface of a rock in the presence of other fluids that are usually immiscible [120]. It therefore plays a vital role in the residual oil saturation and recovery efficiency determinations in water flooding processes as it affects the fluid distribution in a porous medium. It depends on the surface chemistry of the porous medium, oil composition, and aqueous phase composition in relation to pressure and temperature. Wettability alteration is due to the dynamics of electrical charges at the fluid/rock interface. This will be investigated within the body of the research because the test core sample contains reactive clays that will certainly have significant impact on the wettability alteration through ionic exchange.

Interfacial tension (IFT), on the other hand, can be defined as the interface or boundary between multiple immiscible fluids co-existing in a system. The forces of cohesion and adhesion play a significant part in this phenomenon since the characteristics of the individual molecules of the multiple fluids that are present in the system at the interface are different. An important parameter that facilitates oil trapping in the reservoir pore spaces are capillary forces [129]. The detailed mechanism of wettability alteration is explained in the next Section.

2.8.1 Wettability Alteration

It has been inferred by McMillan et al. [70] and literature therein that the ionic strength of a fluid flowing through a porous medium influences the measured permeability. This led to many researchers investigating the causative factors for this phenomenon. It was understood that different wetting states of different fluids employed in oil recovery laboratory experiments caused significant distinction in ultimate recovery. Therefore, altering the wetting state i.e. wettability of the porous medium, is factored as a method of enhancing recovery. Evidence from laboratory experiments and field tests showed that modifying the injection brine salinity of a water flooding process and its ionic composition can significantly improve oil recovery Al-Attar et al. [101]. It was also determined that one of the mechanisms of low salinity flooding to enhance oil recovery is reservoir rock wettability alteration (cation exchange). Others include clay (fines) migration and an increase in pH and interfacial reduction. However, there is still no consensus on how to establish the main mechanism of low salinity flooding, but the most plausible is the wettability alteration [89] that was also established by Al-Attar et al. [101]. He also stated that it is still debatable as to the main mechanism behind low salinity flooding, as other researchers have inferred that low salinity is ineffective in the oil recovery process.

At the reservoir conditions, the formation water pH is about 5 [111] due to the acidic gases (H_2S and CO_2) dissolving in it. The clay minerals at that pH, which are the cation exchange sites, are adsorbed by the protonated or acidic components of the crude oil, especially the divalent cations from the formation water, like Ca^{2+}. The injection of low salinity water, which promotes the desorption of Ca^{2+},will invariably create an increase in pH locally that will be close to that of the brine-clay interface as a result of the H^+ from the water substituting the Ca^{2+}. This phenomenon was observed in the works of Ishiwata et al. [130] who carried out an investigation using core flooding and numerical simulation on low salinity water flooding, where it was found that, with the desorption of the divalent cations, there is a corresponding desorption of the polar components of the oil from the clay surface and, where the H^+ is adsorbed onto the clay surface to bring about equilibrium, it subsequently increases the pH of the effluent. Ishiwata et al. [130] found that a fast reaction between the adsorbed protonated and acidic basic material and the OH^- will facilitate the desorption of organic material from the clay, which improves the water-wet condition of the rock and thereby increases oil recovery.

This dynamic is central to the double layer expansion (DLE) mechanism (a microscopic phenomenon) and it is closely related to the electrochemical interaction among the surfaces of the rock clay minerals. DLE, as reported by Ding and Rahman [131] , is the leading mechanism responsible for the alteration of wettability, both for sandstones and for carbonates. Low salinity water, compared to high salinity water, results in a thicker DLE. It is influenced by the electric surface charge, which is a function of the brine pH. Nasralla and Nasr-el-din [117] carried out an experiment to investigate the possibility of DLE being the primary mechanism for improved oil recovery by low salinity flooding. They tried to eliminate the low salinity brine effects on DLE to ascertain the extent to which EOR by low salinity flooding relates to the electric DLE caused by low salinity water. As stated by Hirasaki [16] rock wettability is dependent on the stability of the water film formed between the rock and the oil. The water film stability is a function of the double layer electrical repulsion that emanates from the electrical charges at the interfaces of the rock/oil/water system. Dubey and Doe suggested that, if these two interfaces have the same charges, a repulsive force will ensue and will maintain a thick film of water that will eventually produce a water-wet condition on the rock surface. It is said that sandstones have a negative charge at pH of about 2. Crude oil is positively charged at lower pH values, while at a higher pH it tends to be negative. Zeta Potential (ζ-potential) is the magnitude at the shear plane of the electric double layer, which is related to the surface charge at rock/brine and oil/brine interfaces and also to the thickness of the double layer [107]. Nasralla and Nasr-el-din [117] performed zeta-potential measurements on oil/brine and brine/rock interfaces to demonstrate the effects of brine pH and the salinity on DLE, and the results show that decreasing the pH of the low salinity brine makes the electrical charges at the interfaces marginally negative, reducing the thickness of the DLE as a result of the low salinity brine. The rock becomes more oil-wet, thereby suppressing oil recovery compared with the original pH of the low salinity brine. Based on their experiments, they concluded that DLE could be a dominant mechanism in low salinity flooding as a method of improved oil recovery. This is backed up by other researchers [107, 132] who, in a similar experiment, stated that results from ζ-potential show that decreasing the salinity and divalent cations results in making the electrical charges at the rock/brine and oil/brine interfaces more negatively charged, which invariably increases the repulsive forces between the rock and oil, and the rock becomes more water-wet as confirmed by their thermodynamic characterisation. They concluded that DLE as a result of highly negative ζ-potential caused by a decrease in divalent cations and salinity is significant in improved oil recovery. Other mechanisms that initiate wettability alteration are multicomponent ion exchange (MIE), pH effects, and salt-in and salt-out effects [131].

Another perspective to view the wettability alteration is the different effect it may have in different reservoir rock types during improved recovery. As sandstones and carbonates are very different rocks in all proportions, several literatures are available that point out these differences. Ding and Rahman [131] have stated that low salinity water containing less multivalent ions is more beneficial for sandstone reservoirs, and that seawater, on the other hand, has more positivity determining ions (Mg^{2+}, Ca^{2+}, and $(SO_4)^{2-}$) and is more profitable for carbonate reservoirs. Nasralla and Nasr-el-din [95] tried to show the impact of cation exchange as a low salinity water flooding mechanism for enhanced oil recovery. Their experiments show that an exchange of certain cations has a significant effect in showcasing the primary mechanism of the technique for higher oil recovery. They found that the absence of Ca^{2+} in the injected low salinity water allowed the water to percolate the Ca^{2+} off the rock surface, leading to instability at the rock surface and giving room for higher oil recovery as a result of higher volumes of oil being released from the rock surface. Their results demonstrated that the existing cations present in the injected brine have more presence when it comes to oil recovery than the concentration of the salts in the water.

Al-Attar et al., [101] performed an experimental investigation on low salinity flooding on selected carbonate reservoirs to identify the oil recovery mechanism. Specifically, they used seawater and two injection waters of different salinities to evaluate the effects of brine salinities and the ionic composition on the impending interaction of the fluid system. The alteration in wettability was determined by contact angle measurement. They found that low salinity flooding has potentials in their application and that increasing the Ca^{2+} concentration in the brine injected resulted in a decrease in the ultimate recovery. This is in agreement with what Jadhunandan and Marrow, which was reaffirmed by Sheng [89], in that the lower the Ca^{2+} concentration results in a more water-wet state in the cores with high initial brine salinity and, invariably, in higher oil recovery. Increasing the $(SO_4)^{2-}$ concentration in the brine injected has the better tendencies of changing the wettability of the rock to a more intermediate level, thereby increasing the ultimate oil recovery as well. Karimi et al. [133] carried out a similar experiment to investigate the impact of Mg^{2+} and $(SO_4)^{2-}$ on the wettability alteration and oil recovery by the imbibition of low salinity brine into carbonates, and confirmed the aforementioned phenomenon in that increases in the sulfate ion tends to increase recovery more than with the increase in the magnesium ion as a wettability modifying agent . Although NaCl and $CaCl_2$ do not significantly affect the wettability of a calcite surface, their presence in high concentration tends to hinder the access of the wettability influencing ions to the surface of the rock. It shows that neither Na^+ nor Cl^- ions are wettability modifying agents. They concluded that the spontaneous imbibition result showed that the modified brine that contained a higher concentration of sulfate ions alters wettability more efficiently than if modified with magnesium ions. This is also supported by Sheng [89] as they inferred that wettability is altered from oil-wet to water-wet in an alkaline phase (pH >9) and from water-wet to mixed-wet (intermediate) (pH <9) i.e. tending towards an acidic phase. This goes on to show that wettability can be altered by low salinity flooding by an ionic exchange between the injected brine and the rock saturated with formation brine.

Nasralla et al. [95] carried out an experiment to investigate the wettability of low salinity flooding in sandstone rocks where they used mica and two different types of crude oil. They concluded that the contact angle increased with the increase in pressure and temperature. High contact angles were observed in high salinity water, while low salinity water decreased the contact angles to a great degree for both types of crude oils. This shows that low salinity flooding can alter the wettability to a more water-wet condition. Additionally, the electrokinetic charges at oil/brine interfaces are sensitive to changes in the ionic strength of the system. Oil/brine system charges are highly negative in the presence of low salinity water, which invariably enacts the repulsive forces between the oil/brine and brine/rock surfaces and transforms the wettability to a more water-wet condition. It is reported in literatures that sandstone rocks and clays are negatively charged with brines [95]. This is because sandstones are primarily quartz, but may contain small amounts of clays that adopt the structural unit of silicon tetrahedral and contain stacked sheets of silicon tetrahedra with oxygen shared between the two tetrahedral. The repulsion between the two highly-charged units (Si_4^+) ensures that the structure of the silicates easily accommodates positive ions (cations). With a substitution of the Si_4^+ with other cations, usually Al_3^+ or Fe_3^+, it results in a net negative charge in the lattice of the crystal. The surface of the silica charges is dependent on the pH of the solution as shown in the reaction [131]:

$$\mathrm{SiOH + OH^- \rightarrow SiO^- + H_2O} \tag{2.5}$$

$$\mathrm{SiOH} + \mathrm{OH}^{+} \quad \rightarrow \quad \mathrm{SiOH}_2^{+} \tag{2.6}$$

Nasralla et al. [95] further reaffirmed that a wettability alteration resulting from changes of electrokinetic charge is the dormant mechanism for enhancing oil production during low salinity flooding.

As shown in some laboratory experiments, there is an inconsistency however in the wettability alteration mechanisms during low salinity flooding. Shojaei et al. [134], carried out an experiment to ascertain relative permeability and capillary pressure curves in low salinity water flooding in quartz-rich sandstone rocks. Initially, prior to aging, the core sample was flooded with oil and the pressure drop was evaluated. Also, after the aging, it was again flooded with oil and the pressure drop was measured; the drop was lower than it was before the aging as a result of the alteration in wettability during the process of aging. Before the oil flooding stage, the core sample was saturated with brine and initial water saturation in the core was affected by flooding with oil. The initial wetting state of the rock sample was water-wet and, during the aging, and subjected to reservoir conditions, some constituents of the oil in the rock sample could overcome the thin water film on the rock surface and be adsorbed. This phenomenon changes the wetting state of the rock from water-wet to more of an intermediate-wet. They showed that, from the contact angles measurement and analysis, the core was oil-wet, and that was not confirmed by their initial results. They attributed this inconsistency to the contact angle measurement and analysis in that most of them are performed on the surface of the rock that is completely aged in oil. They concluded that exponents flow functions from the relative permeability and capillary pressure curves, and residual oil saturation changed linearly with the salt concentration, invariably implying that wettability changed from mixed- or intermediate-wet to water-wet condition, which, in par, indicates that the wettability alteration mechanism is responsible for recovery improvement.

For the most part, it suffices to say that wettability alteration serves as the most profound mechanism of low salinity flooding for enhanced oil recovery. From all the relevant literatures, it shows that the process of low salinity flooding is sensitive to the type of reservoir rock in which the oil is situated. Certain injection brine modifications will not work in sandstones as the ions may behave differently due to the rock composition, but will work on carbonates as a result of the compatibility. There may be common ground whereby single formulated brine will be able to work on both different reservoir rock types.

2.8.2 Interfacial Tension (IFT) Reduction

Barati-Harooni et al. [129] stated that it is significant to reduce these capillary forces in porous media by altering the IFT between water and oil, which will eventually yield higher oil recovery. A dimensionless number, called the capillary number, expresses the general effects of capillary forces and it is expressed as a ratio of viscous forces to capillary forces [135]:

$$\mathrm{N_c} = \frac{\text{Viscous Force}}{\text{Capillary Force}} = \frac{\mathrm{V}\mu}{\vartheta\cos\theta} \tag{2.7}$$

where V is the velocity of the displacing fluid, ϑ is water-oil interfacial tension, μ is the viscosity of the displacing fluid, and θ is the contact angle.

The significance of the capillary number as reported by Ayirala and Rao [135] on the residual oil saturation shows that a significant increase in the magnitude of the capillary number is a prerequisite in any enhanced recovery process in order to reduce, considerably, the residual oil saturation. It can be shown from Equation (2.7) that this increase in the capillary number can be brought about by reducing the interfacial tension (ϑ) or, alternatively, by altering the contact angle (θ), which invariably means altering the wettability of the fluid-rock system. Numerous researches on the effects of several parameters like temperature, pressure and brine salinity on interfacial tension as reported by Barati-Harooni et al. [129] have shown that the trends observed in the IFT determination is dependent on the properties of the system. There was an increase in IFT as pressure increases in one report, and also an increase in temperature led to a decrease in IFT in another report. Ayirala and Rao [135] conducted an experiment to determine the effects of pressure and temperature on IFT using oil and formation brine, and reported that formation brine and oil IFT increased with an increase in pressure, and IFT decreased with an increase in temperature. Interfacial tension (IFT) is one of the key parameters that influence the fluid distribution and the residual oil in place in oil reservoirs. The mobility of oil trapped in the reservoir after the primary, secondary, and even tertiary recovery processes requires an in-depth understanding of the interplay between the confining fluids and the containing reservoir rock.

Aladasani et al. [136] studied the mechanisms and feasibility of low salinity water flooding as an oil recovery technique in sandstone reservoirs using numerous core flooding experiments and simulations. They conducted reservoir simulations to investigate the sensitivities of low salinity recovery effects and concluded that these effects are governed by the initial and final wetting conditions. In various wetting conditions, the increase in oil relative permeability is the underlying recovery effect, except for in weak water-wet conditions. In the weak water-wet condition the low capillary pressure drives the incremental oil recovery in low salinity flooding. However, in weak oil-wet conditions, the recovery effect of low salinity flooding is the change of the non-wetting phase to oil. It is realised, therein, that in all wetting conditions, there is an appreciable decrease in interfacial tension at the breakthrough recovery. This means that the decrease in IFT is the main recovery effect in a strong water-wet condition. This reduction is due to an increase in the pH values as inferred by McGuire et al. [99], which contrasted the experimental findings of Lager et al [121] showing that incremental recovery in brine had a pH value of less than 7.

2.9 Chapter Summary

In all the discussions on the mechanisms of low salinity, it can be noted that there does not exist any agreement with regards to a primary mechanism for low salinity phenomenon. Various examples of data exist for every mechanism. This represents a challenging task to define mechanisms of low salinity water flooding. There is an inconsistency however in the wettability alteration mechanisms during low salinity flooding, as shown in some laboratory experiments. Shojaei et al. [134] carried out an experiment to ascertain relative permeability and capillary pressure curves in low salinity water flooding in quartz-rich sandstone rocks. Initially, prior to aging, the core sample was flooded with oil and the pressure drop was evaluated. Also, after the aging, it was again flooded with oil and the pressure drop was measured; it was lower than the before the aging as a result of the alteration in wettability during the process of aging. Before the oil flooding stage, the core sample was saturated with brine, and initial water saturation in the core was affected by flooding with oil. The initial wetting state of the rock sample was water-wet and, during the aging, was subjected to reservoir conditions; some constituents of the oil in the rock sample could overcome the thin water film on the rock surface and be adsorbed. This phenomenon changes the wetting state of the rock from water-wet to more of an intermediate-wet. They showed that, from the contact angles measurement and analysis, the core was oil-wet and that was not confirmed by their initial results. They attributed this inconsistency to the contact angle measurement and analysis in that most of them are performed on the surface of the rock that is completely aged in oil. They concluded that exponents flow functions from the relative permeability and capillary pressure curves and residual oil saturation changed linearly with the salt concentration, invariably implying that wettability changed from mixed- or intermediate-wet to a water-wet condition, which, in par, indicates that wettability alteration mechanism is responsible for recovery improvement.

For the most part, it suffices to say that wettability alteration serves as the most profound mechanism of low salinity flooding for enhanced oil recovery. From all the relevant literatures, it shows that the process of low salinity flooding is sensitive to the type of reservoir in which the oil is situated. Certain injection brine modification will not work in sandstone as the ions may behave differently due to the rock composition, but will work on carbonates because of the compatibility. There may be common ground whereby single formulated brine will be able to work on both different reservoir rock types, hence the strength of the current study is its ability to develop a unique blend of smart water composition, including chlorides ions, which were previously eliminated for sandstone reservoirs, with the aim of understanding the corresponding improvement in recovery factors using smart water for the Wara field.

Chapter 3: Materials, Experimental Setup and Methodology

3.1 Introduction

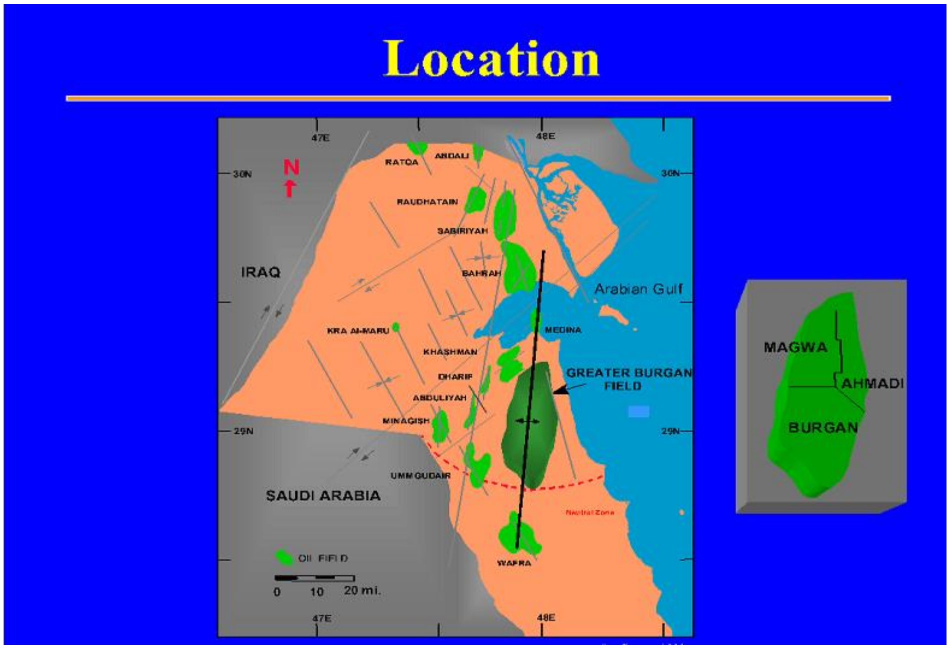
This Chapter details the background design philosophy of the experiments Study, followed by the description of the experimental setup with the sequence of design, which aims to highlight the step-by-step procedure followed in the apparatus, and the method used to fulfil the objectives of the Thesis. The Chapter also provides the specifications of the materials used in the experiments; the methods of preparation will be discussed, including accuracy and sources of errors. The Chapter has been sectioned into three (3), Materials Sourcing and Sampling, Materials Preparations, and Methodology of Conducting the Study.

3.2 Section I: Materials Sourcing and Sampling

The process of experimental design requires the identification of suitable materials based on their relevance. While research has numerous approaches, scientific research usually adopts either experimental investigation or analytical means. In a petroleum engineering discipline, experimental design, using closely associated materials to the field, has been established as a viable means to complement vast numerical simulations of conducting EOR studies [20] using realistic data from the scope of the study. Such data is usually obtained from the candidate field for EOR operations. Descriptions of the candidate field has been provided in the next Section, as a means of providing geological and compositional data from the field used in this Study.

3.2.1 Core Samples Location - Burgan Field in Kuwait

Greater Burgan, which is located in South-Eastern Kuwait (as shown in Figure 3.1), covers a surface area of about 320 square miles and has been ranked as the largest clastic reservoir and the second largest oil field in the world [137]. The field is underlain by, and produces from, Cretaceous age sandstones of the Zubair, Burgan and Wara formations, and Cretaceous and Jurassic carbonates of the Minagish and Marrat formations, respectively as shown in Figure 3.1.

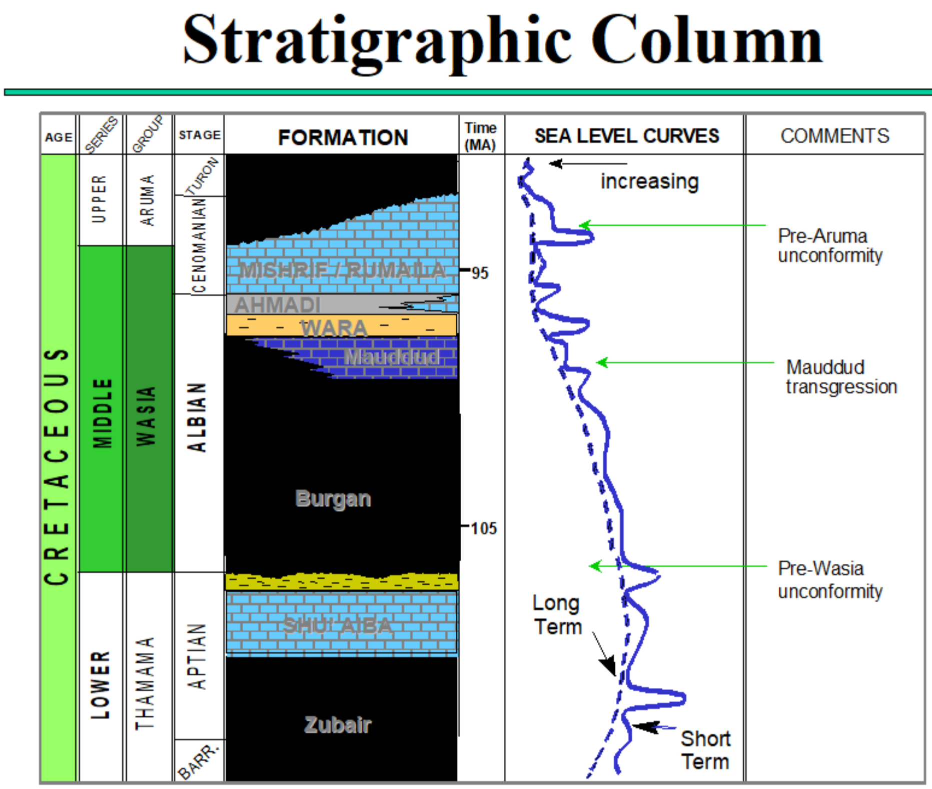


Location

Figure 3.1: Map and Coordinate of the Burgan Field

3.2.1.1 Brief History of the Burgan Field

The Burgan field was discovered on February 23rd 1938, with production beginning eight years later following the end of World War II [137]. The Burgan Formation, which holds the most important hydrocarbon reserves, accounts for about 90% of field production.


Stratigraphic Column

Sea level curves and time scale from Haq et. al., 1988.

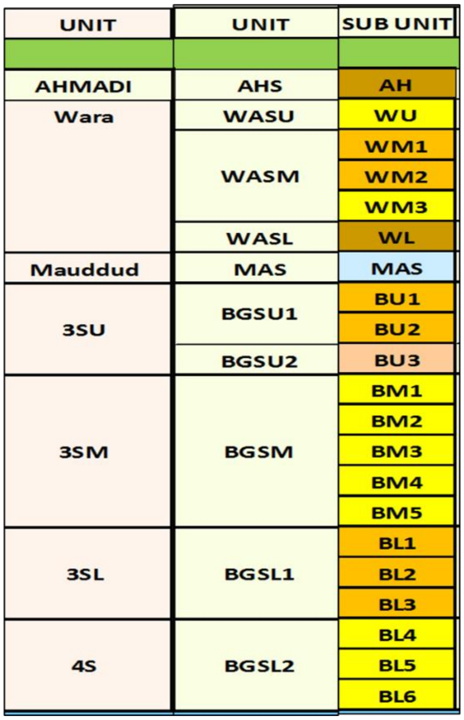
Figure 3.2: Stratigraphy of the Wara Reservoir

3.2.1.2 Field Description

Sandstones of the Burgan formation represent one of three siliciclastic depositional episodes in a Cretaceous section, which was dominated by carbonate sedimentation. A significant controlling factor on the depositional patterns of the platform was the interplay of tectonics, sea level change and climatic variation. Periodic influx of siliciclastic deposits, which were derived from the Western hinterland, displaced the focus of carbonate deposition eastward, resulting in a progression from non-marine to marine clastic, and from mixed carbonate to carbonate shelf facies belts.

