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Experimental Study of Microbial Enhanced Oil Recovery and its Impact on Residual Oil in Sandstones

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Experimental Study of Microbial Enhanced Oil Recovery and its Impact on Residual Oil in Sandstones

by

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Dedication

To my family, friends, co-workers, and Stephanie.

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Experimental Study of Microbial Enhanced Oil Recovery and its Impact on Residual Oil in Sandstones

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The objective of this research project was to determine experimentally, using core floods, whether providing additional nutrients to accelerate the growth of nitrate-reducing bacteria alongside aerobic bacteria would result in an improved oil recovery in sandstone rocks.

The hypothesis was that indigenous reservoir microbes only need additional nutrients to be able to alter the forces enacting within an oil-water-rock system drastically. As a microbial population grows, individual bacteria strains may colonize to form biofilm and produce microbial byproducts. In general, enhanced oil production from microbes can be categorized into three mechanisms, fluid diversion, interfacial tension (IFT) reduction, and solvent production.

Moreover, the distribution and connectivity of the remaining oil could influence the response time and quantity of additional oil production. From the Computed Tomography experiments conducted in this study, it was made apparent that oil distribution does not change considerably when changing brine injection rate after reaching residual oil saturation. However, future experiments are recommended to

determine if the waterflood flow rate before reaching residual oil saturation will influence the distribution of capillary-bound oil.

Conventional Microbial Enhanced Oil Recovery (MEOR) projects involving the injection of surface-produced byproducts to release oil has proven to be costly, inefficient, and unpredictable. Recent research suggests stimulating indigenous reservoir microbes with inorganic nutrients would increase oil production in a cost-effective manner. In this study, an optimal methodology of conducting microbial corefloods with live reservoir microbes and inorganic nutrients is devised.

Corefloods performed in absence of sodium dithionite had overall better microbial growth. Experiments conducted with 1% salinity brine yielded little tertiary oil production (0.1% S_{or} reduction). MEOR experiments in both 2.5 and 5% salinity systems showed significantly more oil release (1 to 6.5% S_{or} reduction). Furthermore, secondary waterflood flow rate did have an impact on the tertiary oil recovery (more than 5% difference in S_{or} reduction). The work presented in this study can be used as a precursor to analyze MEOR performance on high viscosity oil or in heterogeneous rocks.

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Chapter 1: Introduction

Over the past 150 years, the petroleum industry has produced less than 20 % of the world's oil reserves (Westenhaus, 2011). Crude extraction has proven to be an extremely difficult task and it is evident that current technologies do not provide an economical method suitable for all reservoirs. With the current global consumption of oil reaching a historical high (EIA, 2016), improving hydrocarbon production is crucial for sustaining and improving global quality of life.

In the United States, there are estimated over 600 billion barrels of oil remaining in the subsurface, but conventional methods only have the potential to produce 22 billion barrels (Aladasani and Bai, 2010). Many naturally occurring geological factors and unfavorable fluid physics, such as capillary forces and poor mobility ratio, impinge on the ability to produce hydrocarbons. Nonetheless, researchers have developed many advanced enhanced oil recovery (EOR) methods to overcome these hurdles. It is estimated that current EOR processes can unlock as much as 200 billion barrels of oil from existing reservoirs (Aladasani and Bai, 2010); however, producing the large remainder of the reserves require improvements to existing technologies.

EOR processes, otherwise known as tertiary recovery, take advantage of injecting mass or energy not initially present in the subsurface into oil reservoirs via existing wells to mobilize remaining oil. These techniques seek to alter the hydrocarbon properties and/or the interactions between subsurface fluids and their host rock formations. Only a few tertiary methods (e.g. steam and carbon dioxide injection) have reached the "deploy and repeat" level of technological maturity. However, many other promising technologies

are classified in the “research and development” phase; one such method is Microbial Enhanced Oil Recovery (MEOR) (Bryant and Lockhart, 2002).

MEOR is the technique of utilizing bacteria and their byproducts to displace oil. MEOR implementation is categorized into three approaches, stimulation of exogenous microbes, stimulation of indigenous microbes, and injection of microbial byproducts.

Historically, MEOR methods involved the use of laboratory-grown microbes and carbon-based nutrients. Microbial byproducts from molasses stimulation have demonstrated their potential to mobilize oil in several lab experiments (Zobell, 1947; Updegraff, 1957; Edmundson, 1989). However, when subjecting these lab-cultivated microbes to a reservoir, the exogenous organisms oftentimes were not compatible with the native oil/microbe system, or if they were, oil recovery was intermittent (Westenhaus, 2011). Additionally, the high operational costs of large-scale breeding could not be justified with the low additional oil production. These issues with conventional MEOR methods have left a perceived high risk and low success rate and rendered many operators reluctant to execute large-scaled MEOR projects. MEOR methods were one of the least field implemented tertiary processes and only accounted for less than 1% of all U.S. EOR production (The California energy commission, 1999).

Over the last several decades, researchers have refined and developed new methods for applying MEOR processes in hopes of revitalizing bacteria-influenced oil production. Amongst these new MEOR methods is the process of stimulating indigenous reservoir microbes, termed “organic oil recovery” (Sheehy, 1990; Zahner et al., 2012). There exists a higher compatibility with this new MEOR method since extant microbes have already adapted to formation conditions. Analyses of field results from the first 100+ of these “organic oil recovery” applications have shown an 89 % success rate when

activating indigenous microbes. On average, these wells have experienced a 122% increase from pre-treatment rates to post-treatment maximum rates (Zahner et al., 2012).

Another advantage of "organic MEOR" is the relatively low cost to implement the technology. Although almost all EOR projects can circumvent the high costs of drilling new wells, processes such as steam, solvent, and chemical flooding necessitate expensive chemicals and/or substantial changes to field infrastructure, which can result in a large capital expenditure (CAPEX) and operational expenditure (OPEX). A typical maximum project cost for thermal EOR processes can be 25 USD per barrel of additional oil, while carbon dioxide and surfactant injection can be as high as 30 and 50 USD per barrel of additional oil, respectively (Havemann et al., 2014; Town et al., 2010). Current methods of MEOR however, are amongst the cheapest EOR technologies to implement. These projects only require inexpensive nutrient brine solutions and slight modifications to the facilities already in place from secondary recovery processes. The cost of this tertiary process is averaged to be around 6 to 10 USD per barrel of additional oil (Simandoux et al., 1990; Sunde et al., 1992; Town et al., 2010).

In addition to a lower risk, successful "organic MEOR" field trials have been observed with oil gravity as high as 41 °API and as low as 16 °API. Microbes can also survive in extreme reservoir conditions with temperatures as high as 200 °F and salinities as high as 140,000 ppm (Zahner et al., 2012).