3.2.1.3 Wara Formation Background

The Wara formation consists predominantly of shale and sand separated by a low permeability carbonate reservoir (Mauddud Limestone) of about 450ft from the underlying Burgan field [137]. It is a shale-rich formation with about 45% net to gross ratio. There is no communication, due to extensive faulting, between the various units of sands, and the reservoirs share a mutual OWC at 4,471ft below sea level and a pressure of 2,100psi at a depth of 4,000ft below sea level. The first clastic waterflood in Kuwait is the Water Flood Pilot Project. Production from the Great Burgan field initially came from the Wara formation and the reservoir pressure has since fallen below the bubble point in numerous parts of the reservoir [137]. This is because it is the uppermost productive interval in the Burgan field as shown in Figure 3.3. With this phenomenon, free gas will eventually evolve from the oil and a substantial loss in reserve recovery will ensue.



UNIT	UNIT	SUB UNIT
AHMADI	AHS	AH
Wara	WASU	WU
	WASM	WM1
		WM2
		WM3
	WASL	WL
Mauddud	MAS	MAS
3SU	BGSU1	BU1
		BU2
	BGSU2	BU3
3SM	BGSM	BM1
		BM2
		BM3
		BM4
		BM5
3SL	BGSL1	BL1
		BL2
		BL3
4S	BGSL2	BL4
		BL5
		BL6

Figure 3.3: Profile of the Burgan Fields

3.2.1.4 Water Flooding in the Wara Formation

As mentioned in the previous subsection, the pressure in the Wara formation has steadily declined to below the bubble point pressure, which tends to retard the reserve recovery. The need for pressure conservation to improve and implement measures for additional recovery is necessary, given that the Wara formation, which has been on stream since 1946, has recovered only 14% of OOIP [137]. The national oil company of Kuwait, KOC, initiated plans to re pressurise the Wara formation by water injection to arrest further decline in the reservoir pressure and to prevent possible loss of reserves.

The Wara pilot includes an injection pattern of seven spot inverted with one injector, one water source, and six producers, and was designed to inject 5,000 – 10,000bwpd into one injector and get production from six producers that are drilled around the injector. The wells are spaced at 250m and the producers are aided with electric submersible pumps (ESP) to enable production even after water breakthrough [137].

3.3. Section II: Materials Preparation

3.3.1 Core Samples

Actual core samples were obtained from the Wara formation in Kuwait and are shown in Figure 3.4.

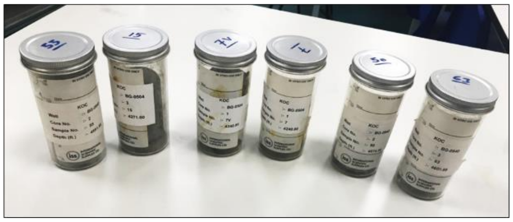


Figure 3.4: Core Samples

The dimensions and depth of acquisition are shown in Table 3.1.

Table 3.1: Dimensions of Core Samples

No.	Sample Name	Length (mm)	Diameter (mm)	Depth(ft)
1	61	58.91	38.05	4607
2	55	55.85	38.35	4591
3	15	60.77	37.92	4271
4	7V	58.91	38.05	4240
5	7	51.73	37.62	4240
6	50	48.10	38.10	4574
7	63	48.56	38.11	4202
8	15V	60.43	38.62	4271

3.3.2 Crude Oil

The crude oil used in this study is a dead oil from the Wara formation, with properties as shown in Table 3.2.

Table 3.2: Crude Oil Property

Water Content	Specific Gravity	Dynamic Viscosity (cP)	API Gravity
9.2	0.895	9.7	22.1

Because it contains harmful volatile compounds, as a safety precaution, it was stored in a canister (Figure 3.5) and in a fume cupboard, Dead crude used in this Study refers to crude oil that has been stabilised by removal of the lighter gas components, thereby allowing ambient and high pressure measurements that are suitable for interfacial tension and flooding systems [138-140].

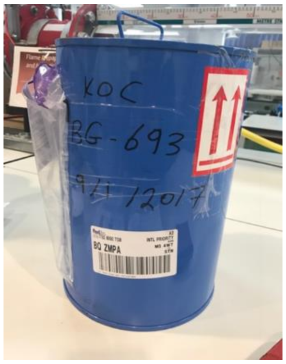


Figure 3.5: Crude Oil

3.3.3 Brines Preparation

A replica of the formation brine from the salt composition was prepared to simulate reservoir water. All the salts were purchased from Fischer Scientific UK. Preparation of the brine was carried out at room temperature by dissolving the measured amounts of various salts in the appropriate volume of distilled water. This was done using a magnetic stirrer and a round bottom flask.

3.3.4 Cleaning and Characterisation of Core Samples

Cleaning and characterisation of the core plugs are vital as they prepare and ensure the proactive and confident results obtained from the experimentation. Soxhlet extraction was used to clean the core sample.

3.3.4.1 Mineralogical Characterisation

This technique aims to ascertain the mineralogical composition of the samples and it involves three techniques in this case. Scanning electron microscopy (SEM) is a technique that examines the morphology of the core sample. This technique is usually used in conjunction with energy dispersive x-ray spectroscopy (EDX), which analyses the elemental composition of the sample of interest. This helps to get a picture of the types of elements that make up a compound present in a given sample, and will be identified using x-ray diffraction (XRD).

3.3.4.1.1 Scanning Electron Microscopy (SEM) and Electronic Dispersive X-ray Spectroscopy (EDX)

This technique is qualitative and is usually utilised for high magnification imaging and elemental analyses at different magnifications. The morphology and texture of a sample can be ascertained with this technique. The SEM technique is very expensive and is usually not available in characterisation laboratories. However, it is frequently employed in obtaining data on the shape, homogeneity, size and crystalline habit, as well as determining the presence of crystalline and amorphous compounds and their various distributions in a sample of interest. The SEM was done on the samples using a FEI Quanta 250 Field Emission Scanning Electron Microscope with EDAZ Genesis Energy dispersive X-ray analyses system attached. The images were obtained using the back scatter electron diffraction technique (BSED).

3.3.4.1.2 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is the method used for extracting structural information from virtually any type of sample, regardless of shape, size or composition and under ambient or non-ambient conditions. The XRD was performed on the samples using a Bruker D8 Advanced Xray Diffractometer with dynamic beam optimisation as shown in Figure 3.6.

Figure 3.6: Advanced D8 X-Ray Diffraction (XRD) Equipment

3.3.4.2 Petrophysical Characterisation

This is performed to evaluate the actual petrophysical properties of the core sample for the core flooding process. It gives vital information on the storage capacity of the core sample and also on the ability of the fluids to pass through the interconnected pore spaces during the injection process; these are essentially the porosity and permeability.

3.3.4.2.1 Permeability

The absolute fluid permeability to the various core samples for this research were determined using a simple core flooding set up. Darcy's Law is the principle of operation of the set-up. The measurement required the following variables: differential pressure (dP), core samples cross sectional areas, core sample length, injection flow rate, and viscosity of the brine used to evaluate the liquid permeability of the core samples.

3.3.4.2.2 Porosity

Pore volume is vital in any laboratory core flooding techniques for EOR, as it provides the carrying capacity of the core samples. It was used to evaluate the measure of the recovery factors of the EOR process and dimensionless analysis of laboratory results, especially when it came to scaling up of the technique in terms of physical or simulation projection. Helium porosimetry and vacuum saturation methods were used to evaluate the property.

3.4 Experimental Methodology

Figure 3.7 shows the Flow Chart of the methodology and the sequence of the experimental process. The method of experiments is classified into four (4) phases to present a concise workflow. Each phase corresponds to the stated objectives described.

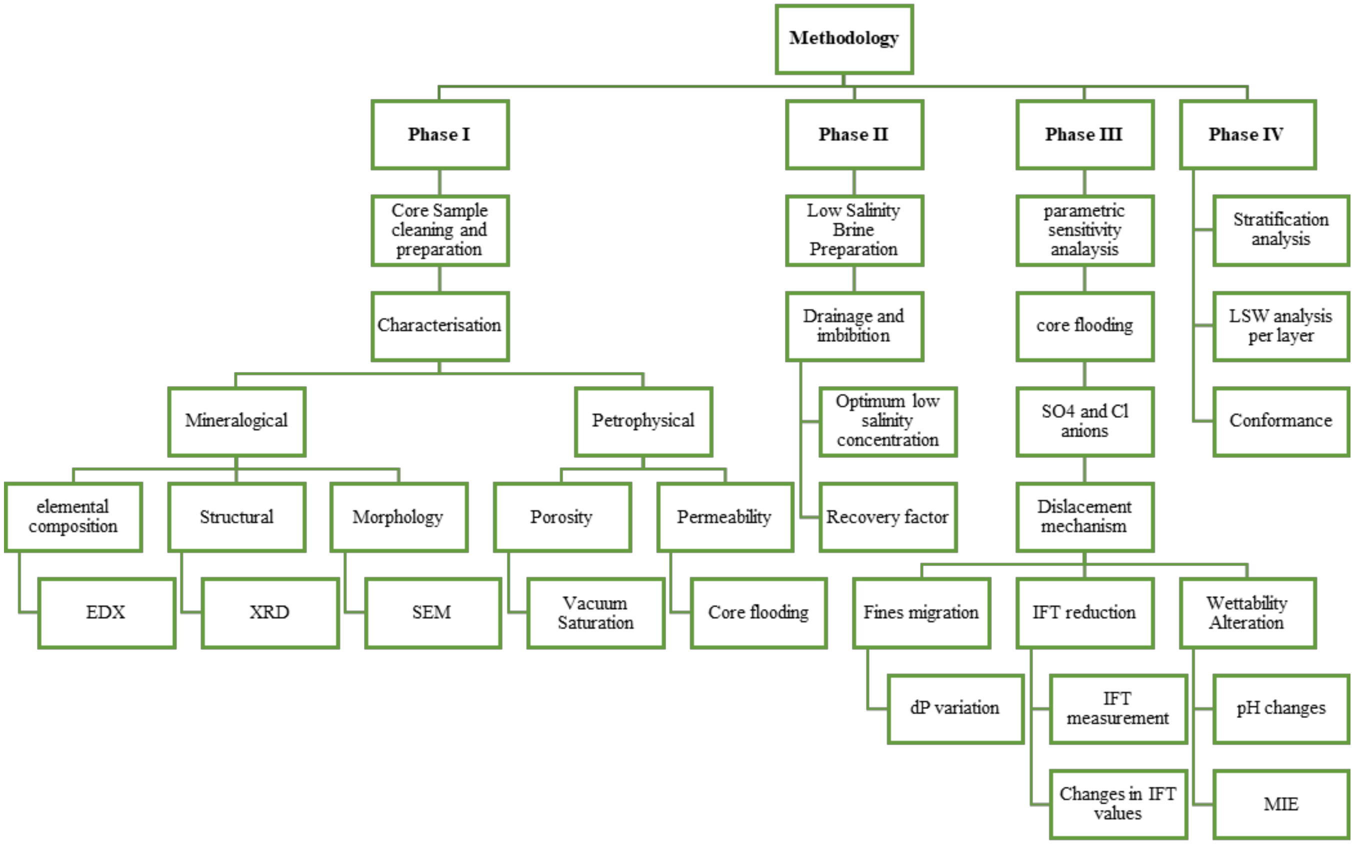


Figure 3.7: Experimental Methodology

3.4.1 Phase I: Core Sample Cleaning and Characterisation

The first step in Phase I of the experimental methodology is core sample cleaning and characterisation. Real core samples were used in this Study and were obtained from the Wara Formation in the Burgan Field in Southern Kuwait. Cleaning of the core sample was carried out using the Soxhlet extraction process to clean the core samples to rid them of any residual organic and inorganic material within the pore matrix that may contaminate the results. This was followed by core sample characterisation, which entails petrophysical and mineralogical assessments of the core plugs to establish a baseline. Various techniques were employed to evaluate the mineralogical properties of the core samples - composition and morphology, such as scanning electron microscopy (SEM), x-ray diffraction (XRD), and electron dispersive x-ray spectroscopy (EDX). This identified the clay types present in the sample, which was beneficial in formulating the most compatible injection water that would present the best-case scenarios of the process. Petrophysical assessment employs the vacuum saturation method for porosity measurement, and core flooding for core sample liquid permeability determination. The essence of this assessment was to obtain the carrying capacity (pore volume) of the core samples, which is vital to the accuracy of the experiments and the ease, or lack thereof, with which the fluids pass through the core sample.

3.4.2 Phase II: Low Salinity Brine Preparation and Optimum Concentration

For this phase, low salinity brines were prepared to suit the system of experiments, based on the results obtained from Phase I. Different brines were prepared, based on established literature, to obtain the optimum low salinity concentration that is tailored for this particular formulation, rock and fluid types. Imbibition core flooding experiments ensued to obtain the optimum recovery factors from all prepared low salinity concentrations that will be most applicable for this rock and oil type. A distilled water imbibition experiment served as a benchmark for parametric sensitivity analysis in Phase III.

3.4.3 Phase III: Sensitivity Analysis

Having obtained the optimum low salinity brine concentrations, the investigation into the effect of sulphate and chloride-based brines was evaluated. This entailed using the dominant salt types within the composition of the actual formation water obtained from the Wara formation, and then performing a core flooding experiment to evaluate the anionic roles in the oil displacement. The determination of the active displacement mechanisms during the smart low salinity process followed. Fines migration was investigated by observing the differential pressure fluctuations during all the flooding scenarios for all the brines tested. The wettability alteration mechanism was examined by measuring the pH of the injected brines and effluents that may indicate a multicomponent ion exchange (MIE) process took place. Interfacial tension (IFT) reduction was also independently evaluated using a rising bubble technique in an IFT measurement cell. Oil and different brines' IFTs were measured and analysed at different operating conditions to investigate the extent to which IFT reduction played a role in additional oil recovery.

3.4.4 Phase IV: Stratification Performance Analysis

As all the rock samples were cored from different depths of the payzone in the reservoir, it was noteworthy to analyse the performance of each layer as it produced oil. This was to envisage the heterogeneity of the reservoir with respect to fluid flow behaviour. To do this, each core plug was subjected to the same imbibition experiment and the result of their performances were overlaid and compared.

3.5 Experimental Procedures

3.5.1 Core Flooding Experimentation

The hydrocarbon reservoirs, which are the storage sites for oil and gas, are naturally porous. The oil recovery process involves the flow of two or more fluids simultaneously in the reservoir. In the secondary process of waterflooding, for example water from the surface, is injected into the reservoir for pressure maintenance in order to displace the oil from the pore spaces of the porous reservoir rock after the reservoir pressure has declined. The core flooding experiments, using the low salinity flooding technique to displace residual oil from the reservoir as a method for EOR, were adopted in this work. A branded core flooding equipment UFS 200 from CoreLab USA was used. The equipment description, the procedures, the possible error sources and, finally, the results of the experimentation will be presented along with the significance of the findings. The pictorial view is shown in Figure 3.8.

Figure 3.8: UFS 200 Core Flooding Equipment

3.5.1.1 Core Flooding Setup

This Section enumerates the detailed experimental procedure for the equipment employed and their operating principles. The procedures adopted in the measurement will also be narrated and presented for every equipment used. The presentation will conform to the sequence of experiments; starting with the core sample cleaning and characterisation, followed by the core flooding process and, finally, the IFT measurement.

3.5.1.1.1 Core Sample Cleaning and Characterisation

The cleaning of the core sample will first be explained in detail from the equipment description to the step-by-step procedure including the compounds used. The characterisation will follow, and will begin with the mineralogical assessment followed by the petrophysical description.

Cleaning using the Soxhlet Extraction Process

Soxhlet extraction is the technique of choice for cleaning core samples, and was employed in this work as it is a thorough cleaning process, albeit time consuming. The experimental set up is shown in Figure 3.9. The set up comprised of four primary components; the round bottom flask (1000 ml), the thimble, the extraction chamber with the siphon arm, and the condenser. A heat source was also required for the process.

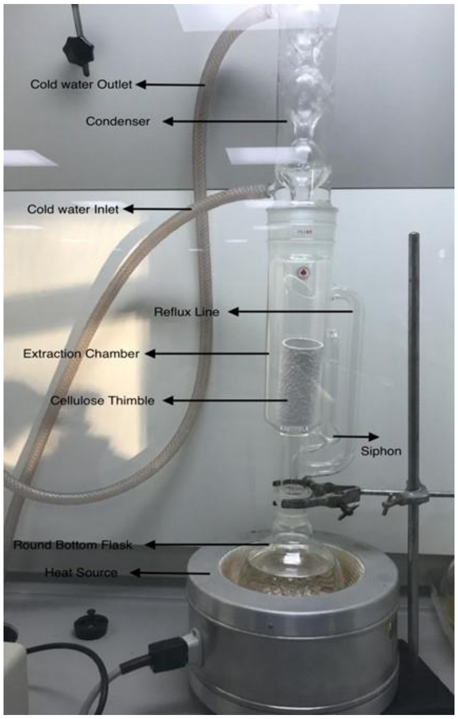


Figure 3.9: Soxhlet Extraction Setup

3.5.1.1.2 Core Flooding Procedure

The core sample was placed in the cellulose thimble and inserted into the extraction chamber. Then the assembly was placed on the round bottom flask, which was on the heat source. The round bottom flask was filled with an organic solvent, in this case Toluene, anhydrous, 99.8% purity ($C_6H_5CH_3$), obtained from Sigma Aldrich. The condenser was then installed on the extraction chamber and the cold water was run through the inlet and drains at the outlet. The electric heat source was then turned on in order to heat up the round bottom flask containing the organic solvent. As soon the boiling point of Toluene was reached, the vapours travelled through the reflux path into the condenser where the temperature was low enough to provide a condition for the solvent vapour condensation. They then drained back into the thimble containing the core sample to be cleaned till it filled it up, automatically siphoning back into the round bottom flask containing the parent organic solvent. This was called a cycle. During the cycle, the solvent warm vapour condensate filled up the thimble containing the core sample and seeped through the sample, dissolving any residual organic solvents like crude oil. The process was left for 48 hours (after numerous cycles) until the colourless organic solvent became very clear and the solvent in the round bottom flask became murky and dirty.

The same procedure was also carried out using the same set up, but with a different organic solvent, methanol, with a purity of 99.8% purity, also obtained from Sigma Aldrich. This was to remove any inorganic deposits from the core samples, ranging from different salt compounds from the formation water, to drilling mud additives.

3.5.1.1.3 Core Sample Drying

After the core sample was removed from the Soxhlet extraction set up, it was dried in an oven for 24 hours to completely get rid of the volatile reagents, leaving the pathways of the pore spaces to allow for absolute petrophysical properties determination. The core sample was weighed after drying to obtain the dry weight, which is an instrumental quantity for subsequent evaluation. Results of the dry core sample weights are shown in Table 3.2.

Table 3.2: Core Samples Specifications

No.	Sample Name	Sample Depth (ft)
1	15	4271
2	15V	4271
3	50	4574
4	63	4202

3.5.1.1.4 Core Flooding Equipment Description

In the laboratory, a CoreLab UFS-200 was employed for core flooding experiments using the schematic shown in Figure 3.10. This system was configured for two phase liquid displacements under unsteady-state or steady-state conditions, and single-phase gas-steady-state experiments. The system is rated to 3,750psig pore pressure and 5,000psig confining pressure at ambient temperature. The inlet pressure into the core sample and outlet pressures on the other side of each core were measured with gauge pressure transducers located on the panel of the control system. Stainless steel tubing with 1/8” OD provided the conduits through which all fluids pass. A computer data acquisition software and control system, and SmartFlood software formed the integral part of the core flooding system, which provided real time display and recorded all measured parameters, ranging from volumes, pressures, flowrates and temperatures, automatically to a data file on the computer.

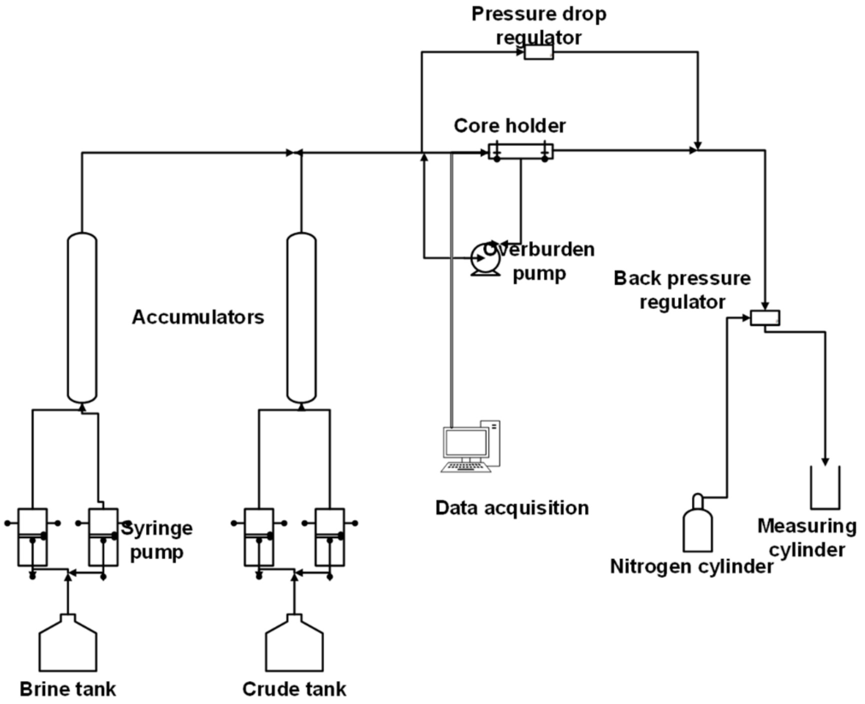


Figure 3.10: Schematic of Experimental Core Flooding Apparatus

The core sample to be analysed was held within a viton rubber sleeve enclosed in a Hassler-type core holder by radial confining pressure, which simulated the overburden pressures in the reservoir. The distribution plugs located at the inlet and outlet of the core holder permitted fluids to be injected through the core sample. All flow lines and internal volumes were kept to a minimum to keep dead volumes as low as possible to allow accurate flow measurements to be achieved. The simulated pore pressure was obtained through a two barrel metering pump system, ISCO model 500D, with a flow rate range variable from 0 to 204ml/min and a maximum pressure rating of 3,750psig. The overburden pressure was simulated by a hydraulic pump, Model S-216-JN-150, with pressure output of up to 10,000psig and provided the desired confining pressure in the system. The back pressure was controlled with a CoreLab dome type back pressure regulator, which controlled the back pressure to whatever reference pressure is supplied to its dome. It was rated for a maximum working pressure of 5,000psig. Floating-piston accumulators were part of the injection system assembly and were rated for 5,000psig pressure and 177°C temperature. The accumulators provided for the injection of fluids into the core sample situated within the core holder to mimic the enhance recovery technique and associated procedures to conform to real-life situations in the field. Fitted on the control panel were 2.5inch dial pressure gauges, with a pressure range of up to 15,000psig full scale, which were used to monitor the overburden pressure and the back pressure dome pressure. A 160psi gauge was provided to monitor the main inlet air going to the pump and other components, like the air actuated valves. A Rosemount transducer provided with the system measured the differential pressure across the core holder. The effluent flowrate and produced volume was measured by a graduated measuring cup, where the volumes will be determined gravimetrically.

3.5.1.1.5 Core Flooding Process

The core flooding process is a laboratory experiment where fluids are injected into a core sample or packed bed for different purposes. It helps in understanding and investigating several parameters or interplay between different parameters in relation to the recovery processes. Some of the aims of the core flooding process are permeability determination, relative permeability measurement, change in rock saturation, rock-fluid interaction investigation and the effect of injection fluid on formation integrity. The core sample usually comes as an outcrop of a hydrocarbon reservoir rock. Generic or artificial rock samples are often used depending on the availability and type of the investigation. The original fluid in place at the onset of the experiment is usually either oil (mineral oil or dead crude oil), gas (in the case of simulating a gas reservoir), a simulated formation brine, or a combination of all of the fluids. The displacing or injected fluids may include gases, simulated formation brine, crude oil, formulated fluids, foam or other chemicals used in the oil field to simulate field conditions/processes. Owing to the purpose of the core flooding experiment, operating conditions may vary; for example, the core flooding can be carried out either at ambient temperature and low pressures, or at high temperatures and pressures akin to that of the reservoir in question. The inlet and outlet pressures are measured and the flow rates of the injected fluid, which causes the pressure differential, are measured. Other integral components for qualitative determination of some parameters may be employed and integrated into the core flooding equipment. A core flood is usually used to determine and assess the optimisation of a method for additional oil or gas recovery through different technologies, or to help facilitate or design novel methods and their feasibilities in field application for enhanced or improved oil recovery.

3.5.1.1.6 Principle of Operation

The UFS 200 core flooding systems work on the principle of Darcy’s Law. Henri Darcy empirically defined fluid flow in porous media in 1856 as being proportional to the differential pressure per unit length. The relationship was derived from data collected during a series of experiments on the vertical flow of water through gravel packs. Subsequent work has proved the validity of Darcy's Law for flow in all directions, and confirmed the experimental observations by derivation from the basic laws of physics.

$$\mathrm{Q} = \frac{\mathrm{kA(dP)}}{\mathrm{\mu L}} \tag{4.1}$$

where, k is permeability (Darcy’s), μ is the dynamic viscosity (cP), Q is the flow rate (cc/sec), L is the length of the flow (cm), A is the cross-sectional area of flow (cm^2), and dP is the differential pressure (atm). Rearranging Darcy’s Law, and changing the units of permeability to millidarcies and pressure to psig, the equation becomes:

$$\mathrm{k} = \frac{14700\mathrm{\mu LQ}}{\mathrm{dPA}} \tag{4.2}$$

where k is in millidarcies (md) and 14700 is a conversion factor.

The next step in the core flooding process was the determination of the instrument dead volumes and other methodical procedures to ensure errors were reduced to a minimum.

3.5.1.1.7 Dead Volume Determination

Before the commencement of any core flooding experiments, it is essential to carry out some preliminary procedures to ensure accuracy of measurements and to minimise errors. These errors could be as a result of dead volumes, which will present an overestimation of the recovery factor and injection volumes, along with other dead volumes-related errors. In this work, accumulator calibration was carried out and fluid losses due to beads and streaks within the tubing were evaluated.

Two methods were adopted to calculate the dead volumes and were compared to ascertain accuracy and conformity. The first method used an experimental approach in which a known volume of distilled water was flooded and the recovered volume was obtained and measured. The difference was evaluated and made up the dead volume. The second one consisted of measuring the lengths of the interconnected tubing and diameters, from which the entire volumes were evaluated.

Firstly, the calibration of the accumulator was carried out in which a known volume of distilled water was injected into the accumulator and then discharged through the first section of the tubing.

An injection of 100cm^3 of distilled water was made into the accumulator from the CC cells. The pumps were run at 10ml/min from the accumulator and the measuring cylinder was positioned downstream of the first section of tubing so that the 100cm^3 volume of distilled water was discharged into it. After the pumps stopped, a volume of 98cm^3 was recovered and this value was recorded. A nitrogen purge was then initiated through the inlet port of the accumulator, which was intended to purge the remaining distilled water within the tubing to be measured. An additional volume of 0.7cm^3 was recovered, given a total volume of 98.7cm^3. This means that a volume of 1.3cm^3 is unaccounted for and, therefore, can be counted as a possible loss through fluid-conduit interaction, particularly adhesion of the fluid to the internal walls of the tubing.

To accurately evaluate the remaining volume, an analytical approach was adopted and the results obtained were compared to the experimental results as aforementioned. The length and internal diameter of tubing of the first section of the setup were measured to evaluate the volume. It was assumed that the fluid transported through the tubing occupied the volume in its entirety. Therefore, evaluating the internal volume gave a good indication of the additional recovery of fluid after the primary discharge:

- The length of the first section measured = 87cm
- The internal diameter of the section = 0.1cm
- Thus, the volume can be evaluated as 0.68295cm^3 (or 0.68cm^3)

Comparing both techniques, there are significant similarities between experimental and analytical methods of dead volume determination - experimental was 0.7cm3 and analytical was 0.68cm^3. Suffice to say that accurate measurement of the dead volume can be carried out using either technique to quantify the volumes of fluids still left in the system.

The dead volume measurement of the entire system was then carried out following the success of the method from the first upstream section. The core sample length was discounted from the length measurement for simplicity, given that its pore volume has already been determined, and also because it has a different diameter from the tubing.

A known volume of water, 500cm^3, was injected into the accumulator. An equivalent length of one end of the core holder to the other was measured, and a tubing of equal length and diameter of the primary tubing was installed in place of the core holder. This provided uniformity when measuring the entire length of tubing in the system for necessary calculation and evaluation.

The water was then injected into the system and 473.73cm^3 was recovered downstream of the system. The same nitrogen purging technique was then adopted to flush out the remaining immovable water within the system. A volume of 5.8cm^3 was recovered. Therefore, the total pore volume in the entire system was determined experimentally and presented as 5.8cm^3. Summing up the volume primarily recovered, and that which was recovered through the nitrogen purge, presented the total recovery of the fluid that was injected - that is, 479.55cm^3. Subtracting this value from the known volume of the initial 500cm^3 gives the total fluid loss in the system. The difference was evaluated as 20.45cm^3.

The analytical method of dead volume determination was similar to the first instance, which involved the measurement of the entire length of the tubing in the system followed by the evaluation of the volumes, with the same assumption that the volume is occupied entirely by the fluid. In this case:

- Entire length of the downstream section = 277.2cm
- Entire length of the upstream sections = 461.2cm
- Total length of tubing = 738.4 cm
- Diameter = 0.1 cm
- Volume = 5.8 cm^3

This value of volume was the same as that which was measured experimentally. After this determination, a core flooding experiment to evaluate using distilled water was carried out. The procedure is discussed next.

3.5.1.1.7 Core Flooding Experimental Design

As surmised earlier, the formation brine was prepared as close to the original brine composition from the field as possible. Then serial dilution of the prepared brine was carried out to create different low salinity concentrations to evaluate the optimum concentration, which was adopted in this body of work. However, for simplicity, the test brine was prepared to a concentration of 100,000ppm. Subsequently, using the relation in Equation 4.3, the amount of the formation water required to create the low salinity counterpart was calculated.

$$\mathrm{V_{add}} = \frac{\mathrm{LS_{conc}} \times \mathrm{V_{Dist\,H2O}}}{\mathrm{HS_{conc}}} \tag{4.3}$$

where V_{add} is the required volume to be added (cm^3), LS_{conc} is the desired concentration of the LS brine (ppm), $V_{Dist\,H2O}$ is the volume brine required for the test (500 cm^3), and HS_{conc} is the original formation water (ppm).

Table 3.3 shows the desired concentrations and the corresponding volumes of formation water required to create a 500cm^3 solution to be used for the core flooding experiments.

Table 3.3: Adopted Concentrations for Optimum LS Determination

No.	Low Salinity Brine Concentration (ppm)	Volume of Formation Water Required (cm^3)
1	15000	75
2	10000	50
3	5000	25
4	1000	10

Having prepared the various low salinity solutions, the core flooding experiment was carried out to evaluate the optimum concentration that will improve oil recovery. The flowchart of the design of the experiment is shown in Figure 3.11.

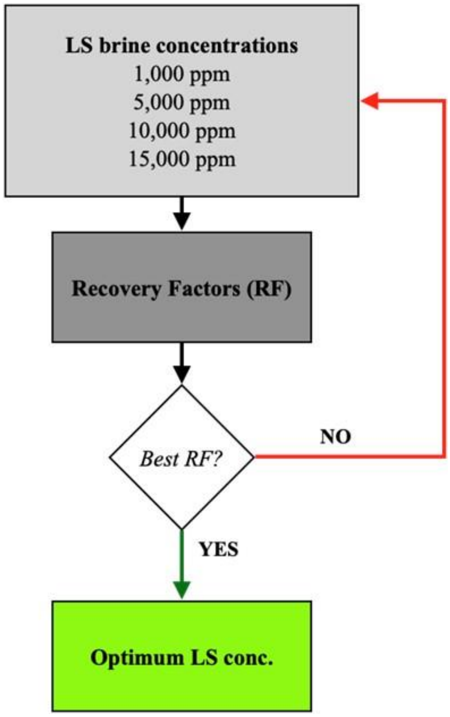


Figure 3.11: Flowchart of Optimum Brine Concentration Determination

The core flooding experiment was carried out in three stages. The first stage was saturating the core sample by injecting the simulated formation water at a constant injection rate after external brine saturation. Secondly, oil was injected into the core sample to establish initial water (S_{wi}) and oil saturations (S_{oi}). The third and final stage was the water displacement using a controlled low salinity brine to mimic an imbibition process. Distilled water was used to establish a characteristic benchmark upon which other tests will be compared. All experiments were carried out at the same temperature and pressure conditions. After establishing the optimum concentration, sulphate- and chloride-based brines were prepared from the species available in the original composition. The categorisation is shown in Table 3.4.

Table 3.4: Salts Used in the Preparation of the Brines

No.	Sulphates	Chlorides
1	Na_2SO_4	NaCl
2	$CaSO_4$	$CaCl_2$
3	K_2SO_4	KCl

Procedure

First stage (core sample saturation with water)

The core lab UFS core flooding module was switched on and the air pressure in the system was set to 95psig. This air controlled the pneumatic systems from the pump metering systems to the refill systems. A distilled water volume of 500cm^3 was decanted into the CC cells in preparation for the accumulator filling. A pressure of 20psig was applied to the CC cells to drive the water into the accumulator. The metering pump was purged from the panel to accommodate the influx of the distilled water into the accumulator. After the volume was completely injected into the accumulator, the pressure in the CC cells was vented. The core sample was inserted into the viton sleeve to establish a seal to channel all fluids into the core sample longitudinally or in the direction of flow (conduit). This was then placed inside the core holder and the distribution plugs were engaged. A heating jacket was then placed over the core holder to establish the temperature of the operating condition of interest. A Tempco temperature controller was used to keep the temperature constant at 40°C. The metering pumps were engaged, which injected the distilled water from the accumulator into the core sample situated within the core holder at a flowrate of 1ml/min. Small increments were made to bump the injection rate in order to ensure full saturation. The injections were made after the back pressure of 1600psig was engaged to keep the system at that condition of interest. This process was monitored on stream and on screen through the SmartFlood software integrated component of the UFS equipment. The software automatically recorded all the parameters during the core flooding for evaluation and monitoring. The run was stopped after a constant dP was observed across the core holder.

Second stage (oil saturation for Soi and Swi determination)

The second accumulator was filled with crude oil using the same procedure, as earlier stated in the first stage, using the CC cells. Accumulator A was isolated during the injection process to minimise the dead volumes during computation because it was injected through a different tubing. The injection rates were varied for a better saturation of the core sample. A range of injection rates of 0.2, 0.5, 1 and 2ml/min were adopted, keeping the same conditions of 1600psig system pressure and 40°C temperature. A long drawdown was made to ensure that the core sample was fully-saturated and that there was no mobile water within the system. An overburden pressure of 2200psig was maintained in the annulus of the core holder using the overburden pump. As a precaution, it was earnestly monitored due to the unpredictable rise in pore pressure delivered by the ISCO pumps. By design, the overburden pressure should be maintained at at least 500psi above the pore pressure to avoid rupturing of the viton sleeve through which flow is established. The displacement was observed as water was ejected from the system by the more viscous crude oil. This volume recovered was recorded in a bid to establish the initial water saturation in the core sample and also the initial oil saturation prior to the displacement in the third stage. The importance was to evaluate the recovery factor and, invariably, the recovery efficiency. A given volume of water was recovered before oil breakthrough and was measured/recorded. The run was stopped when the dP across the core holder became constant.

Third stage (oil displacement)

Prior to this stage, the core sample was aged in the system at elevated temperatures of 80-90°C and pressures of 1600psig for 7 days in order to restore the wettability of the core samples to their original state. Their states could have been altered after using different reagents for the Soxhlet extraction. This stage depicted the oil displacement of the core flooding process, in that a volume of a displacing fluid was injected to displace the in situ fluid for the drive of additional recovery. An injection rate of 0.5ml/min was used for the purpose of the displacement process. This was in a bid to avoid viscous fingering and other injection-related undesirable phenomena, and may have a low areal sweep efficiency. The same procedure as mentioned earlier was followed, with the only difference being the injection rate. The run was stopped or terminated when the water cut was more than 70%.

3.5.1.1.8 Petrophysical Determination

The determination of the petrophysical properties of the core samples provide vital information in core flooding experiments to evaluate the efficiency of a flooding technique in question. For low salinity flooding, porosity and permeability measurements are paramount in determining the pore volumes of the core samples and their respective fluid conductance respectively. Pore volumes provide the carrying capacity of the simulated reservoir, which gives an indication of the oil and water saturations. A step-by-step procedure for acquiring these petrophysical properties will be discussed.

3.5.1.1.9 Porosity Measurement

The porosity measurement process employed the use of a constructed saturation rig and a high-accuracy digital weigh balance. The rig was made up of a high-grade stainless-steel containing vessel, a beaker and a vacuum pump with Swagelok valves with a pressure range of 15psi, 1/4" OD plastic tubing and Teflon tubing as shown in Figure 3.12. The procedure was as follows.

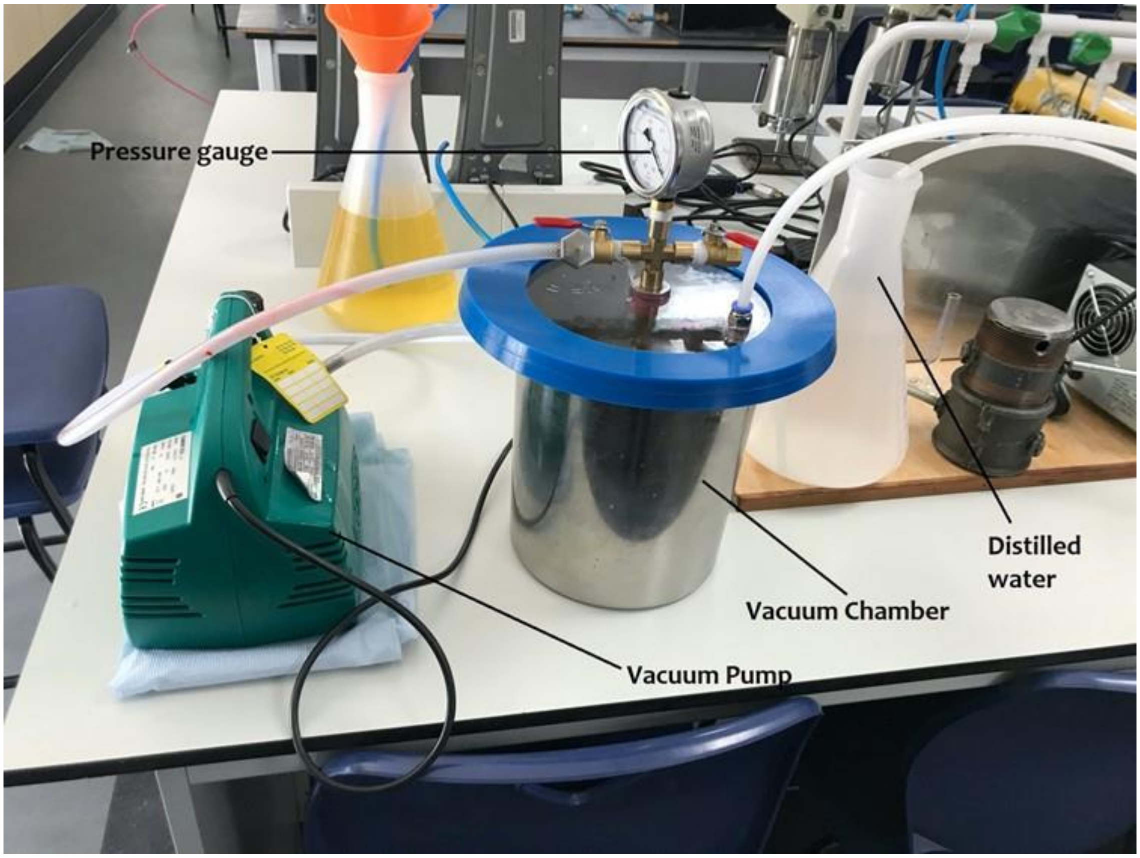


Figure 3.12: Porosity Measurement Apparatus

Procedure

The core sample was placed upright in the containing vessel as shown in Figure 3.12. The lid was then clipped on tightly to form a perfect seal within the vessel. Distilled water/brine was poured into the plastic beaker, valve 1 was opened and the plastic tubing was immersed into the distilled water in the plastic beaker. Valve 2 on the line leading to the vacuum pump was opened. The switch on the vacuum pump was initiated and then the vacuum created in the sealed containing vessel created a suction and delivered the distilled water/brine into the chamber; it continued to do so until the level in the chamber was above the top end of the core sample. Valve 1 was shut off and the vacuum pump was stopped. Valve 2 was also then shut off. Tiny beads of air bubbles could be observed on the surfaces of the core sample.

After 24 hours, this allowed enough time for full saturation of the core sample, and valve 2 was opened to remove the vacuum in the containing vessel.

3.5.1.1.10 Permeability Evaluation

The permeability measurement setup (Figure 3.13) comprised of a Hassler-Type core holder ECH series, a static pressure gauge, a backpressure regulator and an injection pump. The injection fluid was supplied from the accumulator from the PREL 300 core flooding apparatus. The Eldex pump supplied the injection pressure in the required increments to evaluate the permeability at different pressures and flow rates. These are the required parameters for permeability evaluation. The regulator applied the upstream pressure and the pressure gauge recorded the downstream pressure.

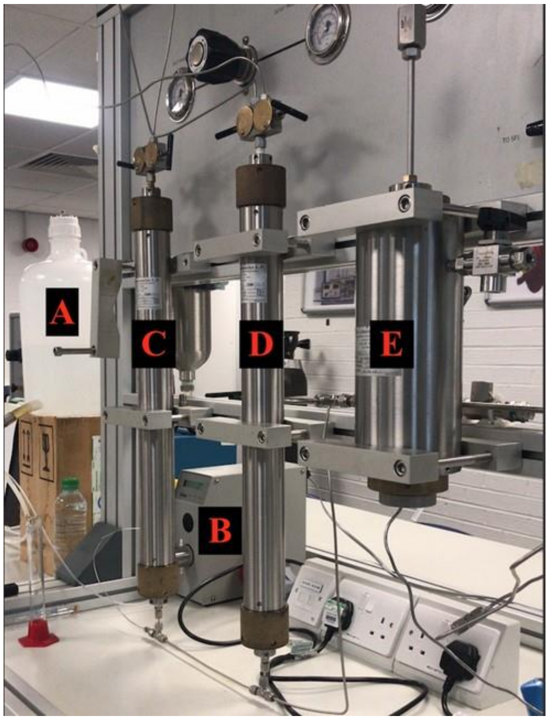
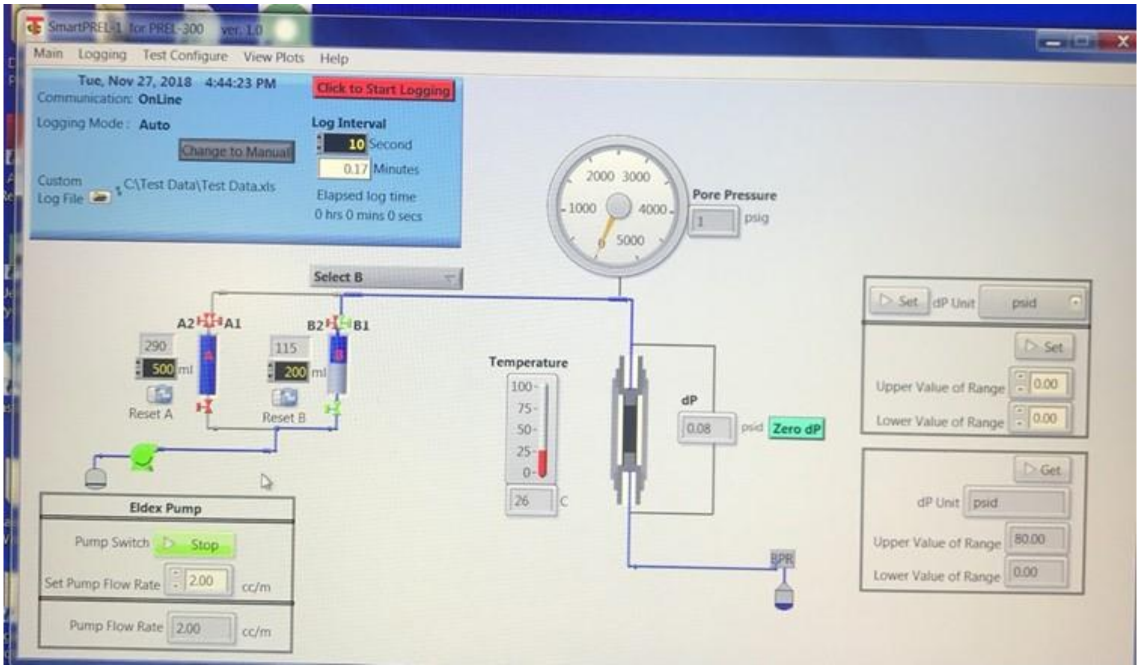


Figure 3.13: Permeability Measurement Rig

Procedure

The accumulators (C and D) were filled with the desired brine and the core sample was loaded into the Hassler core holder (E). Prior to loading the core sample into the core holder, it was slipped into a viton sleeve to avoid the overburden hydraulic oil contaminating the core samples and the injected fluids. The Eldex pump (B) was then set to the desired injection rate, and the fluid flowed into the core sample. dP fluctuations were then monitored using the SmartFlood software (shown in Figure 3.14). Effluent was collected in a calibrated test tube, downstream of the equipment setup.



SmartPREL-1 for PREL-300 ver. 1.0

Tue, Nov 27, 2018 4:44:23 PM

Communication: OnLine

Logging Mode : Auto

Custom Log File C\Test Data\Test Data.xls

Log Interval 10 Second 0.17 Minutes

Elapsed log time 0 hrs 0 mins 0 secs

Pore Pressure 1 psig

Temperature 26 C

dP 0.08 psid

dP Unit psid

Upper Value of Range 0.00

Lower Value of Range 0.00

dP Unit psid

Upper Value of Range 80.00

Lower Value of Range 0.00

Eldex Pump

Pump Switch Stop

Set Pump Flow Rate 2.00 cc/m

Pump Flow Rate 2.00 cc/m

Figure 3.14: SmartFlood Software Interface

The experiment was only stopped when the dP fluctuations became stable; a sample is shown in Figure 3.15. It was ensured that substantial volumes of brines were injected to ensure that the core sample was fully saturated to obtain a steady dP reading. The principle of operation is the same as in the UFS 200 core flooding setup used for the low salinity displacement experimentation as explained in the next Section. The Darcy relation was used to evaluate the permeability, k, for all the core samples used in this Study.

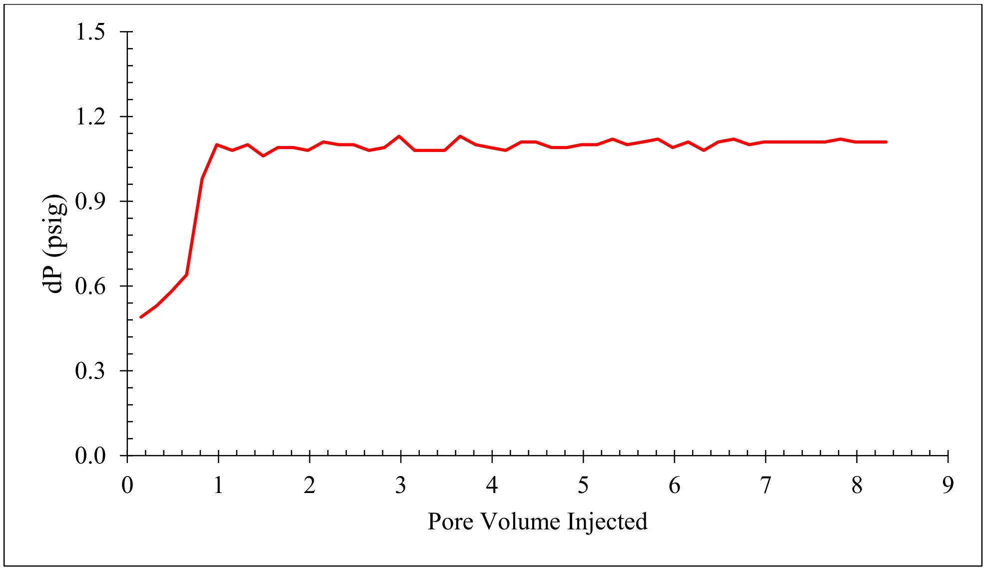


Figure 3.15: Sample of dP Fluctuation During Permeability Measurement

3.5.1.1.11 Interfacial Tension Measurement

A Corelab high-pressure, high-temperature surface interaction energy experimental setup was used in this research. The setup is shown in Figure 3.16 below.