Although successful in many reservoirs, MEOR implementation is still hindered by many factors. Fields need to be carefully screened for the presence of a suitable microbial population and movable remaining oil. The absence of either prerequisites has historically resulted in failed attempts. Out of the 100+ treatments studied by Zahner et al. (2012), seven of the wells did not see any incremental oil even though microbial growth was sufficient. These outcomes remain inexplicable and no correlations can be

concluded between these failed projects. In addition, both lab and field studies have indicated that MEOR processes generally do not recover as much remaining oil as other EOR processes (Bryant and Lockhart, 2002). Further research on microbes and their behavior in subsurface reservoirs is needed to surpass these limitations.

Although stimulating indigenous microbes is termed "organic oil recovery," it only references to the native microbial population and should not be confused with the carbon contents of injected nutrients. Conventional methods of MEOR utilize sugar-based nutrients, as they are able to stimulate bacterial growth quickly. However, these organic nutrient solutions have many disadvantages. Shipping large quantities of sugar to remote locations can be extremely problematic and expensive especially in offshore fields. Injection of carbon-based nutrients may result in uncontrollable microbial growth throughout the entire contacted area. This can lead to wellbore plugging and/or a decrease in water injectivity (Sunde et al., 1992).

Inorganic nutrients can serve as an inexpensive alternative to these issues. Since no external carbon is introduced to the reservoir, injecting inorganic nutrients limits the carbon food supply available to reservoir microbes to only the formation's hydrocarbons, thus, forcing microbes to conglomerate and grow on the oil and water interface. The advantageous microbial growth location allows biosurfactants to be produced directly on the oil and water interface, making the oil releasing process much more efficient (Sunde et al. 1992). However, the absence of additional carbon makes this type of stimulation comparatively slower to that of organic stimulation.

MEOR oil production mechanisms can be grouped into three categories: fluid diversion, reduction of interfacial tension (IFT), or an increase in fluid mobility. A combination of these mechanisms can be achieved through the metabolic conversion of

nutrients into oil releasing agents such as biosurfactants, biopolymers, solvents, acids, and gases (Lazar et al., 2007; Rashedi et al., 2012).

These oil-producing mechanisms have been thoroughly researched through computer simulations and laboratory experiments. Those who utilized simulations have devised computer and mathematical models to predict microbial growth and their effects on remaining oil (Islam, 1990; Sarkar, 1992; Xu et al., 1992; Delshad et al., 2002; Stewart, 2004; Skjaelaaen, 2010).

Most MEOR lab experiments involved observing microbial changes to static systems; only a few experiments involved the use of rock cores. Yakimov et al. (1996) demonstrated the effects of stimulating specific strains of *Bacillus licheniformis* with a sucrose-based nutrient. Other core flood experiments showed the ability of microbial products, such as biosurfactants, to mobilize oil by reducing IFT (Bailey et al., 2001; Ayirala, 2002; Xu, 2005). However, few researchers have tested the effects of stimulating a broad bacterial population with an inorganic nutrient solution. For corefloods performed in the absence of organic nutrients, the main constraint of the rock/fluid/microbe system is the compatibility of in-situ oil as a usable carbon food source.

The goal of this research was to test experimentally the hypothesis that the injection of inorganic nutrients can stimulate bacteria growth and produce additional remaining oil. A suitable methodology for observing the effects of inorganically simulating microbes in a porous medium was developed. The experimental procedure consisted of injecting microbes and nutrients into Bentheimer sandstone cores that have already undergone waterflooding.

Chapter 2: Background

This chapter is divided into five sections. It first highlights the life of a reservoir and example production strategies that are used in various production stages. The second section introduces the necessary components for bacterial growth and the resulting behavior. The third section focuses on the three main mechanisms of microbe assisted oil recovery: fluid diversion, biosurfactants, and solvent production. The fourth section compares the different approaches for stimulating microbes. The final section discusses two different models that can be used to predict the performance of oil recovery processes.

2.1 Oil Recovery Process

2.1.1 Primary Recovery

Primary recovery is the process of extracting subsurface oil from the expansion of naturally pressurized hydrocarbons. When an oil field is first produced, the driving force that induces fluid flow is the pressure gradient between the higher-pressure rock formation and the lower-pressure production wells. In this phase of production, various pump jacks and other artificial lift devices are often utilized to lower the pressure of production wells, which consequentially increases the pressure differential and mobilizes additional oil.

Oil recovery for a reservoir is strongly dependent on its rock properties, fluid characteristics, and geological heterogeneities. Only a small fraction, typically 10 %, of the reservoir's original oil in place (OOIP) can be recovered during primary recovery. Once the natural reservoir energy is depleted, it is necessary to supply external energy to the producing formation in order to boost or maintain oil production.

2.1.2 Secondary Recovery

Secondary recovery is the practice of injecting external fluids in one wellbore and producing hydrocarbons in another wellbore. This production phase involves the process of injecting either immiscible gas or water into the subsurface. The most common practice of secondary recovery is waterflooding due to water's availability, low cost, and high specific gravity.

As a waterflood project matures, oil ganglia are separated and become trapped by capillary forces. Formation heterogeneity can cause water to channel into high permeability zones and bypass large areas of hydrocarbon. Poor mobility ratios may result in fluid fingering and early water breakthrough. These geological and fluid factors hinder secondary processes' oil displacement efficiency and prevent the complete recovery of subsurface hydrocarbons. Successful waterflooding only recovers an additional 10 to 20% of the OOIP. When sustaining secondary recovery becomes uneconomical, many wells are shut in, leaving behind vast amounts of unproduced resources.

2.1.3 Tertiary Recovery

Although the global demand for petroleum resources increases almost every year (U.S. Energy Information Administration), only a fraction of the world's oil fields have undergone additional stages of recovery. Tertiary recovery, or enhanced oil recovery (EOR), is the process of recovering oil left behind from secondary processes (remaining oil). The ultimate goal of tertiary processes is to increase the microscopic and/or macroscopic oil displacement efficiencies of injected fluids. Microscopic efficiency is the displacement of oil at the pore scale, while macroscopic efficiency refers to the

effectiveness of displacing fluids in contacting the entirety of an oil producing formation. Fig 2.1 shows a schematic of microscopic and macroscopic sweep efficiencies.