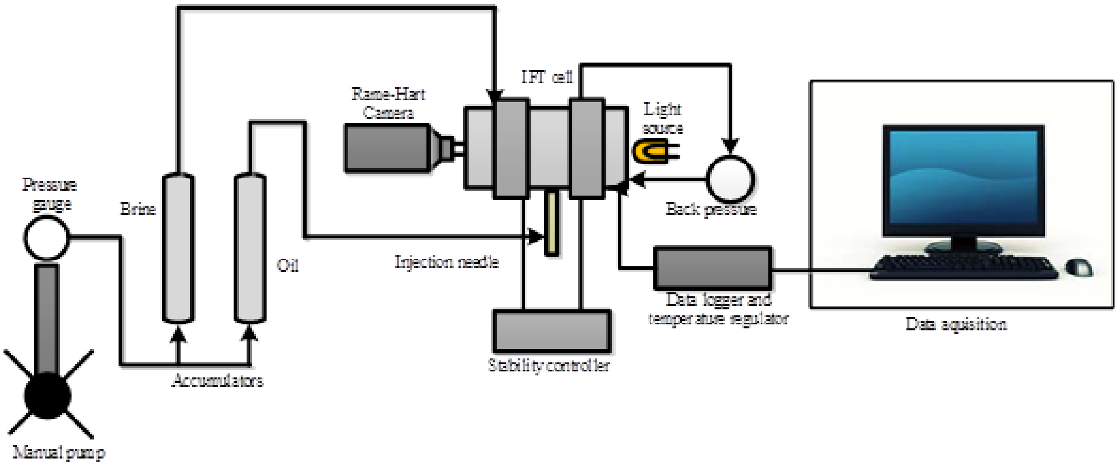


Figure 3.16: Schematics of IFT Measuring Equipment

It is made up of a high-pressure measurement cell with a pressure rating of up to 12,000psig; a Rame-Hart optical video camera system for onscreen real time image display. This is connected to a computer and interfaced with digital image processing software (DropImage software developed by Rame-hart Instruments Co.), which is used for the IFT determination using image analysis of the gas bubble captured by the camera; a high-pressure HiP 62-6-10 manual pump with a pressure rating of 10,000 psig for charging the external phase (brine), and a Temco temperature controller used to set and maintain the temperature of the system within a range of ± 0.3°C of the set temperature. The IFT was measured using DropImage software, which uses a theoretical algorithm to evaluate the IFT based on the bubble profile generated and the dimensions.

3.5.1.1.12 Principle of Operation

The experimental fluid-fluid IFT measurement was carried out using the rising bubble technique. This technique exploits on the buoyancy of the gas bubble with respect to the brine used, in that its ability to rise through the denser fluid is exploited. The IFT measurement was evaluated based on the profile of the gas bubble in the brine created in the IFT cell, which was deduced using the Young-Laplace equations:

$$\gamma = \frac{\Delta\rho g d_e^2}{H} \tag{4.4}$$

where:

$$\frac{1}{H} = f\left(\frac{d_s}{d_e}\right) \tag{4.5}$$

$\Delta\rho$ is the density difference between the two fluids, γ is the interfacial tension, g is the acceleration due to gravity, de is the equatorial diameter of the drop, ds is the diameter of the bubble at de from the apex, H is the bond number, which is a function of the ratio of ds/de. The densities of the phases were evaluated using PVTsim V20 at the test conditions of 1600psig and 40°C. The IFT was first measured when the external phase (different brines) stabilised with the drop phase (crude oil) to observe the development and collapse of the bubble generated.

Procedure

Before each measurement, precautionary steps were taken to sanitise and sterilise the system to ensure good and reliable experimental results. The accumulators, the IFT cell, the injection needle and the delivery tubing were soaked in acetone for 2 hours; this step was repeated for all new samples being investigated. These components were coupled back together and then evacuated using a vacuum pump. Hot distilled water was then placed inside the accumulators and was injected into the IFT cell to flush the whole system. Dry compressed air was then used to dry the entire system. Next, the external phases (brines/distilled water) were charged into the cell using the manual pump and until the desired pressure was attained. The temperature was set using a CoreLab temperature controller. After the pressures and temperatures stabilised, the oil was introduced into the drop phase accumulator. Then the manual pump was used to pressurise the oil to the desired test pressures. Creating the bubble inside the IFT cell was done by gently opening the injection needle valve and monitoring the development of the oil bubble. The bubble development and collapse were recorded.

This bubble measurement was repeated for five bubbles in each experiment using the DropImage software for repeatability and acquired data reliability, and the IFT measurement was made repeatedly on each bubble image obtained.

3.5.1.1.13 IFT Measurement Process

The IFT between oil and the different brines concentration and types was measured using a CoreLab IFT measurement cell at different conditions, which will be discussed in the next Chapter. This will be used to determine the role of IFT reduction as a mechanism of oil displacement and the elucidation of the variation of the results obtained from the core flooding. The setup is shown in Figure 3.17.

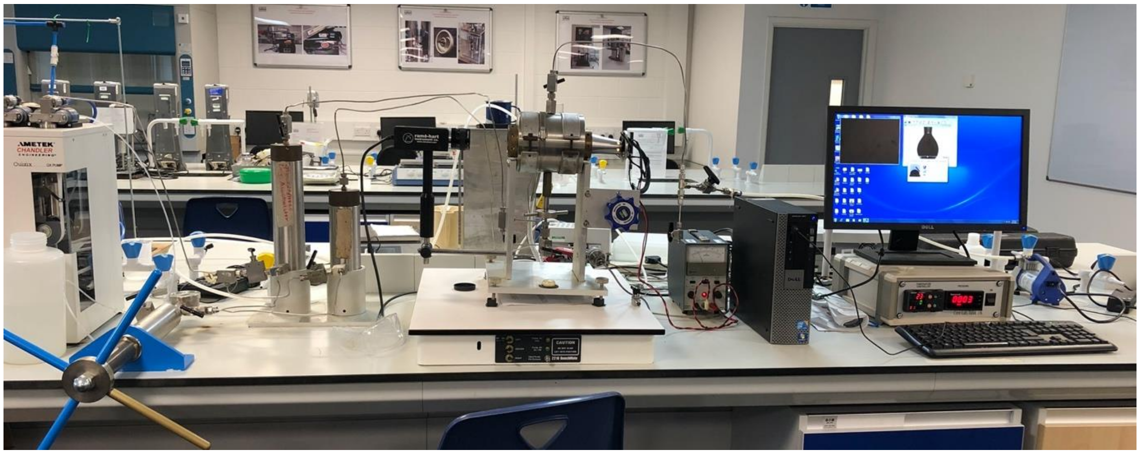


Figure 3.17: CoreLab IFT Measurement Setup

3.5.2 Data Analysis and processing

Microsoft Excel 2019 was used to evaluate and visualise the data obtained from all the experiments. SmartFlood software was used to control and input the parameters in the core flooding process, which is integrated into the UFS 200 core flooding software. On-the-fly recordings of the injection rate, time, dP fluctuations, pore pressure, pump pressures and overburden pressures were made by the software in an Microsoft Excel spreadsheet. DropImage software was used to measure the IFT between the fluids and the data was presented in an HTML format, which was converted into text form and finally imported into Microsoft Excel for data processing. To analytically measure the viscosity of the oil at the desired condition, PVTsim software was used and the data was exported into Microsoft Excel for visualisation and reproduction.

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Chapter 4: Results and Discussion

4.1 Overview

This Chapter highlights the results obtained from the characterisation of the core samples and the core flooding experiment carried out in the prevailing Chapter. These results will be discussed in a sequence depicting the precedence of the experiments according to the phases. The first experiment carried out was the core sample cleaning and characterisation and, as such, the results obtained will be analysed first, and will be followed by the core flooding experimentation.

4.2 Phase I: Characterisation of Core Samples

From the characterisation of the core samples using the aforementioned mineralogicals depicted in Chapter 3, a series of results were obtained and will be shown next.

4.2.1 Scanning Electron Microscopy (SEM)

The result of the SEM analyses, shown in Figure 4.1, is an indication that the core sample was small-grained and had aggregates cementing the grains. This could potentially pose a problem of sand production during enhanced recovery techniques, therefore, measures were taken to augment this potential problem of sand production for a hassle-free oil recovery process.

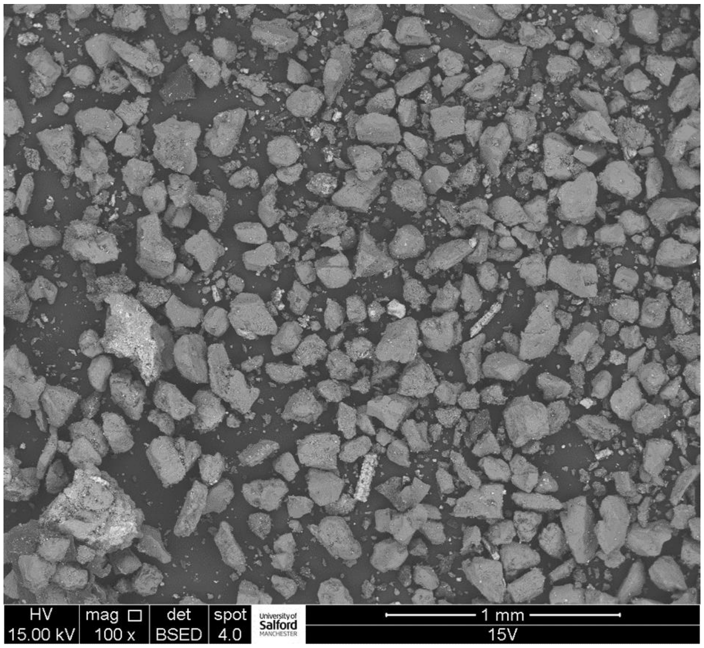


Figure 4.1: SEM Images of the Core Sample

4.2.2 Energy Dispersive X-Ray

As shown, the core sample comprises of the elements shown in Table 4.1, which will help in identifying the type of compounds that are present in the sample using the XRD.

Table 4.1: EDX Results with Elements Present in the Sample

No.	Element	Name	No.	Element	Name
1	C	Carbon	7	Al	Aluminium
2	O	Oxygen	8	S	Sulphur
3	Fe	Iron	9	Cl	Chlorine
4	Si	Silica	10	K	Potassium
5	Ti	Titanium	11	Na	Sodium
6	Mg	Magnesium	12	Mn	Manganese

Figures 4.2 to 4.6 show the elemental composition of the core sample from different angles.

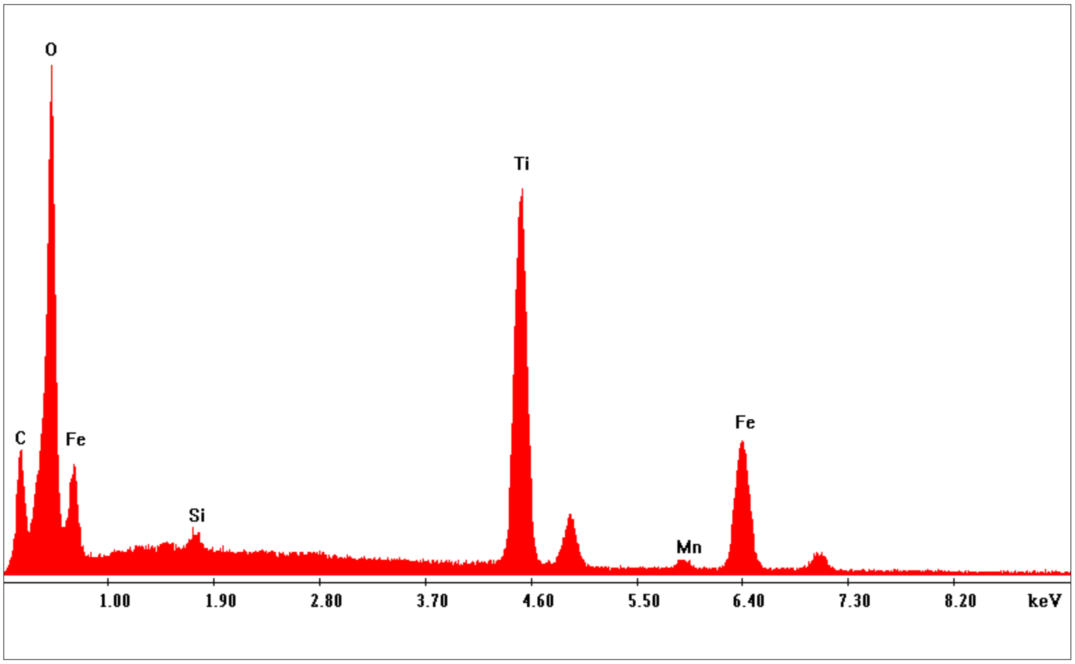


Figure 4. 2: EDX Spectrum – Slice Phase (0°)

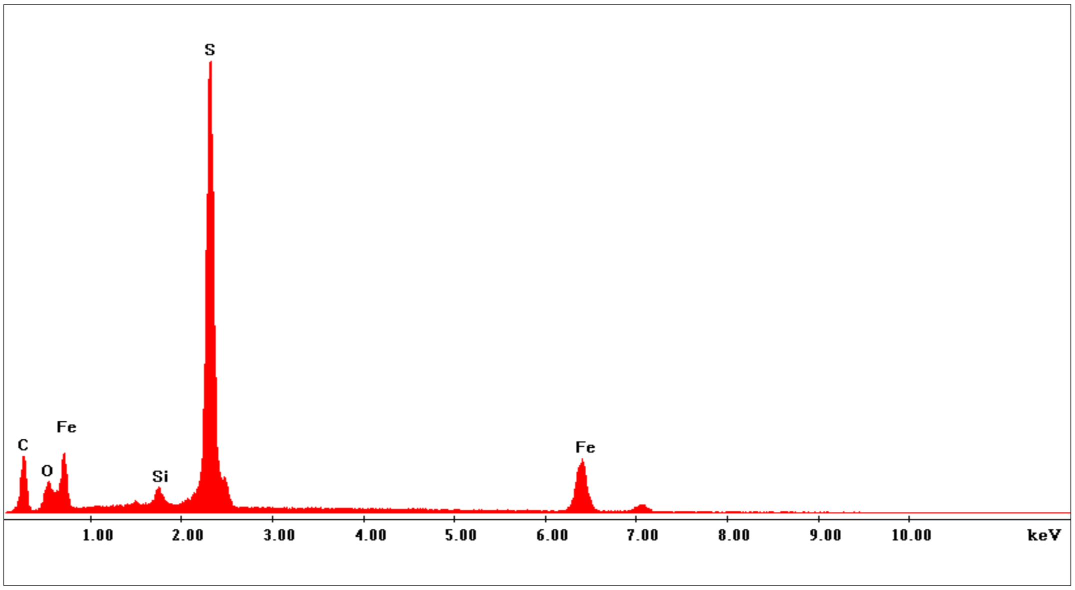


Figure 4.3: Figure 4.4: EDX Spectrum – Slice Phase (90°)

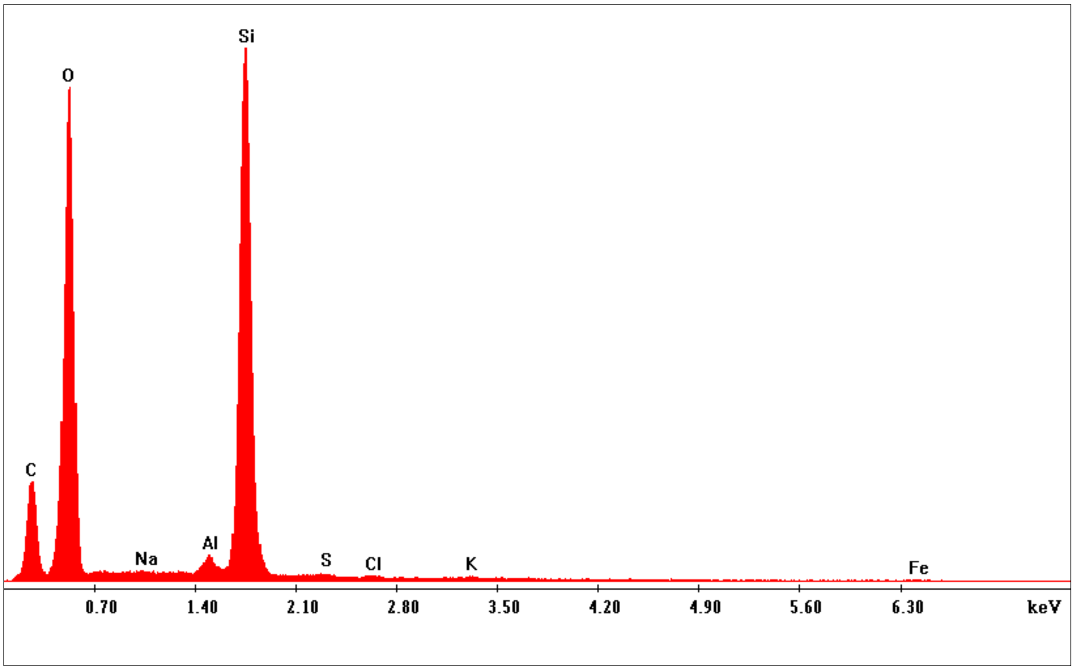


Figure 4.4: Figure 4.6: EDX Spectrum – Slice Phase (180°)

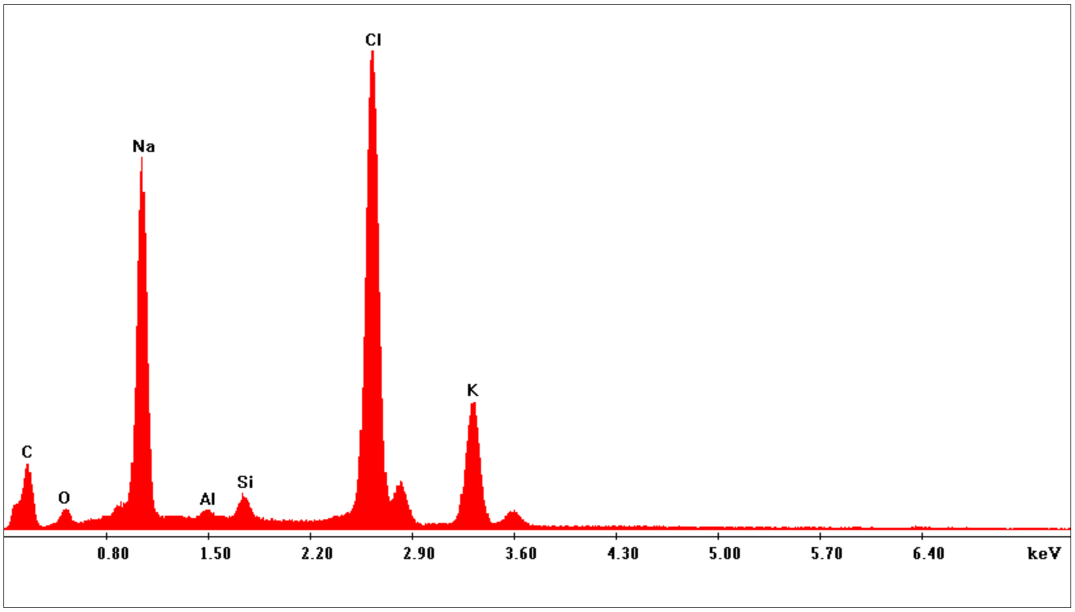


Figure 4.5: EDX Spectrum – Slice Phase (270°)

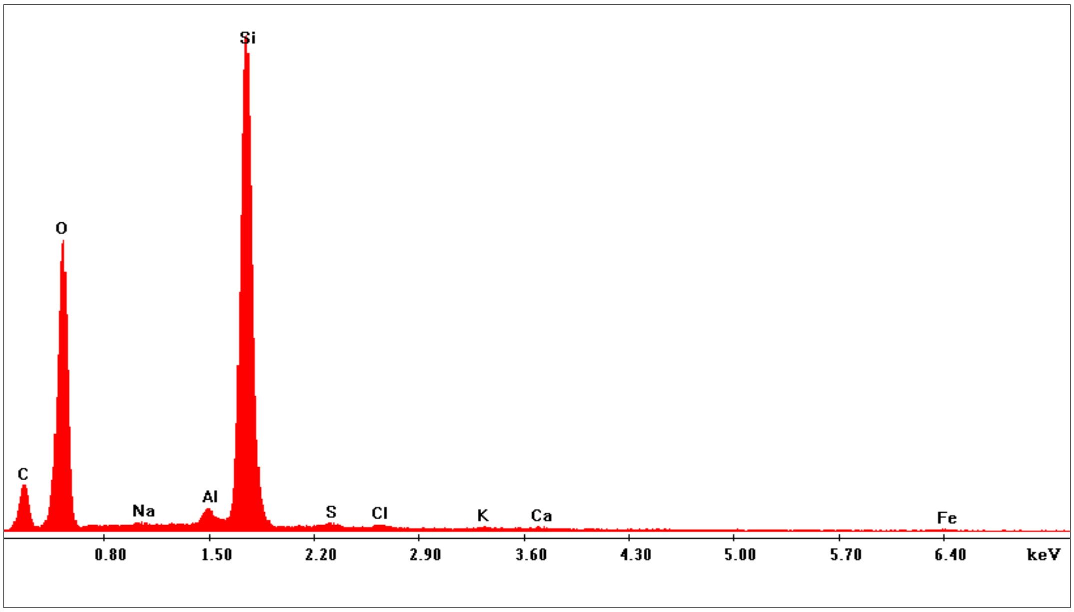


Figure 4.6: EDX Spectrum – Slice Phase (360°)

Figures 4.2 to 4.6 show the spectra from the back-scatter diffraction technique and presented the elemental composition of the core sample probed from different angles. The combination of these spectra provided the overall composition of the rock mineral.

4.2.3 X-Ray Diffraction

From the results obtained from the EDX elemental analyses, a good indication of suspected compounds was acquired, and identification of the matched compounds was made. There are trace amounts of Kaolinite clay in the sample, which is the compound of interest in this work, shown in the raw spectrum - Figure 4.7.

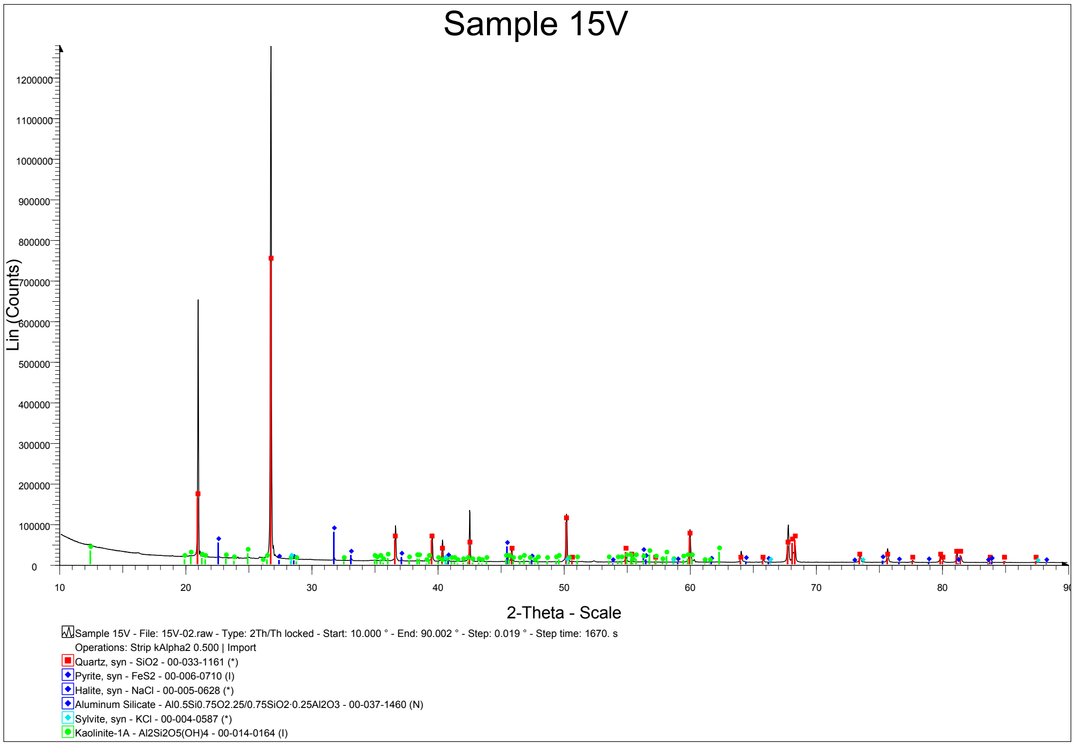


Figure 4.7: Results from XRD Analysis

This is a quartz-based rock sample with traces of other compounds therein. The composition of the core samples is shown in Table 4.2.

Table 4.2: Components of Clay Analysed by XRD

Compound	Chemical Formula	Content (%) ± 0.4
Quartz	SiO_2	88.8
Pyrite	FeS_2	4.2
Halite	NaCl	0.1
Sylvite	KCl	0.1
Aluminium Silicate	$Al_{0.5}Si_{0.75}O_{2.25}$	1.2
Kaolinite	$Al_2SiO_5(OH)_4$	5.6

From the results of the characterisation, Kaolinite was shown to be present in the core samples, and it was vital to the development of the low salinity injection brine to identify the dominant displacement mechanism. Kaolinite is also a non-swelling clay that does not impair permeability.

4.2.4 Porosity

The weights of the dry core samples before the saturation were measured. As explained in Chapter 3, they were then saturated under vacuum with distilled water and their weights were measured after every 30 minutes until there was no change in the weights. This indicated that the core samples were fully saturated. The wet core samples were weighed after saturation, and the results were obtained and recorded as shown in Table 4.3.

Table 4.3: Specification of Core Sample

No.	Sample Name	Sample Depth (ft)	Wet Weight (g)
1	15	4135	137.9
2	15V	4148	129.1
3	50	4161	150.1
4	63	4202	133.1

The bulk volumes of the core samples were evaluated analytically by measuring individual dimensions of the core samples as shown below in Table 4.4.