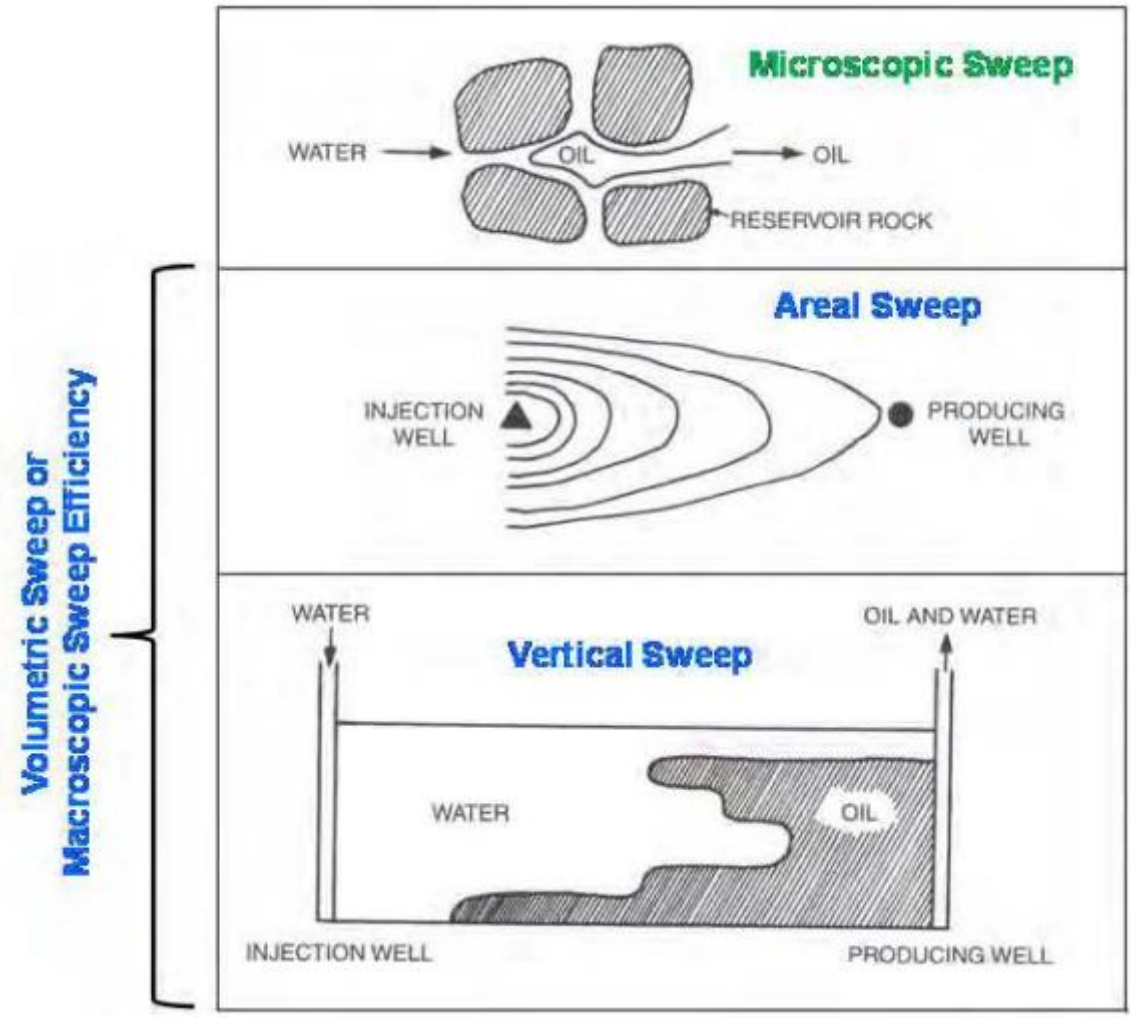


Fig 2.1-Schematic of sweep efficiencies (Lyons and Plisga, 2005)

2.1.3.1 Microscopic Displacement Efficiency

Microscopic displacement efficiency measures the effectiveness of the displacing fluid in moving the oil at locations where the displacing fluid contacts the oil. Microscopic efficiency can be improved by increasing the capillary number, N_{vc}, which is the ratio of viscous to capillary forces. One definition is as follows:

$$N_{vc} = \frac{viscous\ forces}{capillary\ forces} = \frac{v\mu}{\sigma} \tag{2.1}$$

where v is the interstitial velocity of the displacing fluid, μ is the viscosity of the displacing fluid, and σ is the interfacial tension between the displaced and the displacing fluid. Most sandstone reservoirs are water-wet, meaning capillary forces work to keep oil trapped in the rock pores, whereas displacing viscous forces work to release trapped oil. Any hydrocarbon bound by capillary forces is given the name residual oil.

Many EOR methods produce capillary-bound oil through various mechanisms of increasing capillary number. The relationship between residual fluid saturation and capillary number is demonstrated in a capillary desaturation curve. For values greater than the critical capillary number, residual saturation decreases with increasing capillary number until very low capillary number values around 10^{-2} (Berger and Lee, 2002). Below the critical capillary number, the residual non-wetting saturation is constant. An example capillary desaturation curve is depicted in Fig 2.2.

At low capillary numbers, it is hypothesized that, once bypassed, the non-wetting phase is trapped as disconnected blobs (Niordson & Olhoff, 1985). If viscous forces dominate (above the critical capillary number), the viscous drag creates pressure drops that mitigate capillary trapping. For waterfloods, a typical value for the capillary number is 10^{-6} (Berger and Lee, 2002), which oftentimes is significantly less than the critical

capillary number and a moderate improvement on capillary number will have no appreciable decrease in residual oil saturation

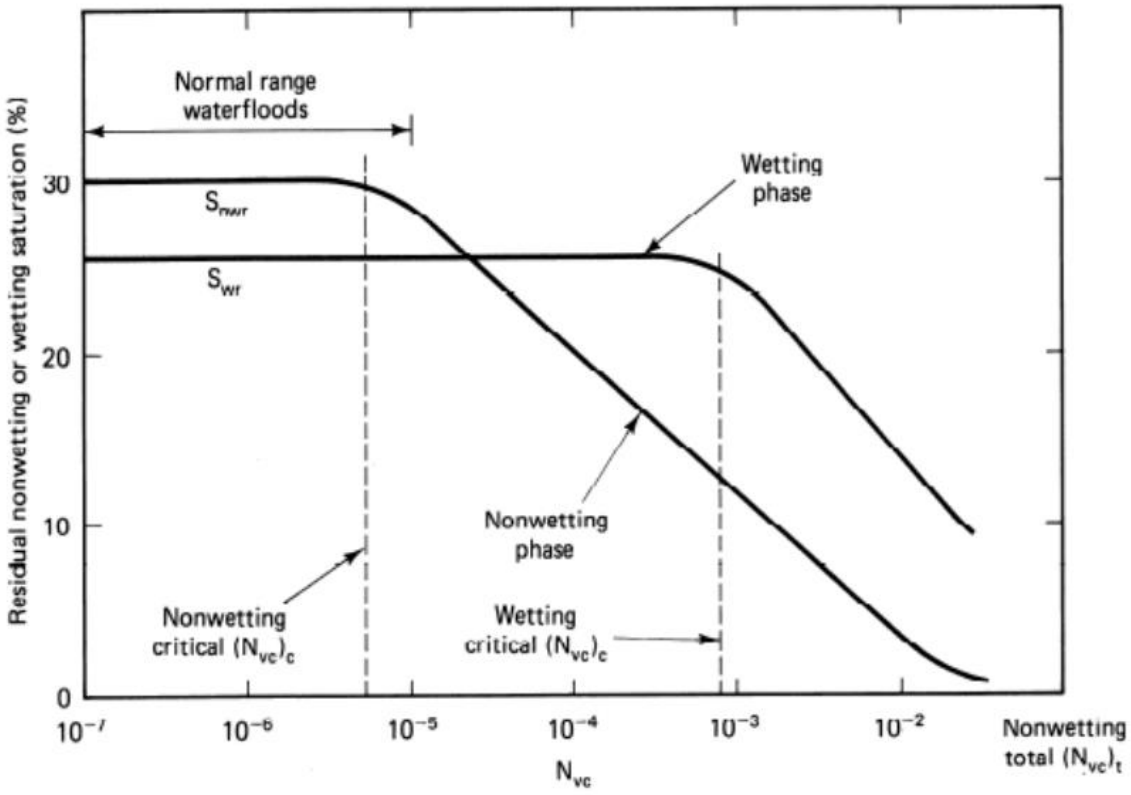


Fig 2.2-Capillary desaturation curve (Lake, 1989)

2.1.3.2 Macroscopic Displacement Efficiency

Macroscopic displacement efficiency is a measure of the effectiveness of the displacing fluid in contact with the pore volume of the reservoir. Macroscopic efficiency can be improved by decreasing mobility ratio, *M*, which is the ratio of displacing (water) to displaced (oil) fluid mobilities defined as follows:

$$M = \frac{Mobility_{Water}}{Mobility_{Oil}} = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}/\mu_w}{k_{ro}/\mu_o} = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \tag{2.2}$$

where λ_w and λ_o are the water and oil mobilities, respectively, k_{rw} and k_{ro} are the rock's relative permeabilties to water and oil, μ_w is the water viscosity, and μ_o is the oil viscosity. Oil bypassed by a poor macroscopic sweep efficiency is termed remaining oil.

The sweep efficiency of the displacing fluid increases as the mobility ratio decreases. When $M > 1.0$, a non-uniform displacement of fluid is present and will promote the fingering of displacing fluid (i.e. water) through the more viscous displaced oil (i.e. oil). Fingering of injection fluid will channel through high permeability zones, bypass areas of oil, and breakthrough at an earlier time. Thus, a large contrast in viscosity between water and oil will result in high amounts of unswept oil due to its unfavorable mobility ratio. Fig 2.3 compares the remaining oil profile after an unfavorable to that of a favorable mobility ratio.

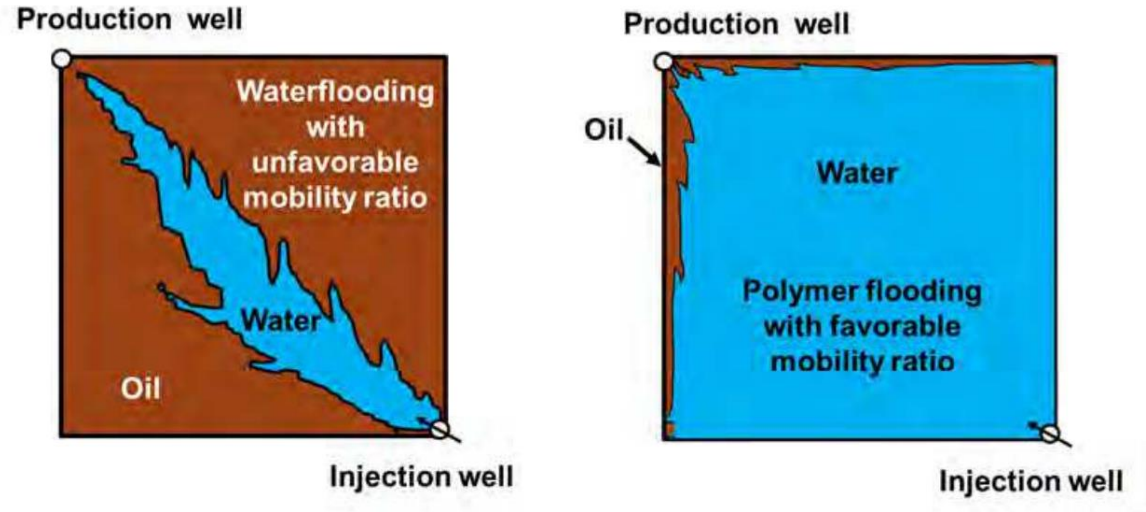


Fig 2.3-(left) Displacement of oil with unfavorable mobility ratio (M > 1), (right) displacement of oil with favorable mobility ratio (M < 1) (Sydansk & Romero-Zerón, 2011)

2.1.4 EOR Applications

EOR methods seek to produce oil left behind from secondary processes by improving the microscopic and macroscopic oil displacement efficiencies. The various applications of EOR all produce additional oil through the means of increasing the capillary number, decreasing the mobility ratio, or exploiting both fundamental principles. In general, EOR processes can be categorized into four main categories: thermal methods, chemical flooding, solvent injection, and microbial stimulation.

2.1.4.1 Thermal Methods

The principle behind thermal EOR is to utilize thermal energy to increase the reservoir temperature. This approach is especially useful for formations with a heavy or viscous hydrocarbon phase. Thermal EOR techniques occur in two main forms, steam injection and in-situ combustion, otherwise known as fire flooding. Steam injection involves the introduction of steam at about 80% quality to a reservoir. As the steam condenses in the subsurface, its heat is transferred to the reservoir rock and fluids. This leads to the thermal expansion of oil, which decreases its viscosity and improves its mobility. Steam flooding is heavily used throughout the energy industry and is the most advanced EOR process (Romero-Zerón, 2012). In-situ combustion processes also seek to lower mobility ratio but by burning some of the reservoir oil to increase formation temperature. Although, this process is theoretically more efficient than steam flooding, it is not widely used due to its complex operational problems (Regtien, 2010).

2.1.3.2 Chemical Flooding

In chemical flooding processes, chemicals such as polymers, surfactants, or alkaline solutions are added to the injection brine to change the displacing fluid behavior. Water-soluble polymers are used to increase the viscosity of the injected water. The injection of a thickened solution lowers the mobility ratio and improves the macroscopic displacement efficiency (Seright, 2010; Sheng, 2011). Similarly, polymer slugs can be injected into high permeability zones and divert any subsequent injection fluids into otherwise unreachable zones for better conformance control (Al-Muntasheri, 2012). Synthetic surfactants can be used to reduce the IFT between the oil and the displacing water as well as the IFT between the rock and the oil (Pope et al., 1978). These chemicals can drastically increase capillary number and allow for the recovery of residual oil. In alkaline flooding, the alkaline compounds, such as sodium carbonate, can react with natural organic acids within the oil to generate petroleum soap in-situ. These chemical products work in the same way as synthetic surfactants to mobilize oil. When combined, these three processes form the Alkaline-Surfactant-Polymer (ASP) method and have synergistic effects to mobilize residual oil (Sheng, 2011; Sheng, 2014).

2.1.3.3 Solvent Injection

Solvent injection processes consist of injecting miscible gases, most commonly carbon dioxide, nitrogen, exhaust gases, or hydrocarbon solvents. Miscible processes reduce the IFT between oil and displacing gas. Additionally, an oil's viscosity decreases as more gases are dissolved into it. The underlying issue with gas injection has been its poor mobility control since injection gas is much less viscous than most crudes. The mobility of the solvent can be improved by a water-alternating-gas (WAG) injection

schemes (Zekri and Alshobakyh, 2011). Carbon dioxide flooding has been the most widely used EOR method (Verma, 2015).