Table 4.4: Dimensions of Core Samples

No.	Sample Name	Length (cm)	Diameter (cm)	Bulk Volume (cm^3)
1	15	4.87	3.81	55.32
2	15V	4.81	3.81	55.19
3	50	5.98	3.81	66.99
4	63	4.86	3.81	55.40

Obtaining these quantities enabled the quantification and evaluation of the pore volumes of each core sample through simple deductions as follows:

$$\text{Pore volume (PV)} = \frac{\text{Wet weight of sample} - \text{Dry weight of sample}}{\text{Density of distilled water}} \tag{4.1}$$

The density of distilled water is 0.9982g/cm^3. Table 5 5 presents the evaluation of the individual pore volumes of the core samples.

Table 4.5: Pore Volume Measurement

No.	Sample Name	Wet Weight (g)	Dry Weight (g)	ΔW (g)	Pore Volumes (cm^3)
1	15	137.90	121.51	16.39	16.39
2	15V	129.10	115.40	13.70	13.70
3	50	150.10	134.49	15.61	15.61
4	63	133.10	121.89	11.21	11.21

Furthermore, the porosity of each sample can be evaluated using the pore volumes as shown below and as presented in Table 5.6.

$$\text{Porosity} = \frac{\text{Pore Volume}}{\text{Bulk Volume}} \tag{4.2}$$

Table 4.6: Porosity Measurement

No.	Sample Name	Initial Pore Volumes (cm^3)	Final pore volume	Bulk Volumes (cm^3)	Initial Porosity (%)	Final porosity	%Change in porosity
1	15	16.39	15.98	55.52	29.5	28.78	-2.44
2	15V	13.70	13.01	55.19	24.9	23.57	-5.34
3	50	15.61	15.11	66.99	23.3	22.55	-3.21
4	63	11.21	10.98	55.40	20.2	19.82	-1.88

The next step is the description of the core flooding experiment, which is central to this research and which is employed throughout the entirety of this investigation.

4.2.5 Permeability

Using the setup as detailed in Chapter 3, the absolute permeability to liquid was computed based on Darcy's law. The core samples were flooded with 9 pore volumes of water to ensure full saturation in order to obtain steady dP during the process. The dP vs pore volumes injected are shown in Figure 4.8.

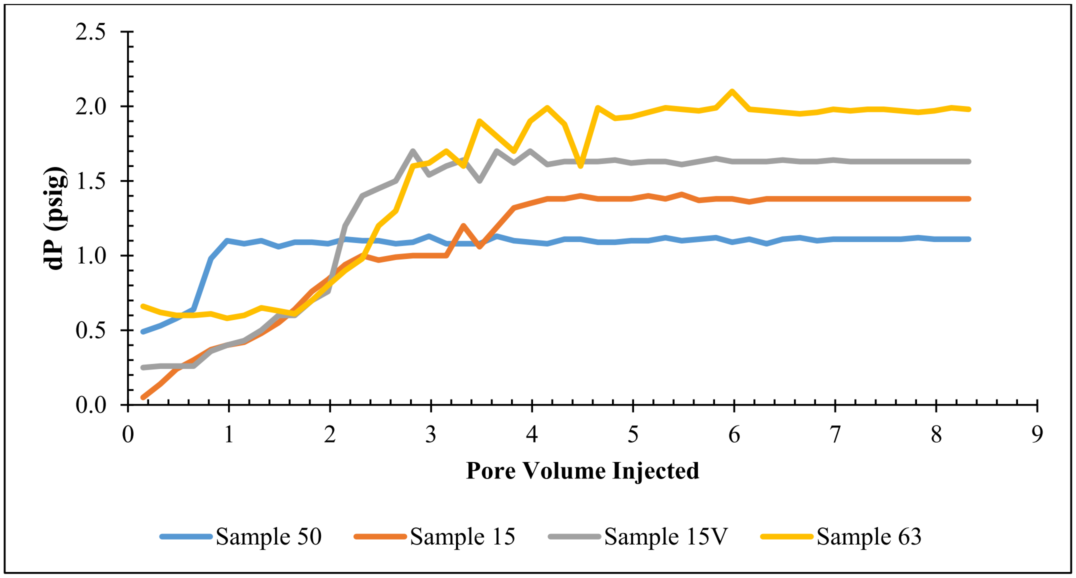


Figure 4.8: Permeability Determination from dP Fluctuations

The permeability values were evaluated using Darcy's Law and are presented in Table 4.6.

Table 4.7: Results of Absolute Permeability

No.	Sample Name	Depth (ft)	Liquid Permeability (md)
1	15	4135	131.3
2	15V	4148	112.5
3	50	4161	189.7
4	63	4201	92.32

4.3 Phase II: Drainage and Imbibition Process

The petrophysical determination is a prerequisite for the core flooding process as the reservoir properties are needed to evaluate the performance of the displacement process. Optimum flow properties had to be established to provide a baseline on which the subsequent parametric sensitivity analysis lies. The first was to determine the optimum injection rate, which was thus used to determine the optimum low salinity concentration.

4.3.1 Determination of Optimum Flow Rate

The common injection rates found in literature are between 0.2 to 2 ml/min, depending on core sample type and geometry. Given the uniqueness and nature of the core samples employed in this Thesis, it is befitting to determine the best injection rate upon which the aim of this Thesis is achieved. This entailed using the original formation brine to perform a simple imbibition test (depicting secondary technique) on the same core sample. After each test, the sample was cleaned and prepared for the next test for injection rate determination. The analysis was based on the recovery factor. The injection rate with the highest recovery factor was the optimum injection rate for the subsequent experiments. The recovery factor was determined using the following relation:

$$\mathrm{RF} = \frac{\text{Total Volume of Oil Recovered}}{\text{Original Oil in Place (Soi)}} \tag{4.3}$$

Each experiment was performed in stages:

- ***<u>Stage-1:</u>*** external vacuum saturation of core sample using high salinity (HS) – 100,000 brine followed by flooding in the flooding setup.
- ***<u>Stage-2:</u>*** Drainage process with crude oil to establish Soi and Swi and followed by ageing.
- ***<u>Stage-3:</u>*** Using HS for imbibition process and oil recovery at specific injection rates.

Due to the core samples measuring only about 5cms in length, the injection rates tested were 0.25, 0.50, 0.75 and 1.00ml/min. Conditions employed remained at 1600psig and 40°C to mimic the reservoir conditions. The result from the core flooding experiments is shown in Table 4.8.

Table 4.8: Optimum Injection Rate and Recovery Factors

Test No.	Injection Rate (ml/min)	S_{wi}	S_{oi}	RF
1	0.25	0.28	0.72	0.42
2	0.50	0.25	0.75	0.58
3	0.75	0.29	0.71	0.31
4	1.00	0.27	0.73	0.27

Interestingly, Figure 5.9 presents the results obtained from the core flooding experiments and the trend observed conforms to the various postulates in literature. As can be seen, as the injection rate increased, the water breakthrough time decreased. This can be attributed to the residence time of the injection fluid within the core sample where higher injection rate lowers the time it takes to traverse longitudinally through the core sample. Consequently, the lower the injection rate, the longer the residence time and the longer the drawdown, as presented in the Figure. The 0.25 ml/min test had the longest drawdown as it took substantially longer to reach the high water cut, which marks the end of the displacement test. This was followed by the 0.5 ml/min run. The lowest time for the high water cut was realised in the 1 ml/min run.

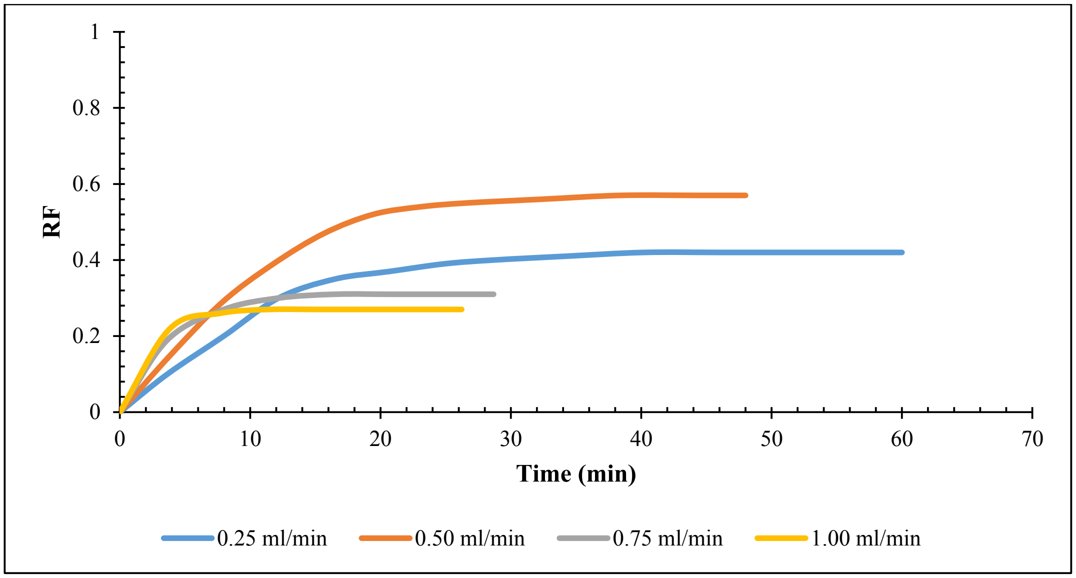


Figure 4.9: Recovery Factors vs. Time at Different Injection Rates

Incidentally, Figure 4.10 shows the ultimate recovery from all of the tests carried out to evaluate the optimum injection rate for the experiments. It is clear that a test that showcased the highest recovery factor was chosen as the optimum injection rate for the subsequent tests. The 0.50ml/min injection rate showed promising results for this specific setup and core samples. The least RF was realised with the highest injection rate owing to poor volumetric sweep and, as stated earlier, gave a shorter residence time. Usually, a short residence time is analogous to poor recovery as there is no room for the fluids to interact with one another; it also affects any significant displacement mechanism.

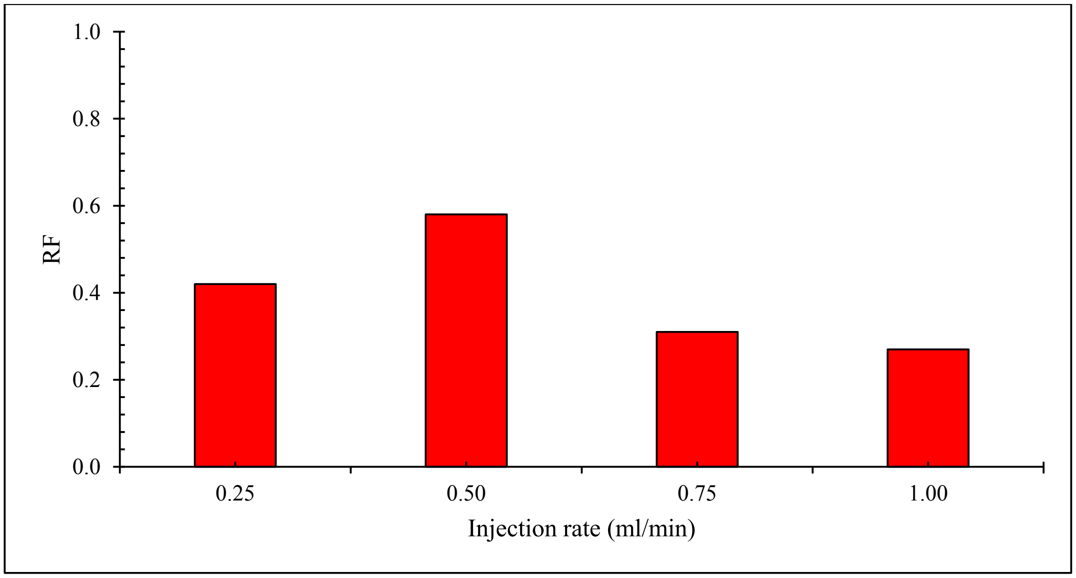


Figure 4.10: Recovery Factors for Different Injection Rates

4.3.2 Optimum Concentration of Low Salinity Brines

Using serial dilutions, different low salinity brines were prepared in the concentrations of 1000, 5000, 10000 and 15000ppm. With the optimum injection rate of 0.5ml/min obtained in the previous Section, imbibition tests were carried out using the prepared brine concentrations to evaluate the optimum concentration. This was also based on the best recovery factor from the predefined low salinity brine ranges. Similarly, the same core sample was used. It was cleaned and prepared prior to each test. For the ageing, it was saturated, and a drainage experiment was performed to establish S_{wi} and S_{oi}. It was then placed in crude oil and pressurised in an ageing cell with N2. The assembly was then placed in an oven at a temperature of 80°C, as in the works of [141], to expedite ageing and restoration of the core sample's original wettability. The results from the imbibition tests are shown in Figure 4.11.

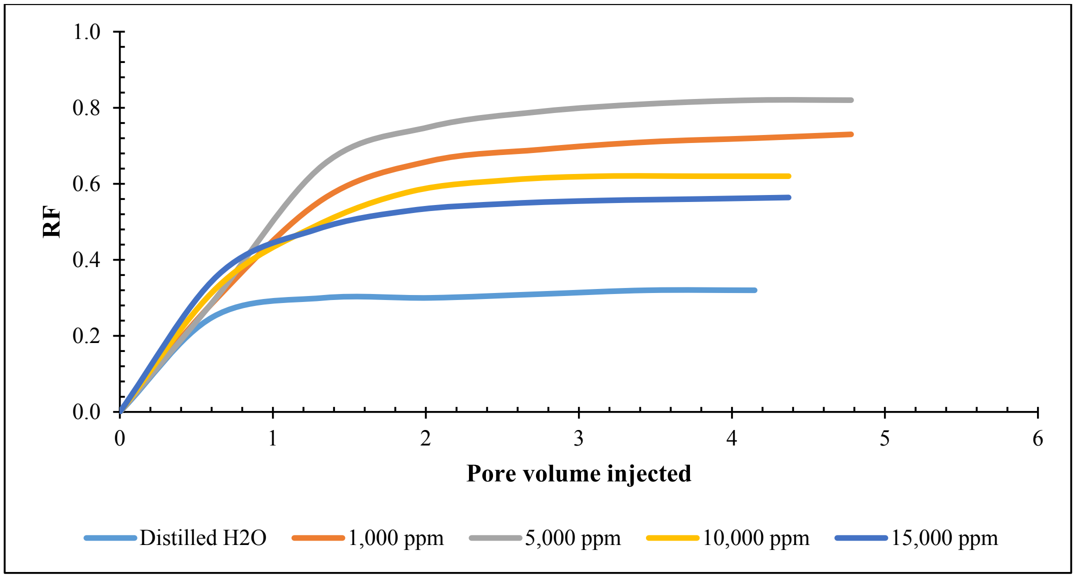


Figure 4.11: Recovery Factors vs. Pore Volume Injected for Optimum Salinity Determination

These results further reiterate the practicality of low salinity flooding in improving oil recovery. This salinity agrees with several works in literature [96] as displacing water is considered low salinity at concentrations of less than 5,000ppm [142], albeit there was some settling with lower concentrations of 2,000ppm [111]. Distilled water performed the worst in all the tests showcasing poor oil recovery attributed to poor volumetric sweep efficiency. The 15,000ppm test also performed lower than the 10,000ppm brine scenario. The ultimate recovery of the results obtained is shown in Figure 4.12 to better present the performance of each brine concentration scenario.

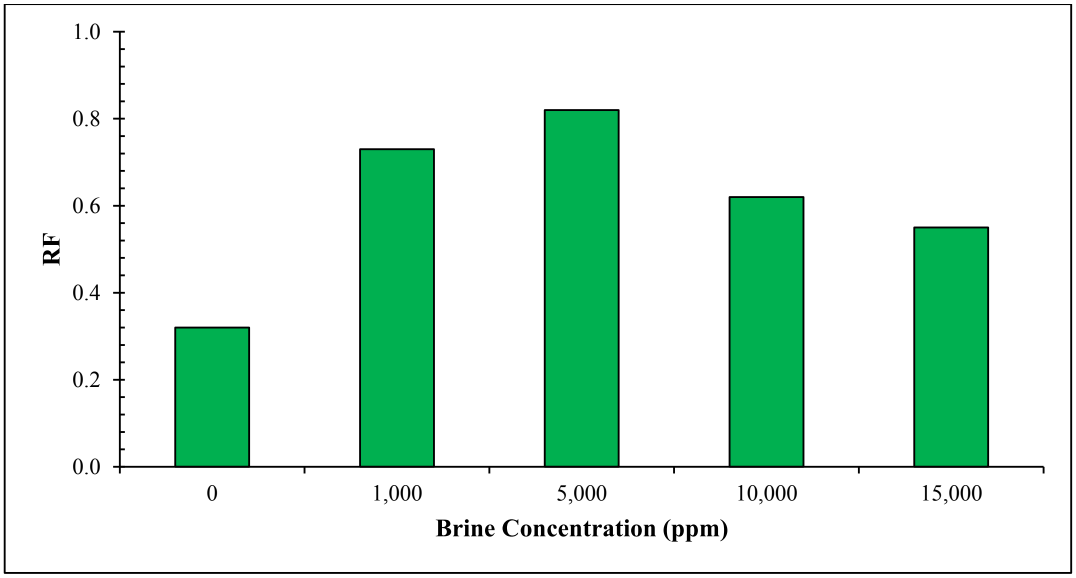


Figure 4.12: Recovery Factor for all Brine Concentrations

Appreciable improved oil recovery was depicted by the 1,000ppm brine, but was not enough to surpass the 5,000ppm test. As can be seen, the presence of salt in the displacement brine thus has the tendency to offset the balance within the pore matrix trapping the oil, typically depicted in the recovery factors of distilled water and the rest of the scenarios with different salinities. Several factors may have been responsible for the improved oil recovery in all cases. Thus, the investigation into the individual effects of different brine components were investigated next.

4.4 Phase III: Parametric Sensitivity Analysis

The parametric sensitivity analysis was carried out through the imbibition process using the core flooding technique. Conversely, the injection rate that was adopted in this Thesis was 0.50 ml/min and the optimum low salinity concentration was 5,000ppm.

4.4.1 Effect of Sulphate and Chloride Ions on Improved Oil Recovery

Given that the optimum flow conditions for the core flooding experiments have been determined, the salt formulation with respect to anion type was thus prepared. High salinity brines (both chloride and sulphates) were prepared in concentrations of 100,000ppm. This served as the formation brine. Then the same formulations were used to prepare the low salinity counterpart in 5,000ppm. The composition was formulated based on the dominant salt types in the original formation water. As NaCl is the most abundant salt type in all underground water, the formulation matched the proportions of the salt distribution within the reservoir. This was attempted to evaluate the individual effects of the anion type on improved oil recovery as seen in the previous Section. Salt compositions used in this study are presented in Table 4.9.

Table 4.9: Composition of Brine Formulations

Components		Hi Sal Sulphates	Hi Sal Chlorides	Low Sal Sulphate	Low Sal Chlorides
cations	Na^+	12550	25560	480	980
	Ca^{2+}	7360	13260	440	800
	K^+	2890	5200	290	520
anions	$(SO_4)^{2-}$	77200		3790	
	Cl^-		55980		2700
TDS		100000	100000	5000	5000
Ionic Conc. (M)		2.28	1.92	0.12	0.10
Brine pH (25°C)		6.6	6.8	7.8	7.9

For contrast, high salinity brines (100,000ppm) displacement tests (imbibition) were carried out followed by the low salinity (5,000ppm) counterpart, separately, to evaluate the extent of improved oil recovery.

4.4.1.1 High Salinity Imbibition Tests

The 100,000ppm sulphate and chloride brines were used to saturate the core sample and displace the initial oil (S_{oi}), using the aforementioned conditions, to evaluate the displacement efficiency. Prior to the displacement test, distilled water was used as the displacing fluid after saturating the rock with high salinity brine and oil, and S_{wi} and S_{oi} were established. This, as already stated, serves as a benchmark for other displacement tests. The result is shown in Figure 4.13. The displacement efficiency was characteristically poor owing to the poor sweep efficiency of distilled water as a displacement fluid.

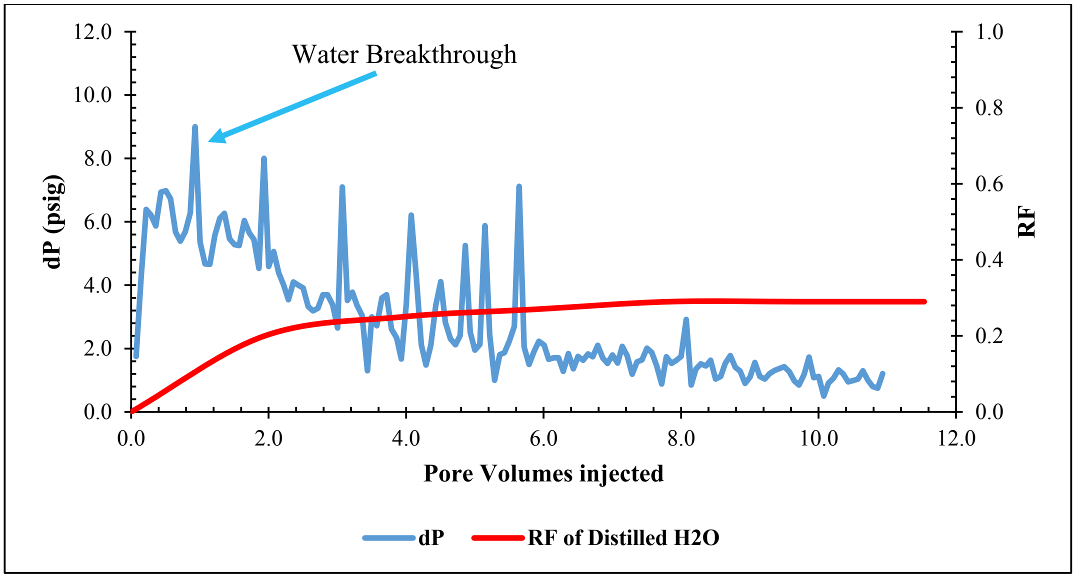


Figure 4.13: Distilled Water dP and Recovery Factors vs Pore Volume

Subsequently, oil was displaced by the high 100,000ppm sulphate and chloride-based brines. Their results are shown in Figure 4.14 and Figure 4.15, respectively. Better recovery efficiency was realised in the high salinity (HS) brines compared to that of the distilled water. This is further evidence that the presence of ions in the displacement fluid tends to upset the equilibrium established by the formation fluids within the pore matrix of the porous medium and, as such, improves oil recovery through different mechanisms. There was obvious substantial bypassing of the oil in the distilled water scenario as seen in the dP fluctuations in Figure 4.13 and the early breakthrough of distilled water during the displacement.

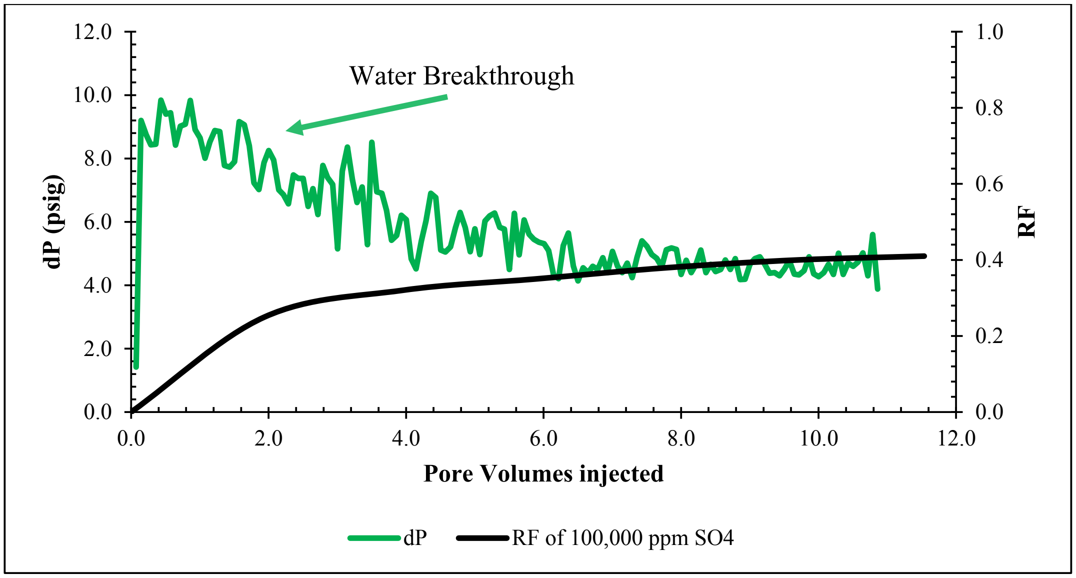


Figure 4.14: Results dP and Recovery Factors vs Pore Volume (of 100,000 ppm SO_4)

The only explanation for this observed trend is the interplay between the ions in the injected fluid and the oil-rock system. Rezaeidoust et al. [126] reported that, when there is a relative concentration of the injected brine of the active ions compared to the formation water, there could be an exchange of ions that could alter the wettability of the rock sample and thus mobilise the trapped oil and improve oil recovery. This, however, was not the case as there was no dilution of the injected brines. The anionic components from the carboxylates of the crude oil adsorb onto the positively-charged rock surface in sandstones reservoirs through cationic bridging. Therefore, the influx of the high salinity displacing brine, with the same concentration as the connate water, do little to upset the equilibrium between the rock-fluid interface.

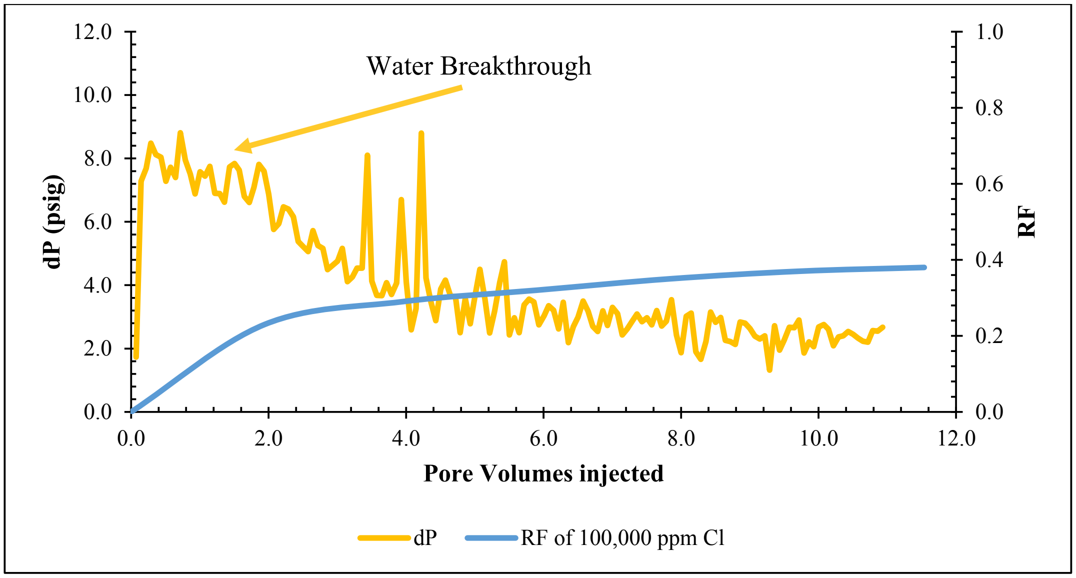


Figure 4.15: Results dP and Recovery Factors vs Pore Volume (of 100,000 ppm Cl)

Furthermore, using the same concentration of 100,000ppm for both Cl and SO_4 brines, better recovery was observed with SO_4 brines compared to the Cl flooding scenario as can be seen in Figure 4.16.

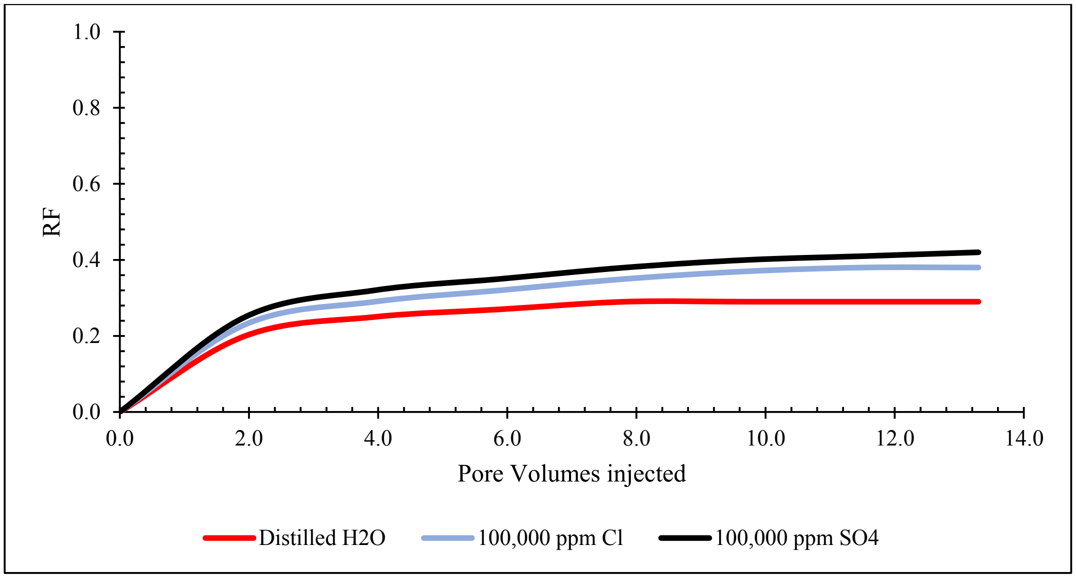


Figure 4.16: Comparison of RF for High Salinity and Distilled Water

This can be attributed to the Ca^{2+} concentration in Swi in both cases (see Table 4.9). Because of the nature of SO_4 ion, a lower amount of Ca^{2+} is needed to balance the aqueous solution, unlike the Cl solution, which require more. It has been established that the higher the concentration of Ca^{2+} in the initial saturation, the more oil-wet the core plugs will be [143]. Thus, the increased concentration of the Ca^{2+} ion in the thin water film between the rock and the oil infers a more positive interface, which decreases the electrostatic repulsion between the rock surface and the anionic components of the crude oil. As such, the Ca^{2+} bridges become stronger than the van der Waals forces in the Cl flooding scenario and, invariably, less oil desorption, which leads to poor recovery compared to the SO_4 scenario. Therefore, the higher the Ca^{2+} concentration in the formation water, the more the adhesion of the carboxylate component of the crude oil to the rock surface, thereby rendering it more hydrophobic. This is one of the reasons why the recovery in high salinity Cl brine displacement was lower than with SO_4 at the same concentration. Additionally, this confirmed the statement by Rezaeidoust et al. [126] that high salinity brines should not show low salinity effects in sandstones.

In Figure 4.14, the displacement efficiency and dP fluctuations during a high salinity SO_4 run are presented. There was improvement in the breakthrough time of the flooding compared to the distilled water and Cl-based scenarios; the flow behaviour showed less dP fluctuations meaning there was, to some degree, a homogeneous movement in the binary system. Admittedly, the interplay between the fluids in the Cl-based displacement showed similar trends as in the distilled water run, characterised by high fluctuations and early breakthrough of water. In Figure 4.17, the dP fluctuations were intense for the Cl run, indicating there was no synergy between the transporting fluids, invariably showing that lower displacement efficiency is expected from such runs.

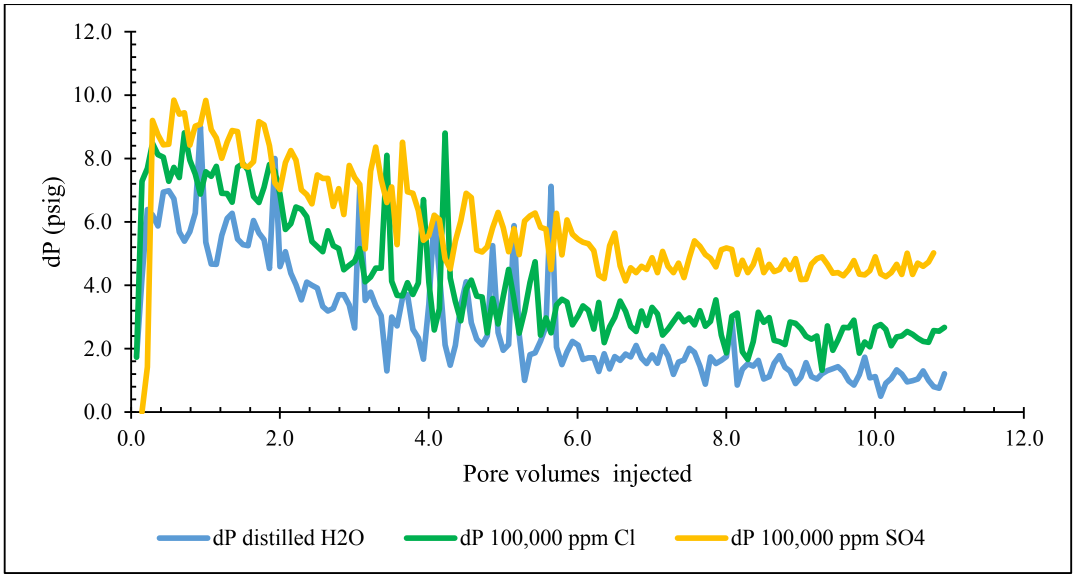


Figure 4.17: dP Fluctuations vs Pv Injected for 100,000ppm of SO_4, Cl and Distilled Water

To evaluate the flow behaviour of the injected brines as they traverse the core sample and displace the oil from the pore spaces, the dP fluctuations were merged and are presented in Figure 4.17. From Darcy's flow point of view, the permeability (which is inversely proportional to dP) of the distilled water to the core sample is highest when compared to the HS brines. This resulted in poor macroscopic sweep efficiency characterised by poor recovery efficiency, as discussed earlier. The fluctuations in distilled water and HS Cl scenarios were most pronounced when compared to the HS SO_4 scenario. The lowest fluid permeability to the core sample was exhibited by the HS SO_4, which elaborated the restrictive flow of the fluid through the core sample. This was, however, accompanied by the better recovery of oil, meaning that there was an interaction between the injected brine and the in situ fluid, which led to increasing the mobility of the oil and, thence, improved recovery. This was characterised by the resistance to flow, which created a gradient between the brines and the oil within the pore matrix. Apart from the earlier explanation of the ions in the fluids being responsible for the desorption in the HS cases, another possible explanation is the reduction in IFT between the oil and the injected HS brines. This will be discussed in the ensuing Sections.

4.4.1.2 Low Salinity Imbibition Tests

Consistently, when the displacement brines concentrations were switched to 5,000ppm, with initial oil water saturation (S_{wi}) at 100,000ppm (to fulfil one of the conditions of the low salinity effect – presence of connate water according to Rezaeidoust et al. [126]), a different and interesting trend was observed. Figure 4.18 shows the comparison between 5,000ppm brines. There was a substantial improvement in oil recovery compared to the 100,000ppm runs, with SO_4 brines exhibiting better recovery than with Cl brine at 5,000ppm, just as with the 100,000ppm counterpart. Water breakthrough was almost the same for both Cl and SO_4 scenarios at the 3 pore volumes injected mark. The late breakthrough and characteristically higher dP values depicted better sweep efficiency and, thus, improved oil recovery. Higher fluids and rock interactions were evident, with several low salinity displacement mechanisms being suspected.

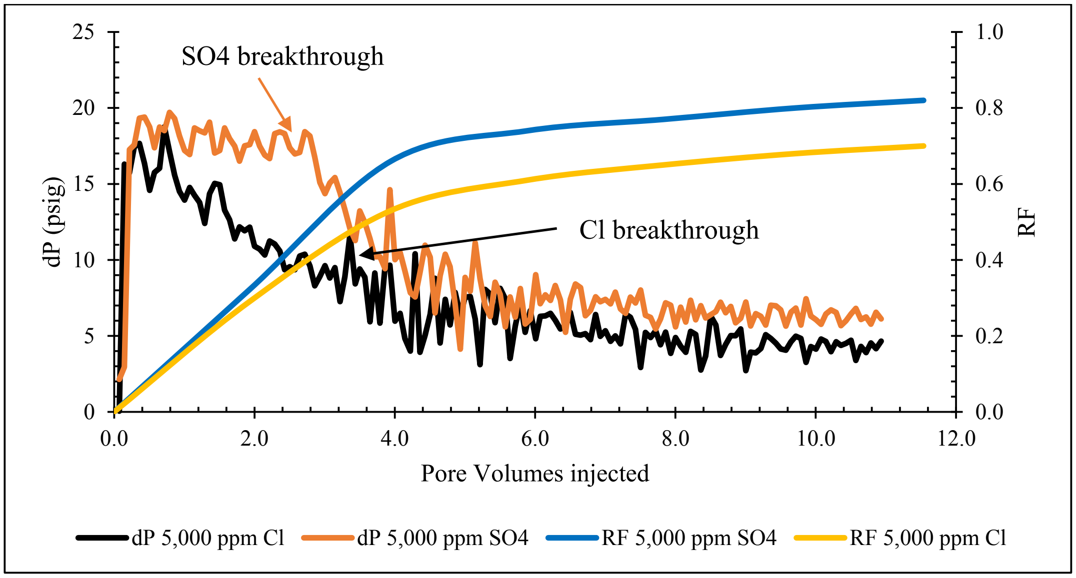


Figure 4.18: Comparison Between RF of 5,000ppm Cl and SO_4 Brines with Breakthroughs

There was a significant improvement in the displacement efficiencies of each LS injection scenario compared to the HS counterpart, also shown in Figure 4.19. Careful measures were taken to satisfy the conditions of low salinity flooding in sandstone reservoirs. As already established, lowering the concentration has the potential to improve oil recovery.

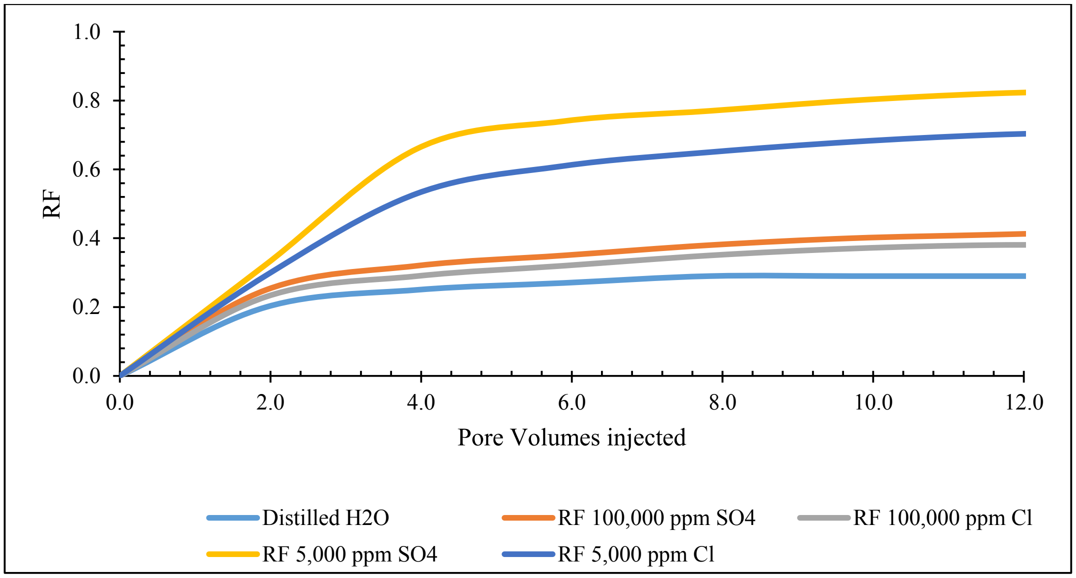


Figure 4.19: Results of all the Imbibition Experiments Performed

To evaluate the production performance of the LS flooding, an instantaneous recovery of low salinity brines is shown in Figure 4.20, which indicates the macroscopic sweep of each brine flooding scenario. The largest initial recovery was realised in the 5,000ppm SO_4 brine and production was sustained longer than in the other flooding scenarios.

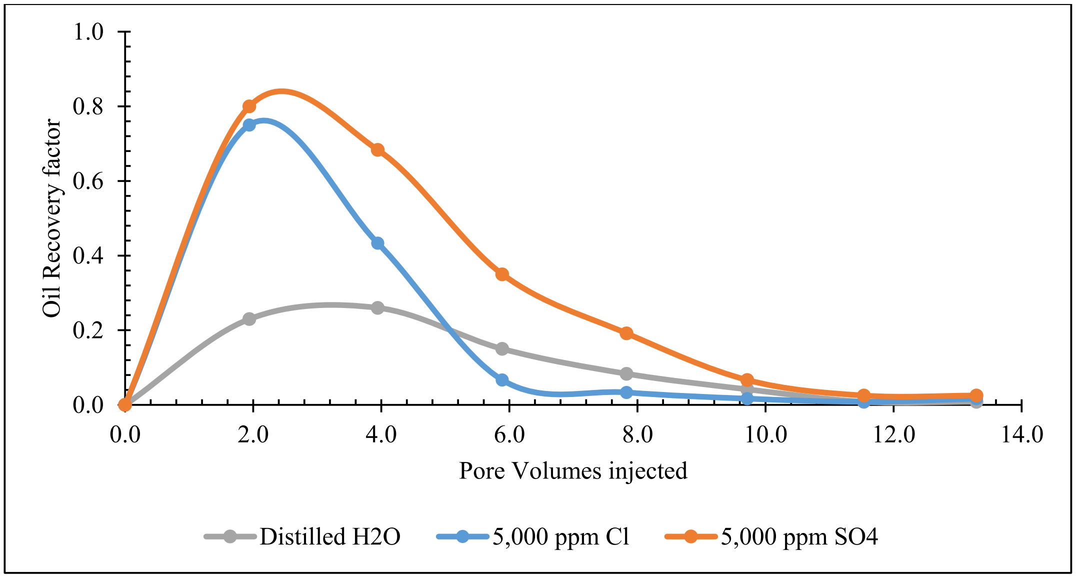


Figure 4.20: Production Performance of 5,000ppm Brines and Distilled Water

The lowest instantaneous recovery was realised after 10 pore volumes of the brine had been injected for the SO_4 scenario, while production peaked at about 3 pore volumes. The worst case scenario was with the distilled water, where production peaked at about 4 pore volumes with about 0.25 recovery efficiency, indicating a poor sweep efficiency. Intermediate recovery was seen in the Cl case with instantaneous production peaking at 2 pore volumes, and where there was no production sustenance as seen in the rapid drop in production after 6 pore volumes of 5,000ppm Cl brine were injected. The intersection between the distilled water and the Cl-based scenario is indicative of the fact that, at that point, the recovery efficiencies of both scenarios were the same. And at no point was there a scenario where production was the same for the SO_4 flooding case and any other brine.

4.4.2 Displacement Mechanism Analysis

Several mechanisms of displacement of oil using LSF can be attributed to this significant oil recovery with low salinity effects, while others can be ruled out. Figure 4.21 shows that there was no increase in dP as the low salinity brine (both Cl and SO_4) displaced the oil in the porous medium, and there were no visible solids upon physical inspection of the effluents. Therefore, fines migration as a displacement mechanism can be disregarded as it is characterised by an increase in dP (indicating lower permeability of the fluids to the porous media) as reported by Tang and Morrow [28], after breakthrough. The increase in the resistance to flow through pore channels indicates that clays and other fines may have been dislodged/relocated and have plugged narrower pore channels within the porous matrix as a result of flooding. This phenomenon was not observed in all the experimental runs carried out in this work.

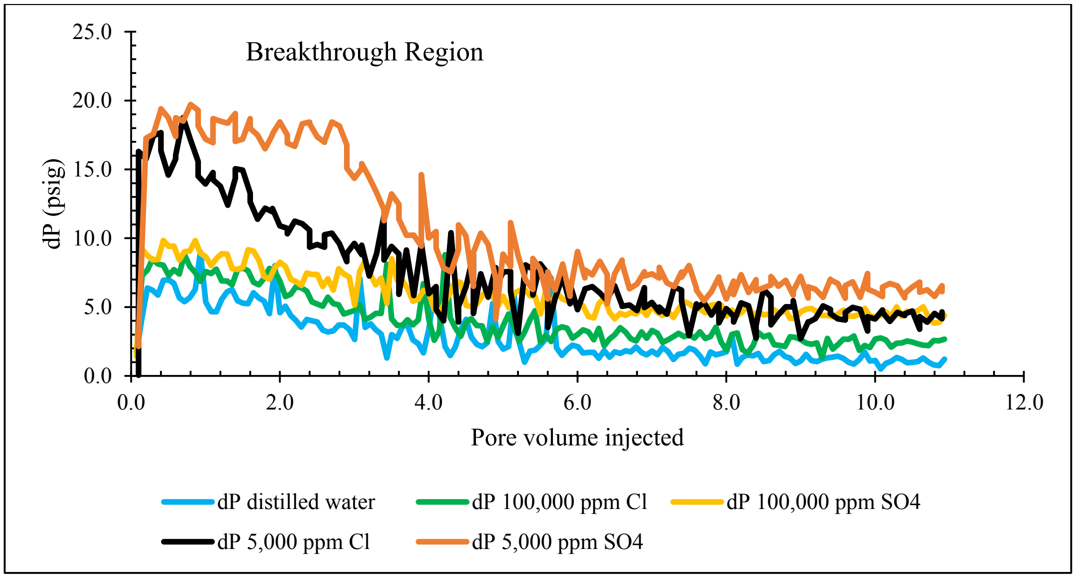


Figure 4.21: dP Fluctuations of all the Imbibition Experiments

4.4.2.1 pH Evaluation

One of the most prominent indicators of the key displacement mechanisms in low salinity flooding was the increase in pH of the effluents after the displacement test. This was brought about by the exchange of ions between the injected fluid and the formation water, which is accompanied by oil desorption from the rock surface, and thereby improved oil yield. The variation of pH of injected brine and the effluent conformed to the postulates made and drawn out in this work. Figure 4.22 shows the pH of the brines before and after flooding. As expected, the high salinity and distilled water runs showed no apparent change in the pH values. This was echoed in the preceding Sections where HS brines were used in the imbibition experiments; SO_4-based HS brine had an edge over the Cl, but without any ionic interaction. Reasons were provided previously where it was stated that there were no interactions between the rock and the injected brines and, thus, there was no expansion in the electric double layer given that the high salinity brines are of the same order of magnitude, in terms of concentration, as the connate/formation water.

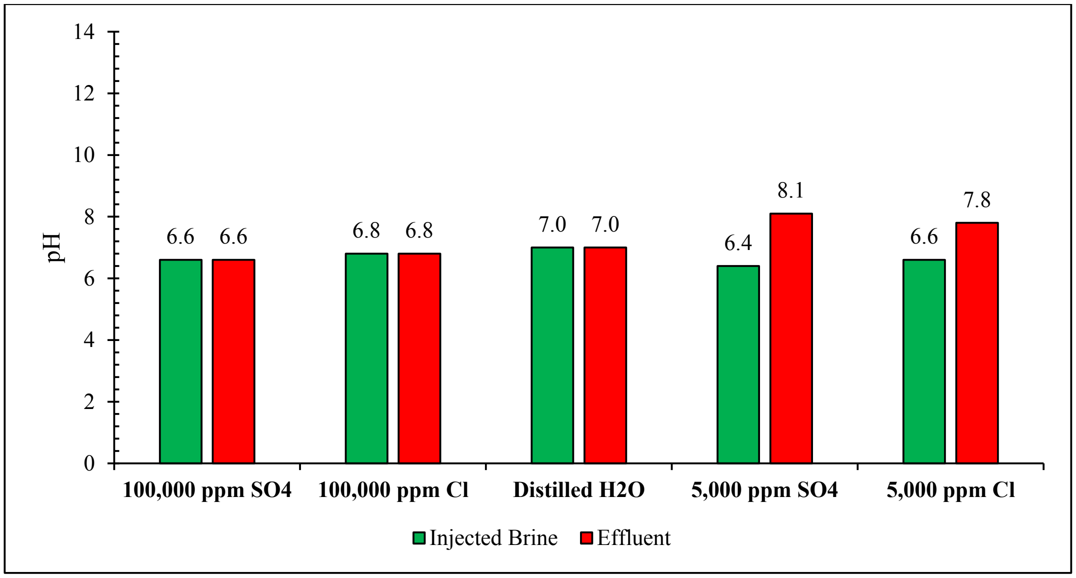


Figure 4.22: pH Changes of all Flooding Scenarios

As for the distilled water, there was poor microscopic sweep in terms of recovery, and poor macroscopic sweep in terms of flow behaviour of the flooding scenario where the distilled water bypassed the oil characterised by the lower dP trend. Distilled water bypassed the oil and exited at the end of the core sample easily compared to the other brine runs with respect to RF. This finding also reiterates the significance of the presence of ions in the displacement brine during any flooding process.

There was an increase in pH of 1.7 and 1.2 units when 5,000ppm SO_4 and 5,000ppm Cl brines were used as displacing fluids, respectively. This increase was as a result of the MIE leading to the desorption of Ca^{2+} and the protonation of the rock surface. The aqueous solution injected into the core plugs dissociated, and the H^+ found its way onto the rock surface and displaced the Ca^{2+} present on the rock surface according to the following equation:

$$\mathrm{Clay} - \mathrm{Ca}^{2+} + \mathrm{H_2O} \leftrightarrow \mathrm{Clay} - \mathrm{H}^{+} + \mathrm{Ca}^{2+} - \mathrm{OH}^{-} \quad (4.4)$$

Because of the abundance of the OH^-, the pH of the effluent increased after the flooding process. This increase in pH was accompanied by the better recovery in the 5,000ppm SO_4 brine compared to Cl, i.e. there was more desorption of Ca^{2+} from the rock surface. This desorption implies that breaching of the cation bridge in the SO_4 flooding was evident.

pH was found to play a vital role in the site density of oil/brine. Pooryousefy et al. [144] observed that the site density of the carbonyl group of the crude oil decreases with an increase in pH. In the presence of aqueous ionic solutions, the variation of the site density of the surface chemical groups alters the interfacial tensions (IFT) between the brine and oil. This is yet another suspected mechanism in this work and for that, the interfacial tension measurement is discussed next.