2.1.3.4 Microbial Stimulation

Microbial Enhanced Oil Recovery (MEOR) is the process of injecting fluids that activate the oil producing potential of microbes. Reservoir bacteria have the ability to produce biosurfactants to lower the IFT between the oil and water as well as improve the mobility ratio between the displacing and the displaced fluids.

MEOR is a technology that has been researched for over 90 years. Beckman (1926) first suggested the utilization of microorganisms and/or their metabolites for producing oil from reservoirs. Zobell (1947) patented the process by which bacterial products produce oil from sandpack columns in laboratory experiments. Further extensive microbial tests established the fundamentals for the first MEOR patent granted to Updegraff (1957). The first field tests using the in-situ conversion of cheap substrates into oil-releasing agents were conducted in the Lisbon field, Arkansas in 1954. Ivanov (1983) later developed an alternate MEOR approach to activate indigenous reservoir microbes.

MEOR remains as an emerging technology that has the potential to produce large amounts of unproduced oil economically. Other forms of EOR application typically necessitate special equipment and a substantial amount of capital and operational expenditures to handle their rigorous procedures. However, stimulating microbes in a reservoir is among the most inexpensive tertiary recovery methods (Simandoux et al., 1990; Biji et al., 2014). Only minimal changes to waterflood facilities and nutrients are

needed for a successful MEOR project. Fig 2.3 shows the incremental cost per barrel for various EOR techniques.

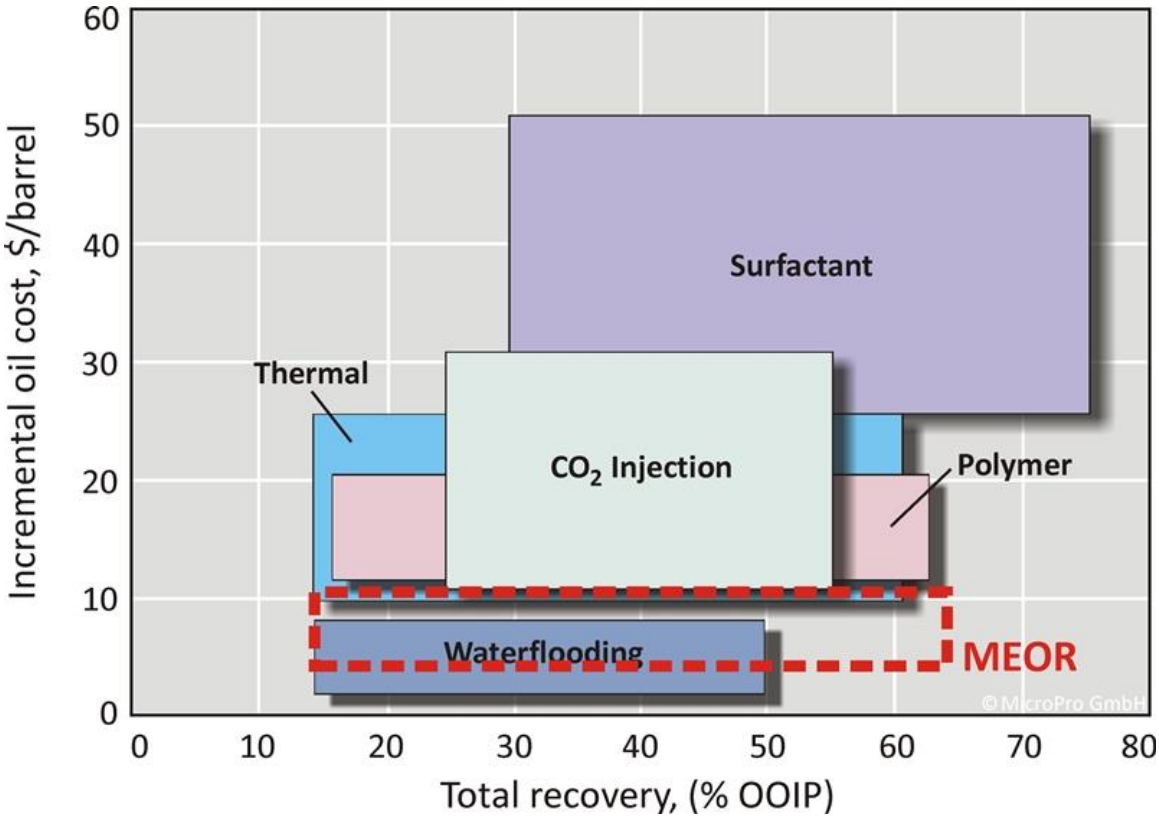


Fig 2.4-Incremental oil costs and potential recovery of various EOR methods (Simandoux et al., 1990)

Although incremental oil cost is relatively low, the applicability of MEOR is not suited for all reservoirs. Microbial growth is favored in reservoir conditions with >50 mD permeability, reservoir temperature of <80 ℃, and <10 % salinity water (Awan et al., 2008). Similarly, the technology has not yet been expanded to accommodate formations outside of sandstone reservoirs.

2.2 Microbial Enhanced Oil Recovery

A standard practice of MEOR does not exist across the energy industry; operators use several different combinations of techniques to extract oil. However, all applications of MEOR can be categorized into one of three main approaches: (i) injection of exogenous microbes followed by customized nutrients for cell growth in the subsurface, (ii) injection of only nutrients specifically tailored to stimulate growth of indigenous reservoir microbes, (iii) production of microbial products ex-situ and their subsequent injection into the reservoir. Furthermore, implementations of each MEOR approach differ within each category based on the presence of carbon in injected nutrients. The objective of this study is to analyze the effects of a particular inorganic nutrient package known as AERO. AERO is a unique technology used to stimulate indigenous microbes in the oil field. Fig 2.5 shows the various options within each MEOR approach.

This section introduces the first two mentioned approaches and the impact of the MEOR stimulants. The intent of approach (iii) is to utilize only the bacterial byproducts to mimic synthetic chemical EOR processes and is excluded from this discussion.