4.4.2.2 Interfacial Tension (IFT) Reduction

As one of the mechanisms of displacement in LS flooding, it is important to investigate the precedence of the possible IFT reduction between the injected brine and the oil in the core samples in this research and, for that, the measurement of IFT of individual salt types in the composition (Table 3.3) of the tested brines and oil was performed; after which the IFT between oil and the combined salt species was then evaluated. This was carried out to see the effect of each salt type on the IFT of the mixture. Using the setup described in the experimental section, the IFT between the oil and different brines was measured at 40°C and 1,600psig. In order to evaluate the response of IFT between the fluids with respect to concentrations, each salt type was prepared in seven concentrations as shown in the matrix in Table 4.10, until 5,000ppm was found to have the lowest IFT, and was therefore adopted for this investigation.

Table 4.10: Brine Matrix

Salt Type	Concentration (ppm)						
$NaSO_4$	90000	70000	50000	20000	10000	5000	1000
$CaSO_4$	90000	70000	50000	20000	10000	5000	1000
K_2SO_4	90000	70000	50000	20000	10000	5000	1000
NaCl	90000	70000	50000	20000	10000	5000	1000
$CaCl_2$	90000	70000	50000	20000	10000	5000	1000
KCl	90000	70000	50000	20000	10000	5000	1000

The results of the IFT between all the brine types at the predefined concentrations and oil are shown in Figure 4.23. A very interesting fact is that the lowest IFT in all the tests that were carried out was at 5,000ppm concentration. All the brines exhibited the same trend at this concentration and reaffirmed the earlier results in the evaluation of the optimum low salinity concentrations. From the tests carried out, certainly, IFT played a significant role in the improvements of oil recovery. The lowest IFT was exhibited by the $CaSO_4$ brine test at 5,000ppm, with $CaCl_2$ brine having the highest IFT at the same concentration.

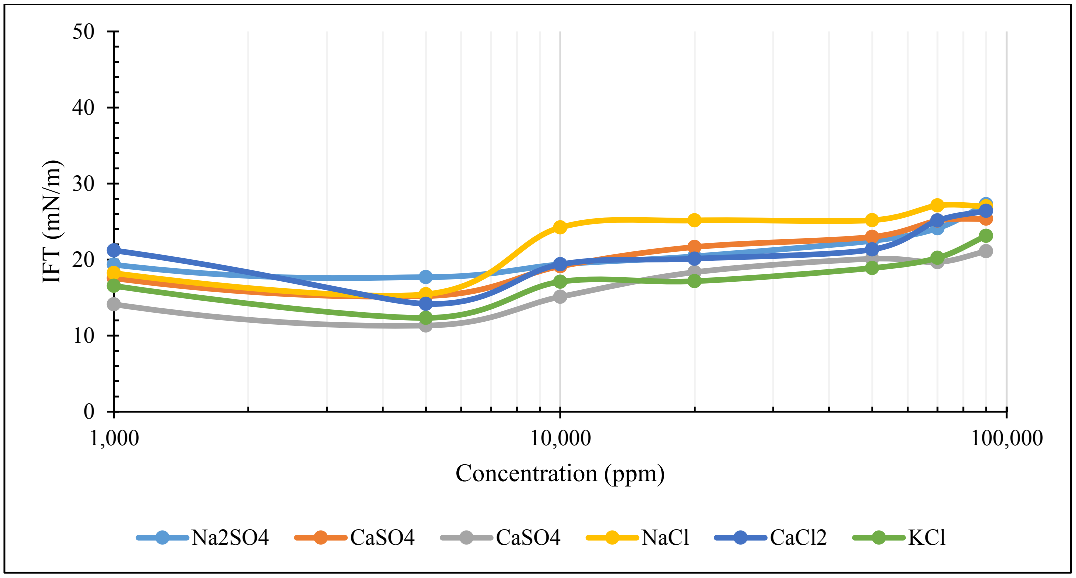


Figure 4.23: IFT Results between Oil and Different Brine Types and Concentration

Additionally, the original formulations of the brines used in the imbibition experiments were tested and a comparison was made between SO_4 and Cl brines in terms of IFT. It is clear from the results that the IFT between the SO_4 brine and oil was lower than its Cl counterpart. Accordingly, these results explain flow behaviour observed during the LS displacement process. The IFT between the brine and oil was lowest in the 5,000ppm SO_4 brine, which yielded the highest recovery in all the runs combined as shown in Figure 4.23. This was followed by the 5,000ppm Cl, with distilled water having the highest IFT, evident with the unstable flow behaviour, early breakthrough and poor recovery efficiency in the displacement process characterised by oil bypass. This variation of IFT between the brines is due to the accumulation of the cations at the crude oil/brine interface, which can be explained by the Gibb's adsorption isotherm as reported by [145]. However, the individual IFT measurement conceded that the SO_4 based brine ($CaSO_4$) had the lowest IFT and the Cl-based counterpart ($CaCl_2$) related to the highest IFT. This, thereby, inferred that the SO_4 ion did play a role in the IFT reduction or, rather, that SO_4-based brines improved the flooding performance of the imbibition process.

Darvish Sarvestani et al. [146] explained that decreasing the concentration of salts in the brine would result in higher stability of the formed emulsion droplets by lowering the rate of coalescence and aggregation, thereby improving the mobility of the oil and water and, hence, improving recovery. This centres around the surface energies of the fluids in contact as can be seen from the results in Figure 4.24.

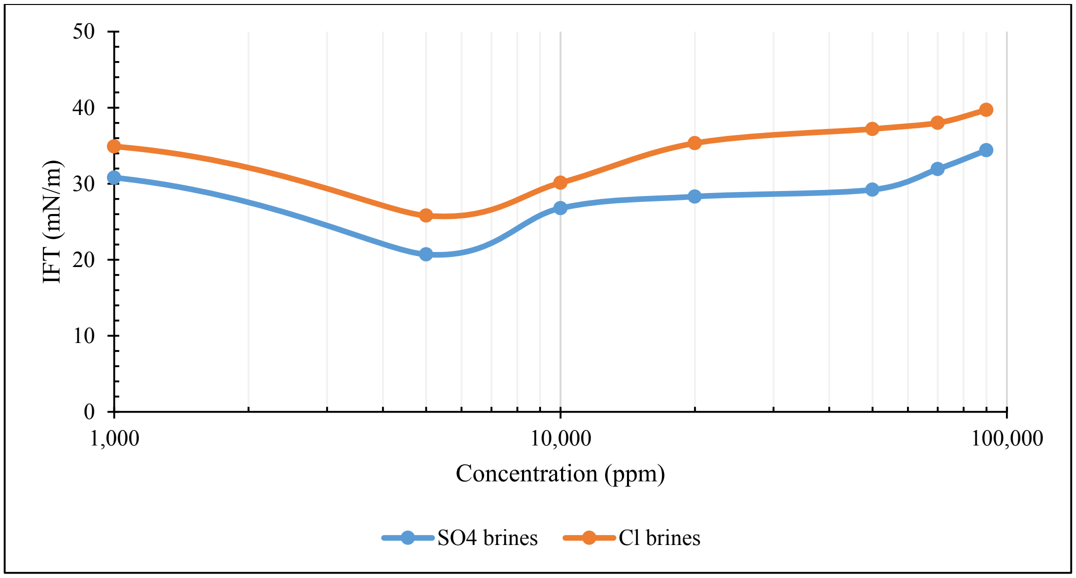


Figure 4.24: IFT between Oil and the Brines at Different Concentrations

These results are consistent with the trends observed in the works of Khaksar Manshad et al. [147] where it was clear that the IFT between the oil and SO_4 brines are significantly lower than those of Cl-based brines at different conditions (pressures, temperatures and concentrations).

One of the reasons that prompted the investigation into IFT reduction resulted from the flow behaviour of the injected brine during the core flooding. The dP fluctuation in all the runs presented a characteristic trend with regards to the stability of the flow. An exemplar of this is shown in Figure 4.21, which showcased a comparison between the flow behaviour of low and high salinity injection scenarios and distilled water. From the Figure, it can be seen that the spiking in the dP plot of the Cl and distilled water scenarios were significantly more intense than the SO_4-based scenarios. This is indicative of the fact that, in the SO_4 runs, the fluids (brine and oil) moved as a single or near homogenous unit compared to the other two flooding runs, with distilled water having the most unstable fluctuations and spiking. The much smoother flow of SO_4 can be explained by either the salting-in effect mechanism [126] or by the emulsification of the oil and brines [146] during the displacement, which were all defined by the IFT between the two fluids. Upon physical inspection of the effluents, the oil in water emulsion showed larger oil droplets in the brine and a distinct layer between their interface in Cl-based brines. This is shown in Figures 4.25 to 4.27.

Figure 4.25: Effluents of Imbibition Experiment using Distilled Water

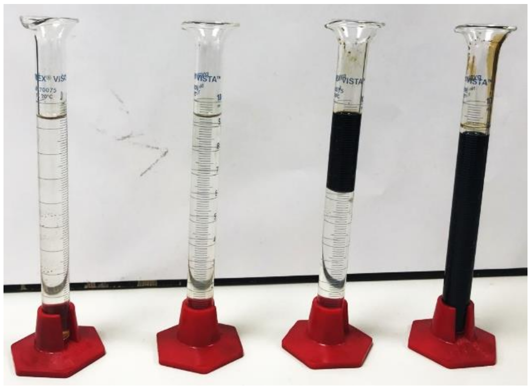


Figure 4.26: Effluents of Imbibition Experiment using 100,000ppm Cl Brine

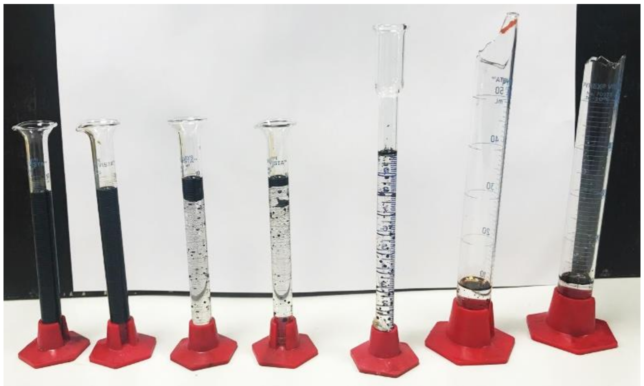


Figure 4.27: Effluents of Imbibition Experiment using 5,000ppm Cl Brine

The effluents from the distilled water run are similar to the Cl-based brines runs (both 100,000ppm and 5,000ppm). The brine was clear, especially in the 100,000ppm scenario and droplets of oil formed in the 5,000ppm Cl run. This infers that minimal interaction occurred between the injected fluids and the in situ oil, and flow characterisation showed intense unsteadiness as the Cl brines displaced the oil. There were no stable emulsions formed during the Cl brines scenarios as the key parameter (IFT) to actualise the homogeneity of the flow conditions was rather meagre.

However, for the SO_4-based brine effluents, there was no distinct layer between the brine and oil and the emulsion showed smaller droplets of oil upon standing. The oil droplets coalesced and became larger droplets. These are shown in Figure 4.28 and Figure 4.29. The realisation is the same for both concentrations of SO_4 (100,000ppm and 5,000ppm). The effluent brine appeared murky, signifying more fluids and rock interaction between the injected brine and the porous system; it is a form of oil in water emulsion that will not pose flow assurance problems during production. The surface interactions between these fluids were responsible for such phenomena.

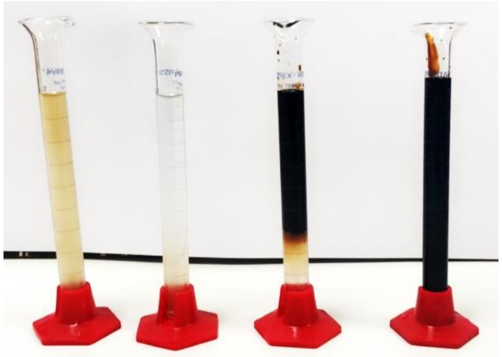


Figure 4.28: Effluents of Imbibition Experiment using 100,000ppm SO_4 Brine

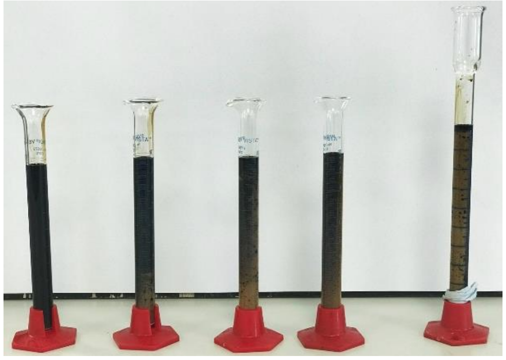


Figure 4.29: Effluents of Imbibition Experiment using 5,000ppm SO_4 Brine

4.4.2.3 Multicomponent Ion Exchange (MIE)

MIE is a mechanism triggered by the expansion of the double layer of the high concentration film between the oil and the rock during LSF [122, 148]. When low salinity water was injected into the reservoir, the double layer tended to expand and opened the diffuse layer, causing electrostatic repulsion between the rock minerals and the oil. Eventually, the repulsive forces exceeded the binding forces formed by the multicomponent cation bridges and the oil desorbed from the rock surface. In a study by Lee et al [122], they highlighted the roles of divalent cations (Mg^{2+} and Ca^{2+}) in the electric double layer expansion during LSF and, from their results, it was clear that SO_4-based brines presented larger thicknesses of water layer when comparing the salts of the monovalent cations at 0.001M concentration.

In the 5,000ppm SO_4 brine scenario, as with the 100,000ppm runs, the recovery efficiencies were higher than for the Cl and distilled water runs, as clearly seen in Figure 4.30 and Figure 4.31, despite the higher ionic strengths of SO_4 in all scenarios (Table 4.9). According to Rezaei Gomari and Joseph [98], when the ionic strength is lowered, it facilitates the improved recovery by altering the wettability of the core rock, both in sandstones and in carbonates, which is contrary to what was observed here. Furthermore, the active cationic count of the low salinity SO_4 was lower than the low salinity Cl. This comes down to the anionic components of the brines, which play vital roles in the improvement of oil recovery. A study by Rezaeidoust et al. [126] postulated that SO_4 can act as a catalyst in a way, and a possible school of thought is that it replaces the carboxyl ion in the cation or ligand bridge with the rock surface at sites where protonation has not occurred.

A proposed mechanism for the role of SO_4 in LSF was demonstrated by Al-Otaibi [149] as follows:

$$> \mathrm{SiOCaCOO} \quad \leftrightarrow \quad \mathrm{SiO^- + Ca^{2+} + COO^-} \tag{4.5}$$

$$> \mathrm{SiO^- + Ca^{2+} + (SO_4)^{2-}} \quad \leftrightarrow \quad \mathrm{SiOCa(SO_4)^-} \tag{4.6}$$

$$> \mathrm{SiOCa(SO_4)^- + H^+} \quad \leftrightarrow \quad \mathrm{SiOCaHSO_4} \tag{4.7}$$

$$> \mathrm{SiO^- + Ca^{2+} + Cl^-} \quad \leftrightarrow \quad \mathrm{SiOCaCl} \tag{4.8}$$

Repulsion of the carboxylate group of the crude oil by the now negative surface of the rock promotes the desorption of the organic material from the rock surface by overcoming the electrostatic van der Waals forces binding the oil to the rock surface. The pH at the rock surface/brine interface is lowered i.e. more acidic ($pH < 7$) where the H+ affinity towards the mineral surface increases as depicted in the works of Chen et. al [150]. This further stimulates the multicomponent ion exchange (MIE) where the surface Ca^{2+} is replaced by the H^+. The desorption of Ca^{2+} from the surface severs the cation bridging and a better microscopic sweep is realised, hence, more oil is recovered.

In Figure 4.30, the 5,000ppm SO_4 brine had the best recovery efficiency. However, the 5,000ppm Cl brine showed significant results.

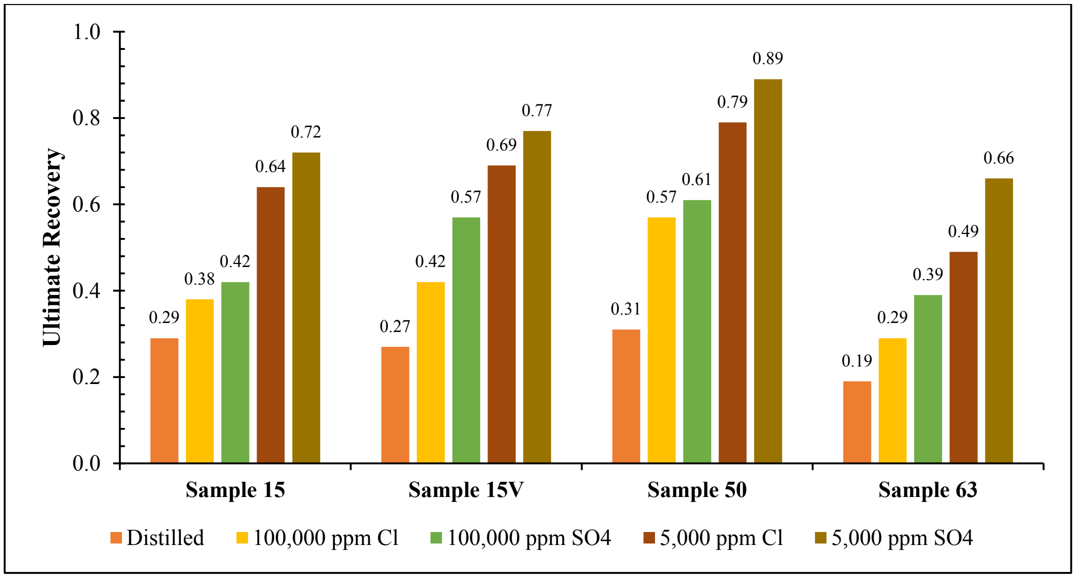
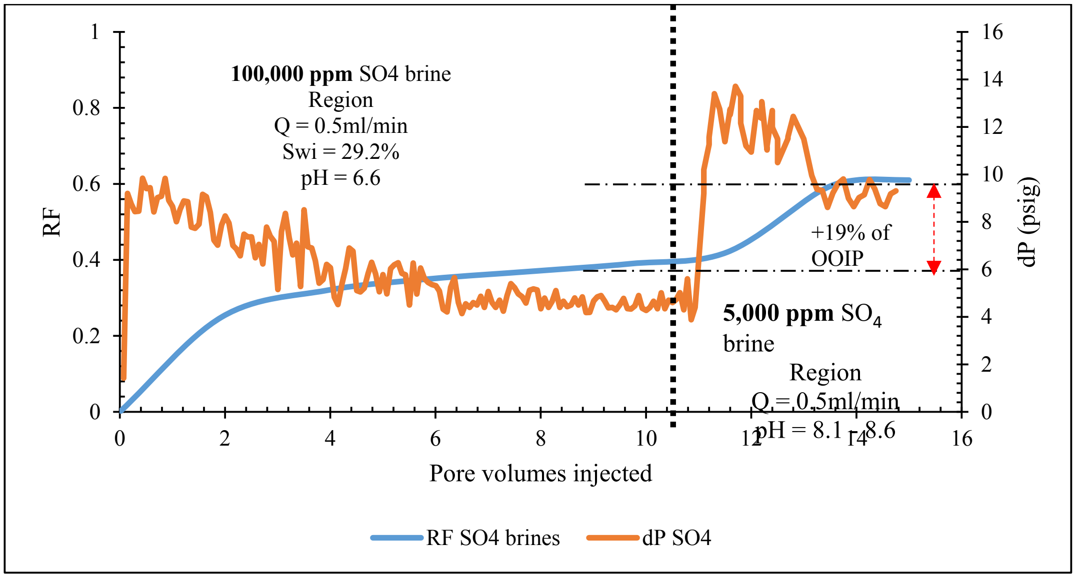


Figure 4.30: Ultimate Recovery at Different Concentrations with Distilled Water as a Benchmark

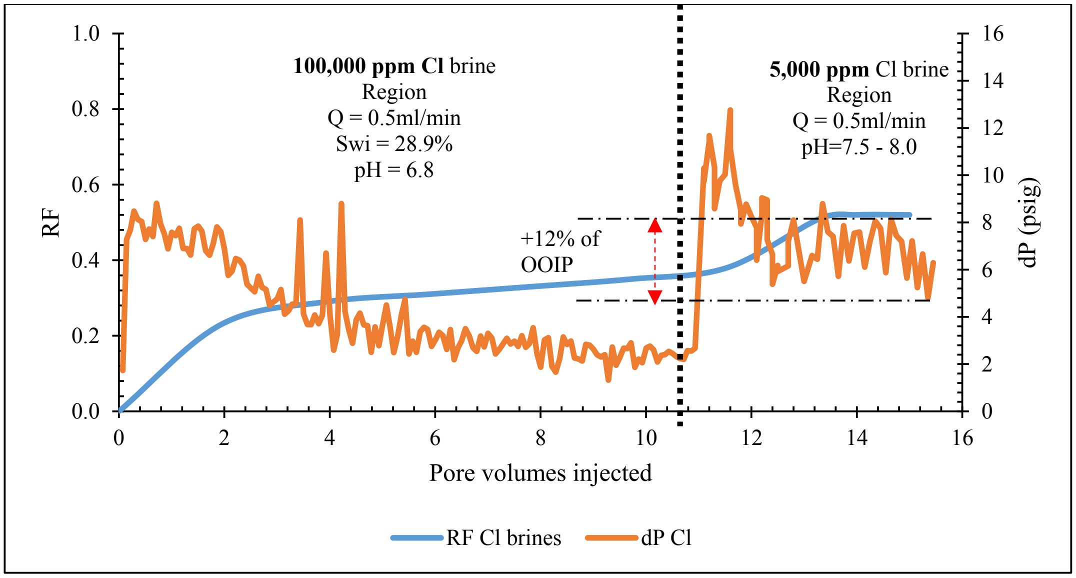
The proposed mechanism by Al-Otaibi [149] can also be adopted but, in this case, the stepwise replacement as seen in SO_4, as shown in Equations (4.6) and (4.7), is not prominent. Therefore, the repulsion created in Equation (6) in the SO_4 mechanism is absent and the promotion of Ca^{2+} desorption is muted in the Cl scenario (Equation 4.8). Therefore, the better recovery here was attributed to other displacement mechanisms. Furthermore, 5,000ppm Cl brine produced significant oil recovery compared to the distilled water as opposed to the assumption that Na^+ and Cl^- and other monovalent do not have any wettability altering properties [146].

Apart from the SO_4 mechanism proposed in this work, it has been proven that the lower the Ca^{2+} concentration in the connate water, the greater the effects of low salinity water [151]. A high concentration of Ca^{2+} in the thin brine film between the rock mineral and the oil leads to less negative surface charges by decreasing the electrostatic repulsive forces between the oil and the rock and increasing the cation bridging that exists between them. This, ultimately, increases the adhesive forces of the oil onto the rock surface and eventually increases the oleophilic nature of the rock. In Table 4.10, the divalent cation (Ca^{2+}) count in the high salinity SO_4 (100,000) brine formulation was lower compared to the Cl brine formulation. This further explains the better recovery seen in low salinity SO_4 flooding over the Cl scenario.

To further explicate the effectiveness of SO_4-based LS brine for oil displacement, a secondary and tertiary recovery process was simulated on Sample 50. This sample was chosen as it presented the best results from all the samples tested. Reasons for this will be detailed in the next Section. An imbibition experiment was first performed using the 100,000ppm brine (for each salt type) and then EOR was affected using the 5,000ppm brine specific to each class of brines for additional oil recovery. The results are presented in Figure 4.31.



(a) SO$_4$ Brines



(b) Cl Brines

Figure 4.31: Recovery Factor and dP Evolution during Different Stages of Oil Displacement

With regards to additional oil recovery, it is evident that the SO$_4$ brine performed significantly better than the Cl brine in the tertiary stages of the flooding process. The pH in the SO$_4$ brine was significantly increased and ranged between 8.1 – 8.6, with the highest pH recorded immediately after the injection of 3 pore volumes in the tertiary stage. This indicated that the MIE was most pronounced at the onset of the wettability alteration of the core sample when LS brine was injected and was accompanied by additional oil recovery. Cl-based salts performed appreciably and an increase in pH was noticed immediately after the LS flooding was initiated. Although the pH variation was not as large as in the SO_4 scenario, substantial oil recovery was realised. Pressure drop (dP) increased in both cases when the LS brine was injected. This was due to the clay layer expansion after the modification of the electrical forces within the oil-water-rock system as a result of lowering the brine salinity. Although kaolinite clays are non-swelling, they bind together to form a conglomerate that will lead to more interaction between the fluids in the system as reported by [108]. Another explanation for the increase in dP observed could be attributed to the formation of oil/water emulsion. An additional 12% of OOIP was recovered using the LS Cl brine, while 19% of OOIP was produced when the SO_4 LS brine was used. As mentioned earlier, the lower the ionic strength of the displacement brine, the higher the chances of wettability alteration, thereby improving oil recovery. Invariably, the SO_4 brines had higher ionic strength at both concentrations than the Cl brines, but they still performed better with even lower cationic counts.

4.5 Phase IV: Stratification Analysis

Conformance is a measure of the uniformity of the displacement front of the injected fluids during an EOR operation as it is being propagated through an oil reservoir. Conformance indicates the effectiveness of the displacing fluid in sweeping out the volume of a reservoir, both horizontally and vertically, as well as how effectively the displacing fluid moves the displaced oil toward production wells [85]. As the layers or strata of the pay zone vary in petrophysical properties, so does the conformance, which poses serious flow-assurance problems during oil transportation. A simple depiction of the displacement front in an EOR process is shown in Figure 4.32.

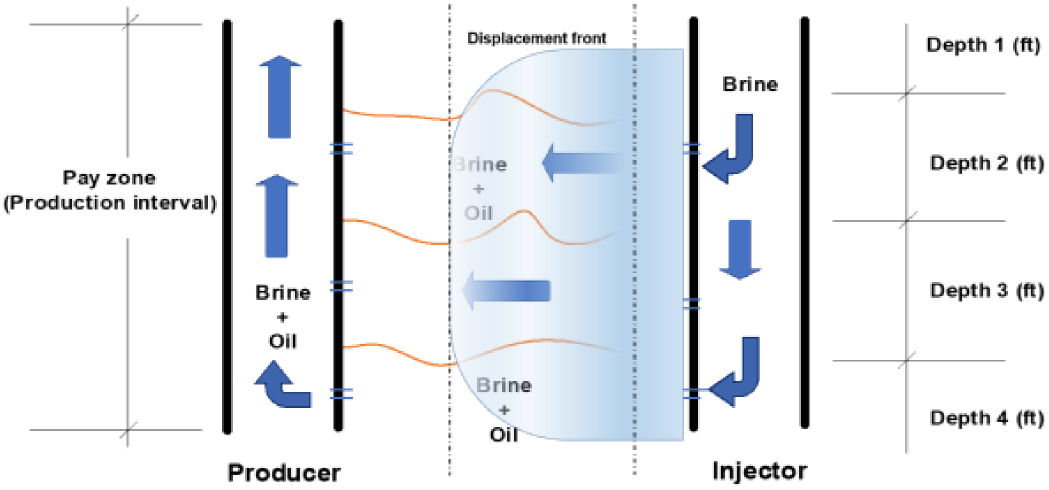


Figure 4.32: Vertical Sweep of the Reservoir

As the reservoir depth increases, the compaction due to overburden increases, which, in turn, reduces the reservoir properties in magnitude. Chief amongst which are the porosity and the permeability, which decrease with overburden/depth. The outcrops of native cores obtained at different depths of the reservoir were characterised and the results were observed to be eccentric. These are presented in Figure 4.33. Sample 50 appeared to have the deviant behaviour as it had a permeability higher than any other outcrop in the group of samples and was located deeper than Sample 15 and 15V. The porosity however did follow the conventional pattern as it decreased with an increase in depth. It stands that all permeable materials are porous, but not all porous materials are permeable. The implication of this unorthodox trend of permeability heterogeneity is a non-uniform flow given that permeability is the most important flow property. Conformance will most certainly affect the displacement front of the injected brines. To evaluate this, the results from individual core samples were analysed based on the production performance.

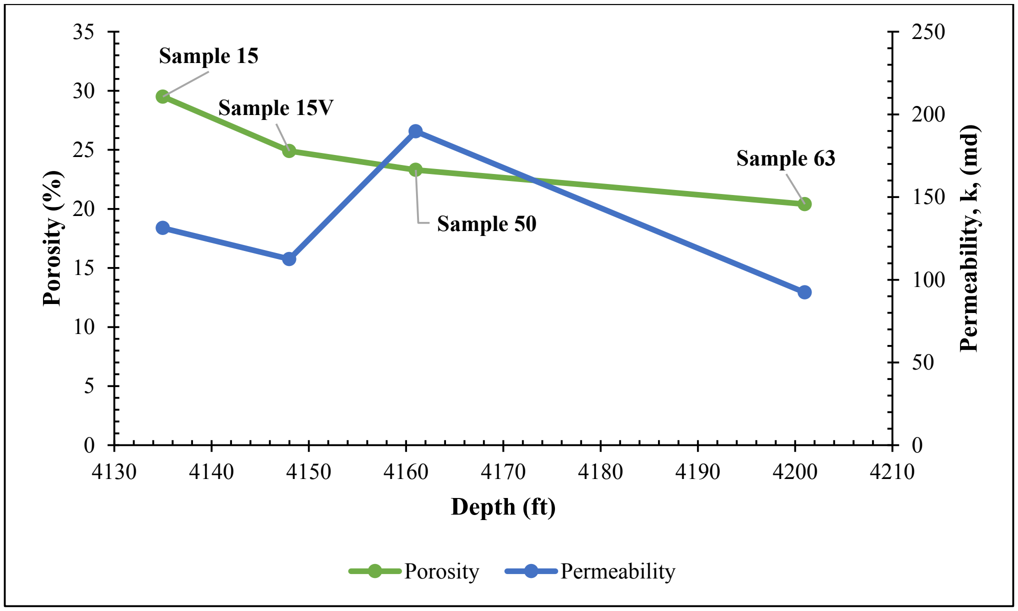


Figure 4.33: Porosity and Permeability vs. Depth of the Core Plugs

4.5.1 Production Performance per Stratum

Using the instantaneous oil production from the LS imbibition tests from each core sample, a sense of the production performance can be explicitly presented. This can be quantified by the amount of oil produced per pore volumes injected and the sustainability of the production during the course of the flooding process.

Figure 4.34 shows the results from Sample 15's instantaneous recoveries for Cl and SO_4 LS brine floods, with distilled water as a benchmark, to measure the performance of the test brines. Production peaked at about 1pv injected for the SO_4 brine flooding scenario and sustained till about 2.5pv. For the Cl case, production peaked when the pore volume of the injected brine clocked about 0.8pv and was sustained till 2.3pv, with the worst case presenting in the distilled water flooding scenario; production peaked at 0.4pv with a recovery factor of about 0.22, and oil production curbed after 1.7pv of distilled water had been injected.

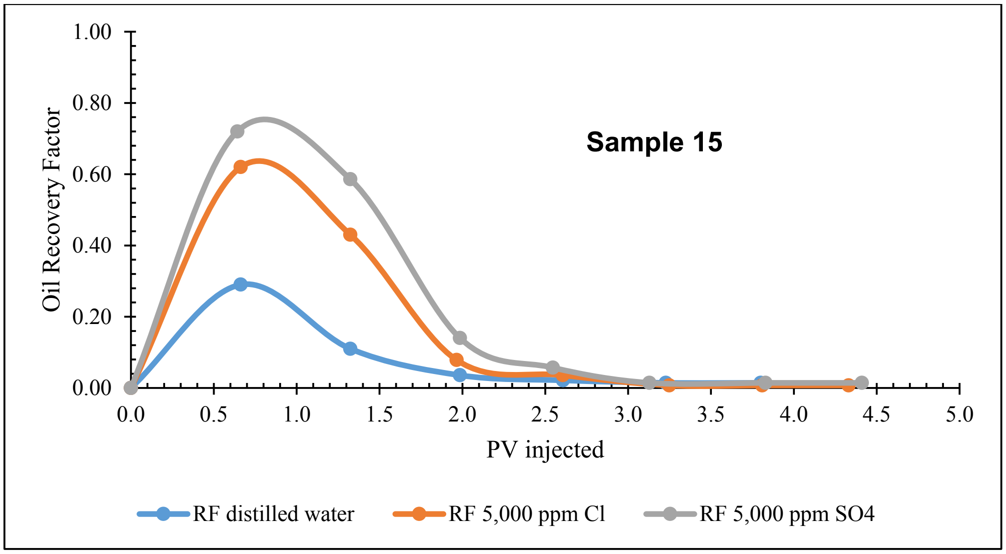


Figure 4.34: Production Performance of Sample 15

Sample 15V, shown in Figure 4.35, presented a similar trend as Sample 15 in the SO_4 brine, but Cl production ceased after 2.1pv of brine had been injected. The recovery factors were similar in both cases to the previous sample analysed. However, oil recovery generally was better in Sample 15 compared to Sample 15V.

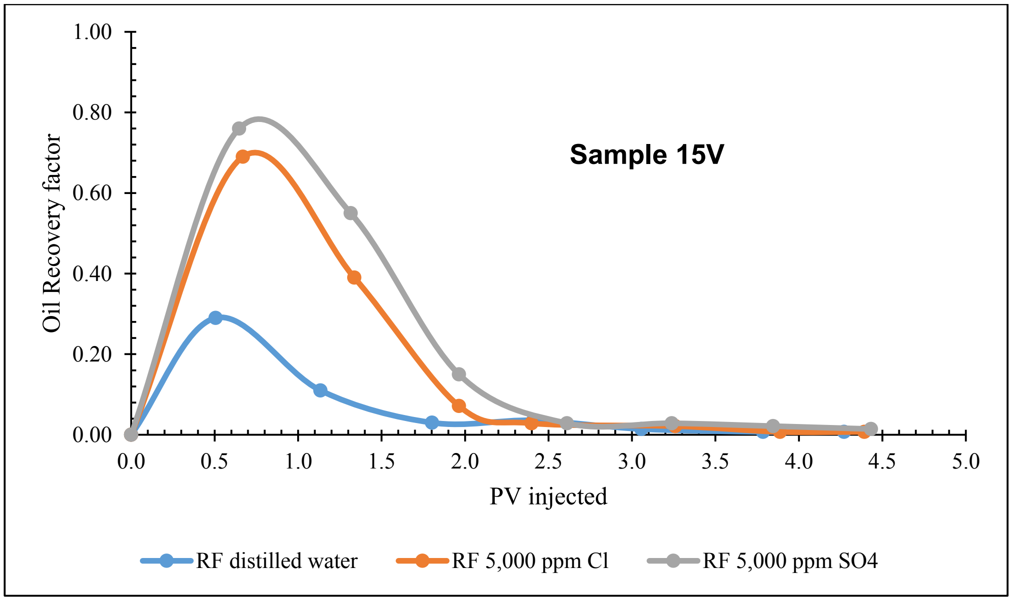


Figure 4.35: Production Performance of Sample 15V

The most interesting results so far are shown in Figure 4.36, where imbibition tests with SO_4, Cl and distilled water were used to investigate the production performance in Sample 50. For the SO_4 case, the oil production peaked after 2.4pv of the LS brine was injected and production was sustained significantly till after 10pv. At that pore volume, water cut was significantly high and substantial oil was recovered. The distilled water scenario also presented a unique trend compared to the previous samples investigated; oil production peaked at 3pv and production sustained till the end of the flooding where water cut was exceedingly high, albeit with a low oil production rate. On the other hand, the Cl case also had stimulating results, such that the production peaked at 2.3pv and was sustained till 8pv, thereby showcasing a longer sustained oil production, which infers good recovery. Overall, Sample 50 appeared to have the best production performance, which can be linked to the unusually high permeability.

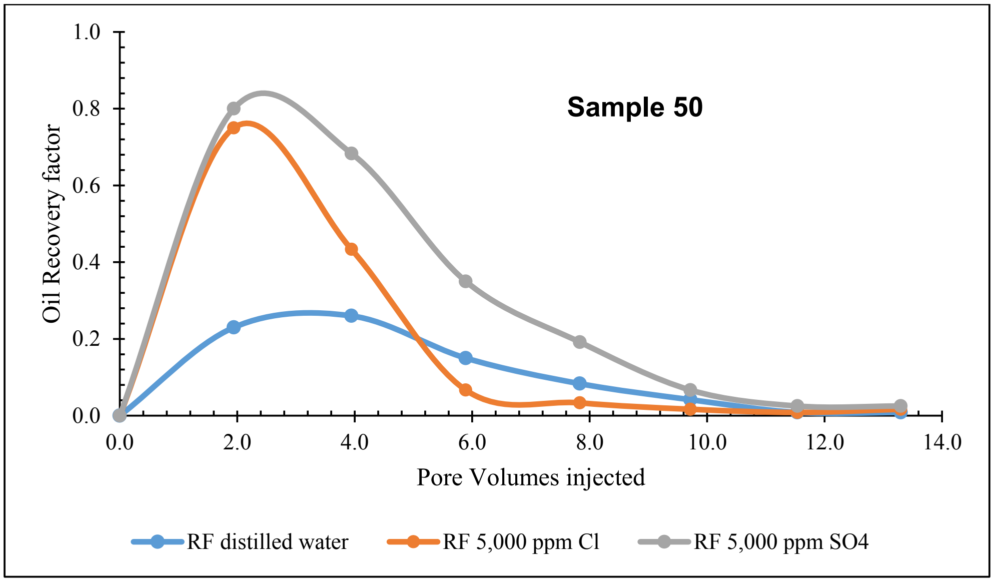


Figure 4.36: Production Performance of Sample 50

The most unusual results when compared to the other samples were realised in the deepest located core plug (Sample 63). The production generally was poor from all the brine scenarios and this may be attributed to the most obvious reason - lowest permeability. From Figure 4.37, production peaked at 1pv for Cl and SO_4 while it peaked at 0.8 for distilled water. In the distilled water case, the production ceased at 1.9pv and sustained for Cl and SO_4 till around 3pv of fluid was injected.

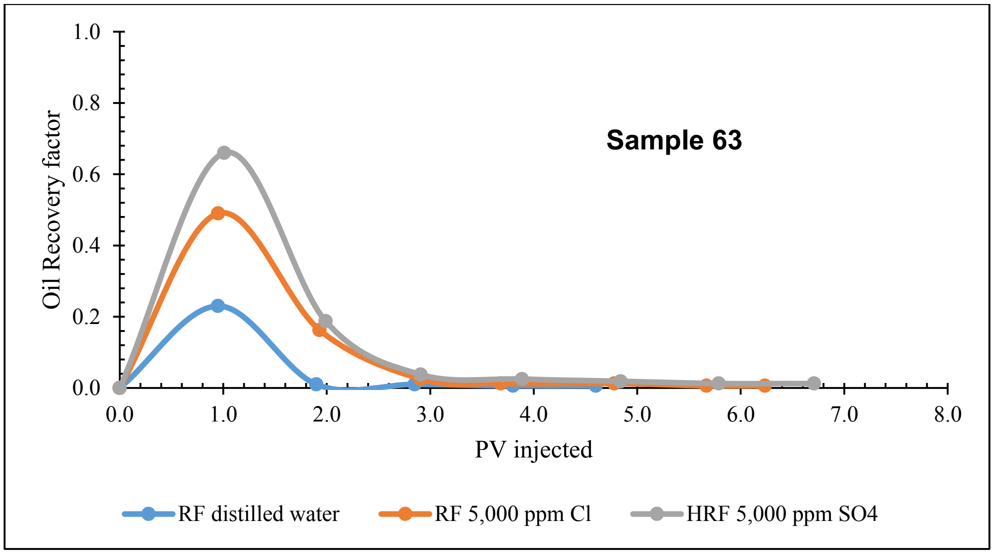


Figure 4.37: Production Performance of Sample 50

These were all insightful results and one of the key reasons why the production in Sample 50 was highest is because of the high permeability, while poor recovery was realised in the sample with the least permeability - Sample 63. This, however, is not the only reason for the good performance in Sample 50. The results from the mineralogical characterisation and the compositions of the core samples do differ, especially the clay content (See Table 4.11). Sample 50 had the highest clay content, with 6.9% Kaolinite. It has been proven that clay content in the reservoir is directly proportional to improved oil recovery by lowering the salinity of the injection brine [96]. Presence of clay renders the rock more negative and increases the ion exchange capacity of the rock surface. This will be a perfect site for the protonation of the rock surface and desorption of the oil as presented in the proposed mechanism.

From all the production performance analysis per layer of the reservoir, there is obviously a conformance problem should an EOR technique be performed. A uniform displacement front cannot be achieved because the permeability variation will hinder the flow efficiency as brine displaces the oil. This can be visualised using the ultimate recovery per layer and the depth from whence the core plugs came – see Figure 4.38. It can be observed that the profile of the displacement front based on the recovery factors is non-uniform and will require conformance control measures. The risk associated with this conformance effect is that the watered zone of the reservoir swept by the injected brine could be diverted and could create a path of low resistance already paved out.

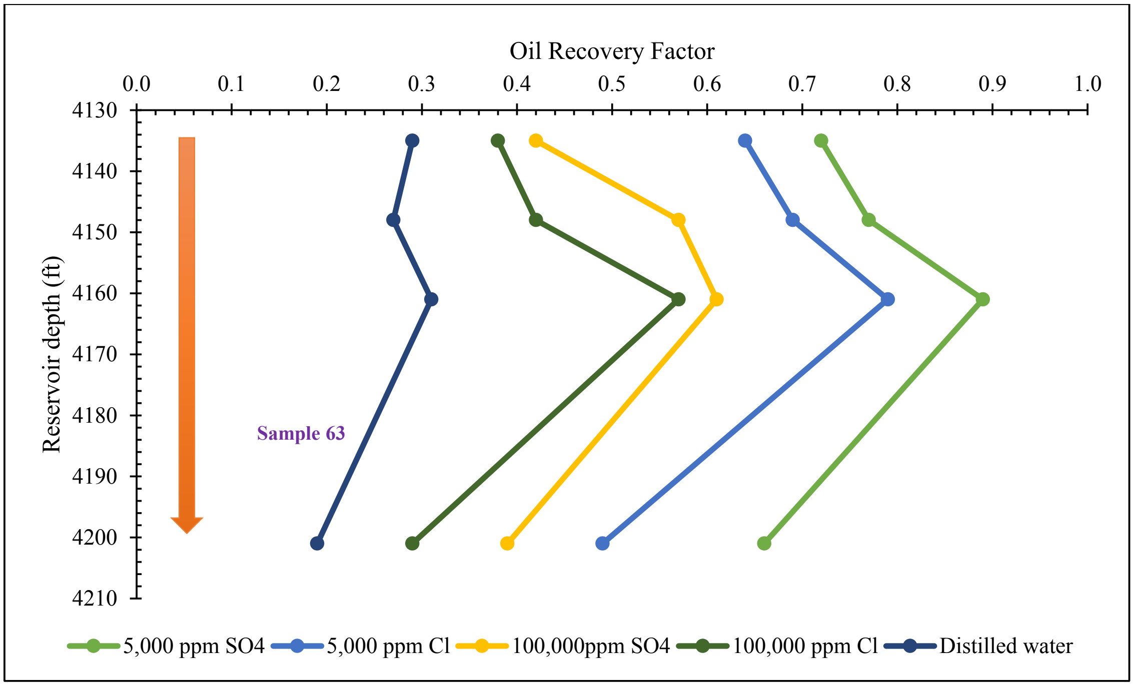


Figure 4.38: Displacement Profile per Layer from RF Obtained from each Brine Scenario

Thus, leaving behind substantial oil in the reservoir as a result of the non-uniformity of the displacement front, vertical sweep efficiency will significantly be hindered as the stratification of the reservoir exhibits a high degree of heterogeneity.

4.6 Chapter Summary

Phase I:

In order to ascertain the potential for mineral scale formation in sandstone reservoirs , the determination of the petrophysical and mineralogical properties for the core samples was conducted and the results obtained before and after the experiment. Findings indicated a maximum decrease of 5% porosity after the core flood, which could not be established related to mineral scale due to the small reduction, as shown in Table 4.6. These will be vital for the parametric sensitivity analysis that will be performed in the ensuing Section, where the establishment of the optimum flow conditions will be carried out. A summary of the results obtained is presented in Table 4. 11 below.

Table 4.11: Petrophysical and Mineralogical Assessments of Core Samples

Samples	Depth (ft)	Porosity (%)	Permeability (md)	Type	Kaolinite Content (%)
15	4135	29.5	131.3	Sandstone	5.6
15V	4148	24.9	112.5	Sandstone	5.4
50	4161	23.3	189.7	Sandstone	6.9
63	4201	20.2	92.32	Sandstone	4.7

Phase II:

The determination of the optimum flow conditions for the parametric sensitivity analysis was successfully completed. The optimum injection rate was determined to be 0.50 ml/min for this application given the nature of the native core samples and fluids to be used. Furthermore, the optimum concentration for the low salinity flooding was determined through carrying out oil displacement using the obtained optimum injection rate where 4 different concentrations were investigated. It was determined that the best concentration for this formulation of low salinity brine is 5,000ppm. The next task was to examine the effects of chloride and sulphate-based ions on the oil recovery improvements.

Phase III:

The roles of SO_4 and Cl-based brines were evaluated, and it was found that SO_4-based brines improved oil recovery substantially in all the four core samples. Figure 4.3 highlights the overall ultimate recovery from all the core samples and it is clear that the SO_4 brines had the potential best recovery compared to the other brines. Sample 63 had the worst performance amongst the core samples tested and this could be as a result of the low permeability compared to the other core samples, as shown in Table 4.11. Additionally, distilled water performance was identical in all the runs and, overall, low salinity brines had the best performance as already established here and in literature. The increase in pH in low salinity brines is highest in SO_4, while there were no significant changes in the effluents after the high salinity and distilled water displacement tests. IFT between the SO_4 brine and oil was lower compared to those of the Cl-based brines. Individually, SO_4-based brines exhibited lower IFT in a brine-oil system. Furthermore, pH variation was most pronounced in the SO_4 brines displacement tests with an approximate increase of 1.8 units. Furthermore, a new mechanism was proposed that showcased the prospects of anionic components in altering the wettability of sandstone core samples and improving oil recovery. This was supported by the results obtained in this work as more oil was recovered in the SO_4-based flooding than in the Cl^- counterpart.

Phase IV:

Conformance effect was analysed in the reservoir and it was found that there is a tendency of a disrupted displacement front during flooding. This was as a result of the variation in permeability of the core samples with the depth, and the reservoir exhibited a high degree of heterogeneity. Furthermore, Sample 50 had the best production performance owing to the high clay content and also had better permeability compared to the other core samples. Core sample 63 presented the worse production performance because it demonstrated the opposite of the desirable properties of the best core sample - Sample 50. However, for a successful EOR process in the case study, a substantial conformance control had to be adopted.

Chapter 5: Conclusion and Recommendation

5.1 Overview

This Chapter provides the leading findings from this study as well as the recommendations to be considered at both laboratory scale and field scale when adopting the findings.

5.2 Conclusions

The aims set out in this research were achieved through the methodical execution of the defined objectives. Core sample characterisation was first carried out to determine the petrophysical properties and mineralogy of the native core samples used. It was gathered that the core samples were wholly silica-based with kaolinite clay. Various salt compositions were used to ascertain the effectiveness of the suspected displacement mechanisms, interfacial tension reduction and wettability alteration brought on by the anionic components of the salt compositions. Furthermore, the role of chloride and sulphate-based brines in low salinity flooding with a hybrid smart water injection technique was also investigated. The results obtained in this research revealed that a combination of sulphate-based brine improved oil recovery to a significant degree. Therefore, the conclusions drawn are:

- Optimum low salinity concentration was determined to be 5,000ppm for an effective low salinity flooding process using the formulation from the native reservoirs, and a practical injection rate that is most ideal for the type of core samples and fluids used was found to be 0.5ml/min.
- Distilled water experiments highlighted the significance of the presence of ions in the displacement brines given the poor microscopic and macroscopic sweeps depicted by the poor recovery efficiencies in all the flooded core plugs, albeit with the presence of kaolinite clays.
- pH substantially increased by 1.8 units when a 5,000ppm SO_4-based solution was used as the displacing fluid during imbibition experiments. 5,000ppm Cl-brine also showed promise with an increase of 1.2 units, from 6.8 to 8.0. There were no pH changes in higher salinity (100,000) and the distilled water runs.
- A possible mechanism where SO_4 ion breaks and replaces the carboxyl group at the cation bridge site in low salinity flooding was postulated, which promotes the desorption of the Ca^{2+} from the rock.

- Low salinity (SO_4) brine was observed to possess the lowest IFT between the oil and brine, and distilled water exhibited the highest IFT, which may be significant in overcoming the capillary pressure of the pore matrix and may contribute to the alteration of the wettability of the rock mineral to a more water-wet state.
- The use of the hybrid smart water low salinity injection technique tested in this research is feasible for large scale EOR in the Wara field provided that the conformance effect is taken into consideration.

This research highlights the importance of anionic components of the brine that have previously been relegated to inactive capacities. They have substantial roles to play in the improvement of oil recovery in a cost-effective manner. The proposed mechanism for wettability alteration kinetics will pave way for more research into the investigation of other pathways apart from the pre-existing ones in order to exploit and enhance this purview.

5.3 Recommendation and Future Work

Despite the considerable findings from this research, it is noteworthy to mention that there are significant avenues to consider that are beyond the scope of this research work. Some of the recommendations are as follows:

- Ionic count and effluent analyses investigation of the injected brines and the produced water, which will provide additional information to make further deductions.
- Permeability test to be conducted in addition to the porosity test already considered in this study to ascertain the scale formation potential after the core flood, especially where high delta P is observed.
- Two phase oil-water relative permeability investigations involving the sulphate and chloride-based brines to evaluate the performance of the entire process.
- Numerical simulation to evaluate the extent of conformance in the reservoir with sufficient heterogeneity.

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