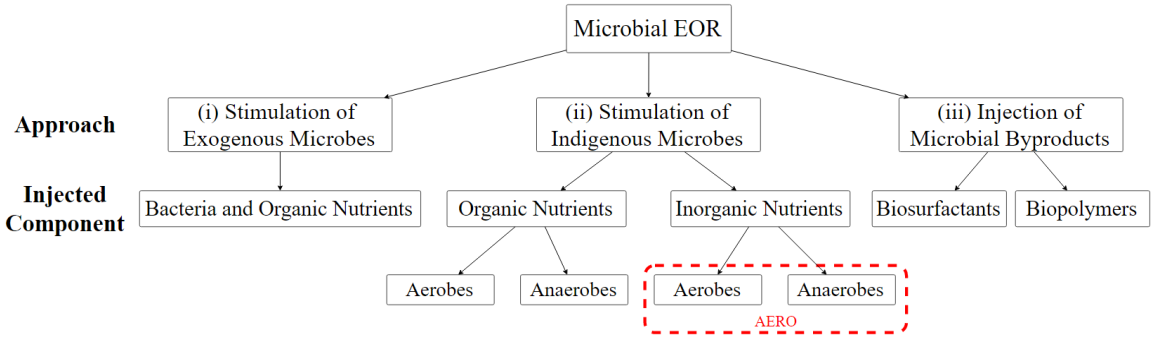


Fig 2.5-Various methods for implementing MEOR

2.2.1 Exogenous Approach

In a review conducted by Donaldson (1991), many of the world's first MEOR field projects utilized approach (i). The advantage of this approach is the byproducts that are generated in the subsurface are determinable. A specific bacterial group presumably produces the same microbial byproducts regardless of their environment.

Johnson (1979) implemented a "huff-and-puff" in 150 stripper wells with the intent that produced gas, acids, and solvents from inoculated *Bacillus* and *Clostridium* bacteria would clean the near wellbore area. Although performance varied across the study, an average of 20 – 30 % additional oil-in-place was recovered from stimulating the exogenous microbes with molasses and mineral salts.

From 1977-82, Petrogen, Inc. conducted field tests with 24 wells. Neither the type of inoculation nor the stimulant was defined. Again, the trial results varied; four wells doubled in oil production rates for 6 months, while 12 other wells experienced an increase of > 50 % for 3 months (Hitzman, 1982).

Lazar (1986) reviewed the results from MEOR field tests in seven reservoirs in Romania. After microbial injections, two of the reservoirs experienced a 200% increase of oil production for a few years; however, the remaining five projects had inconclusive results.

Overall, this conventional MEOR approach showed promise when implemented in the field; however, there were no explanations for the failed projects. Along with inconsistent outcomes, the exogenous approach requires large expenditures for special facilities and equipment for cultivating microbes. It is unclear whether the aforementioned field trials were economical. These two main disadvantages have encouraged many operators to pursue a different MEOR approach.

2.2.2 Indigenous Approach

Some researchers hypothesized that exogenous bacteria are incompatible with the reservoir system or were not capable of penetrating the reservoir (Mcinerney et al., 2005). Reservoirs are the natural habitats to a widely diverse population of indigenous microbes that can vary drastically between reservoirs. These native bacterial populations can impose the issue of out-competing injected cultures for nutrients and carbon, resulting in growth hindrances of the foreign microorganisms.

This triggered the development of an alternate approach, "organic oil recovery," in which in-situ bacterial stimulation shifted to indigenous reservoir microbes (Lazar et al., 2007; Zahner et al., 2012). The first instance of activating indigenous reservoir microbes was recorded by Ivanov and his research group (1983). Their successful implementation was based on introducing oxygen and some salts with injection water.

Stimulating indigenous microbes is a more economical approach. The need and expenses for large-scale cultivation of microbes is removed. Only a few additional equipment is needed to add low-cost nutrients and treat injection brine.

Although relatively inexpensive, there are a few caveats to this approach. "Organic oil recovery" is not applicable to all reservoirs; a suitable microbial population must be present in the producing formations in order to be considered a candidate. Additionally, operators can only presume a group of microbes will be stimulated and not any specific strain. The exact oil-releasing agent can only be surmised and reservoir changes can only be qualitatively defined as a whole.

The five steps of "organic oil recovery" are as follows: (1) initial field screening for suitable conditions, (2) analyze wellbore fluids for indigenous components and microbes, (3) formulate nutrient solution to ensure microbial growth, (4) pilot test in

injection well, (5) field-scale tests. A negative response in any of these five steps will generally result in no additional oil recovery.

Nonetheless, recent implementations were very meticulous and studies indicated this MEOR approach has a higher success rate than the conventional approach (Zahner et al., 2012). From July 2007 through the end of 2010, more than 100 treatments of organic oil recovery were conducted in in the U.S. and Canada. In review, 89 % of these projects were successful with an average oil production increase of 122 % from pre-nutrient production rate.

2.3 BACTERIA BEHAVIOR

Bacteria, like all forms of life, have necessities for survival: water in a usable form, a carbon or energy source, and access to electron acceptors for metabolic processes. In hydrocarbon reservoirs, fluids native to the subsurface provide the resources to support a diverse microbial population.

2.3.1 Water and Carbon Source

Accessible water is the most crucial resource for sustaining life. Approximately 70 % of a bacterial cell is composed of water. Proper hydration is critical for microbes to take in food and to remove unwanted waste products. Additionally, the water can carry various vitamins and minerals needed for cell construction. Thus, single-celled reservoir bacteria live in the aqueous phase and absorb water through their cell membranes.

Most reservoir bacteria are characterized as heterotrophic, meaning the organisms cannot manufacture its own food and instead must obtain energy and carbon by consuming organic substances. Since reservoir bacteria are confined to their host aqueous

phase, the microorganisms can only obtain their organic nutrients from sources in contact with the host water. In carefully controlled sandstone reservoirs, the main source of organic nutrient available is the hydrocarbon phase. Thus, microbes will preferentially grow in areas with high carbon concentrations (oil and water interface). However, providing extra organic nutrients is achievable through the injection of inexpensive substrates such as molasses. These additions may boost cell growth but also deter microbes from settling on the oil and water interface. Water and carbon scarcity is not an issue in oil reservoirs; however, chemical compounds found in injected solutions can alter the bacterial population and growth behavior drastically.

2.3.2 Microbial Metabolism

Metabolism is the chemical process by which a living organism obtains the energy and nutrients in order to maintain life. Reservoir microbes can be categorized by their metabolic processes into aerobic and anaerobic organisms. Anaerobes use inorganic compounds, such as Carbon Dioxide (CO_2), Sulfate (SO_4^-), or Nitrate (NO_3^-), to carry out their metabolic processes, while aerobes use Oxygen (O_2) as their terminal electron acceptor. The four mentioned chemical compounds account for the metabolic needs for almost all reservoir microbes (Skjaelaaen, 2010). The presence and amount of each compound controls the manner in which bacteria can grow.

Over geological timescales, hydrocarbon is degraded by anaerobes, such as methanogens. Methanogens utilize carbon dioxide in the formation for their metabolic processes and produce Methane (CH_4):

$$Oil + CO_2 + \ bacteria \rightarrow CH_4 + more\ bacteria \tag{2.3}$$

Methane produced by methanogens is miscible with the hydrocarbon phase and helps lower oil viscosity. However, this biodegradation process is the least energy efficient of the four metabolic processes. Throughout the timespan of an MEOR project, it is unlikely that methane could be produced in large enough quantities needed for an effective mobility change (Romero-Zerón, 2012).

Sulfate reduction is usage of sulfate as a terminal electron acceptor. When sulfates are present, a group of anaerobes, referred as sulfate reducing bacteria (SRB), can reproduce in months or years. SRB are notorious for their metabolic end products, Hydrogen Sulfide (H_2S):

$$Oil + SO_4^- + \ bacteria \rightarrow CO_2 + H_2S \ + more\ bacteria \tag{2.4}$$

Sulfates can be found in injection water and if left untreated can cause reservoir souring or wellbore corrosion issues. Biocides implemented in oil fields aim to eliminate SRB and their Hydrogen Sulfide production. However, biocides are indiscriminant and may kill both SRB and other beneficial bacteria. Fortunately, SRB can be combatted through the stimulation of more energy efficient groups of bacteria (Hubert and Voordouw, 2007).

Denitrification is the usage of nitrate as a terminal electron acceptor. Nitrate reducing bacteria (NRB) is commonly targeted for stimulation in MEOR projects. Nitrate has a high reduction potential, which means this metabolic process is the most efficient anaerobic process. This respiratory process involves the stepwise reduction of nitrate to nitrite (NO_2^-), nitric oxide (NO), and dinitrogen (N_2):

$$Oil + NO_3^- + \ bacteria \rightarrow CO_2 + N_2 \ + more\ bacteria \tag{2.5}$$

Nitrate treatment is used in many wells to mitigate the corrosion issues related to the SRB. When an adequate amount of nitrate is injected, subsurface microbial activity will shift to nitrate reduction. Since NRB's biodegradation process is more energy efficient than the process of the SRB, the resulting hastened NRB growth will oust the SRB population and reduce Hydrogen Sulfide production.

Aerobic bacteria have the most energy efficient metabolic process and can reproduce at a rapid rate.

$$Oil + O_2 + \ bacteria \rightarrow CO_2 + H_2O \ + more\ bacteria \tag{2.6}$$

Although aerobic bacteria are the quickest to grow, reservoir conditions have limited amounts of usable oxygen. Oxygen must be supplied to the subsurface through injection fluids. However, most field infrastructure and equipment suffer from oxidization issues that must be accounted for when stimulating aerobic bacteria.

2.3.3 Biofilm Growth

Stimulation of reservoir bacteria in a suitable condition will allow bacteria to produce an extracellular polymer substance (EPS). The EPS connect single bacteria to form colonies. In time, colonies of different species may associate for mutual benefits and form biofilms, a group of microorganisms in which layers of bacteria accumulate together. Biofilms may adhere to the fluid-rock surface and at the interface between two fluids. Fig 2.6 shows a biofilm on the interface between oil and water.

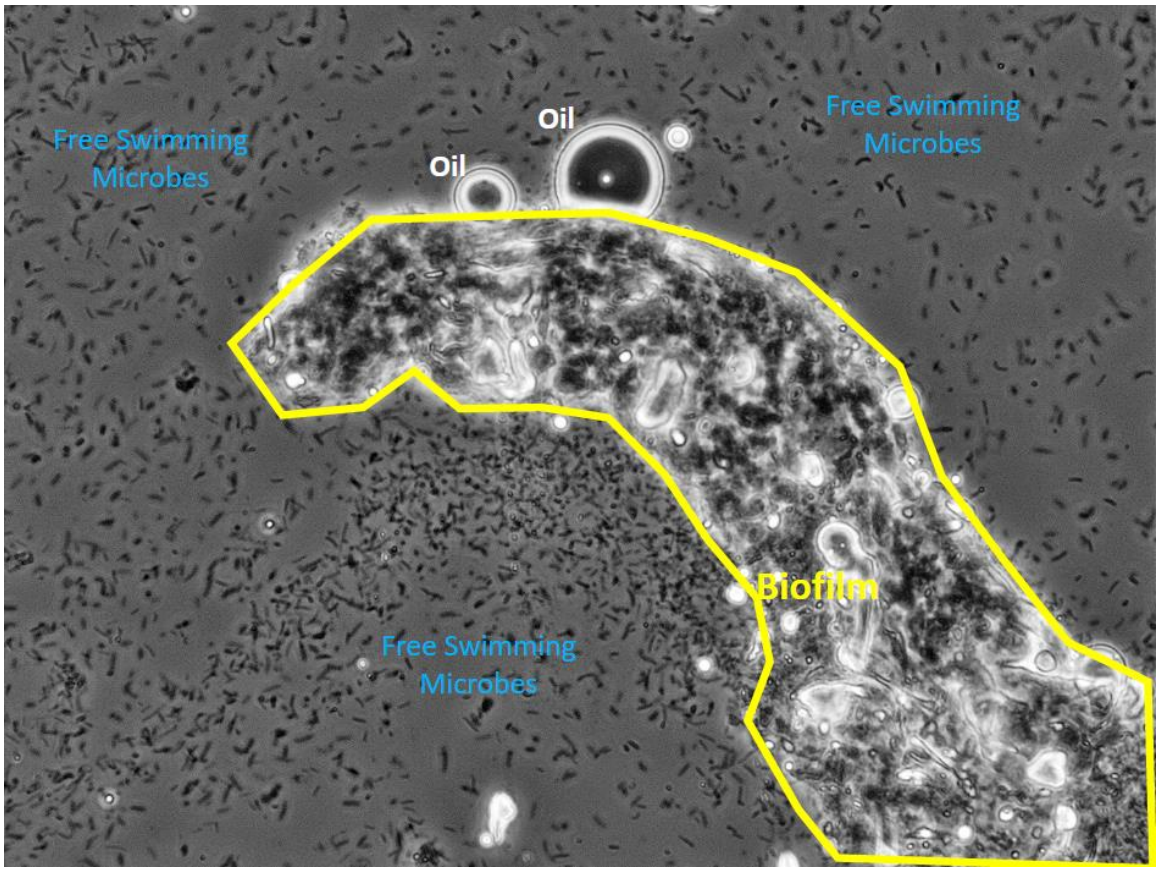


Fig 2.6-Biofilm growth on oil (Glori Energy)

Biofilm growth is dependent on the adsorption rate of cells to the surface, the reproduction rate of microorganisms, and the removal rate of cells lost to fluid flow (Kroukamp et al., 2010). The most successful colonizers would be the cells with the greatest ability to adhere to the surface and multiply quickly. As biofilms grow, cells in the complex three-dimensional structure may become susceptible to fluid flow and disconnected from the biomass. Given the right condition, the detached cells may colonize downstream and form new instances of biofilm. Microbial systems are continuously evolving and their influence on the oil-water-rock systems is oftentimes hard to predict.

2.4 Oil Producing Mechanisms

In MEOR, the microbes and/or their metabolites interact with the system and change the forces that affect the oil. The three main mechanisms by which MEOR releases additional oil are fluid diversion by selective plugging, interfacial reduction through biosurfactants, and solvent production.

2.4.1 Fluid Diversion

The first mechanism involves the modification of the injected fluid flow path. At early stages of a waterflood process, injected brine flows into areas of low resistance or high permeability. As water enters a region and displaces the in-situ oil, that path will require even less energy for subsequent water to follow. As the formation's water saturation increases, injected water requires less energy to displace water than to displace oil, thus a preferential path for injected water is established. This phenomenon diminishes the oil production of secondary recovery methods over time. Eventually, injection costs overcome production profits and the wells are abandoned.

The technique of selective plugging aims to increase the displacing fluid's sweep efficiency by diverting fluid from high permeability zones to lower permeability zones of the reservoir. This is achieved through the injection of nutrients and accelerating biomass growth. The injected nutrients will behave similarly to previously injected brines and follow the pre-established channels. However, as the nutrient concentration increases, bacteria reproduce and conglomerate at a faster rate. As biofilm grows, it constricts pore spaces and increases flow resistance. When the preferential path is no longer the least resistive pathway, the pore space is plugged and injection fluid is forced to divert to previously bypassed oil zones of the reservoir (Bryant et al., 1998).

2.4.2 Biosurfactants

Various surfactants are commonly used to reduce the IFT between the oil and water. This effect lowers the viscous forces required to overcome capillary forces and mobilize the entrapped oil. Although chemically synthesized surfactants can greatly increase the capillary number of a system, they can be expensive and toxic to the environment (Bordoloi et al., 2008; Suthar et al., 2008). Biosurfactants produced by microbes are a possible solution to these issues. Biosurfactants have superior characteristics, such as low toxicity, high biodegradability and tolerance to extreme reservoir conditions (Banat et al., 2000; Cameotra and Makkar, 2004; Desai and Banat, 1997).

2.4.3 Gas and Solvent Production

Some bacteria can produce gases such as hydrogen, carbon dioxide, and methane during their growth phase. Microbes can migrate to pore spaces that would normally be bypassed with conventional gas flooding operations and produce gases to increase reservoir pressure (Bryant and Douglas, 1988). Additionally, Bordoloi and Konwar (2008) have identified the potential of produced gases to dissolve carbonate rocks, which increase permeability and porosity. Microbes can also produce liquid solvents such as acetone, butanol, ethanol, and isopropanol. Both gaseous and liquid byproducts can dissolve into formation oil and lower the oil viscosity. Although this mechanism aids the oil recovery process, it is unlikely that these solvents are produced in quantities needed to mimic the mobility alterations of a carbon dioxide flood (Bryant and Lockhart, 2002).

2.5 Remaining Oil Models

Although MEOR has become more successful over the years, the exact progression by which oil is produced is still debated. In one case of a MEOR pilot (Field X), an increase in oil production rate was observed following the start of nutrient injection but ceased almost immediately after the process was stopped (Sunde et al., 2012, Havemann et al., 2015). The producing formation has an average pay of 3.88 m, showed an average porosity of 23%, and had an average horizontal permeability of 1382 md. At the start of the MEOR project, average water saturation was 35%. Fig. 2.7 shows the oil production of Flied X over the life of the pilot.

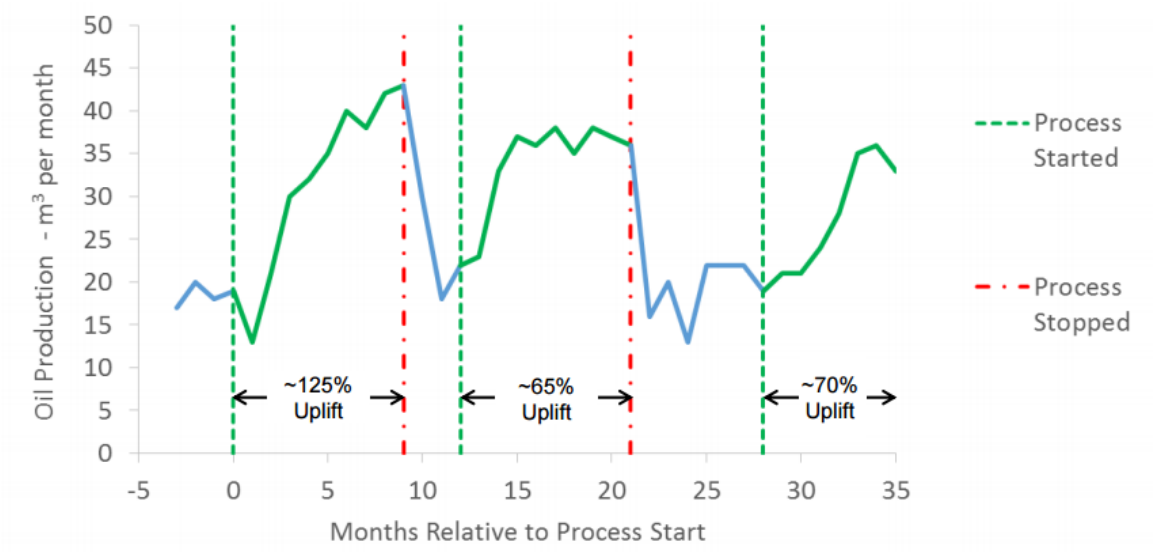


Fig 2.7-Oil production rate rapidly decreases after stopping nutrient processes (modified from Sunde et al., 2012)

Two models of remaining oil are presented, each with its own distinct explanation for this phenomenon. Accurate predictions of the remaining oil distribution and the

identification of oil producing mechanism are crucial to future planning and implementation of EOR projects.

2.5.2 Snap-off Theory

This theory postulates the continuity of the hydrocarbon phase is cut off by the displacing fluid phase (Roof, 1970; Setiawan et al., 2014). For this model, oil snap-off is governed by a threshold pressure, which is expressed as follows:

$$P_s = \frac{\sigma(cos\theta - sin\theta)}{r} \tag{2.7}$$

where P_s is the snap-off threshold pressure, σ is the two-phase interfacial tension, θ is the contact angle, and r is the pore or throat radius (Blunt and Scher, 1995). As water enter a pore, the oil phase becomes unstable from being separated from the pore throat wall. Eventually the water film becomes thicker and breaks the continuity of the non-wetting phase. Fig 2.8 illustrates various oil snap-off processes from an invasion of water.

However, there is a distinction between residual oil and unswept oil. Residual oil refers to the hydrocarbon phase separated as small droplets confined within the rock pores. These disconnected blobs are bound by capillary forces and are immovable by water. Conversely, unswept oil is the hydrocarbon phase left untouched due to the poor mobility ratio between water and oil. Unswept oil can exist as large volumes of untouched oil spanning across nearly the entire distance between wells. If a displacing fluid is able to contact these areas, unswept oil can easily be displaced.

This model's explanation for Field X's rapid production response time is that the microbes were plugging high permeability channels. Rather than releasing capillary bound oil, injection fluid was diverted to areas of unswept oil. As water enters these

zones, oil must be expelled quickly to reach the minimal energy state. Furthermore, once nutrient injection stopped, not enough respiratory components were present to sustain the accelerated microbial activity. Thus, a decay of biomass occurred, injection fluids reverted to flow in high permeability channels, and oil production decreased.

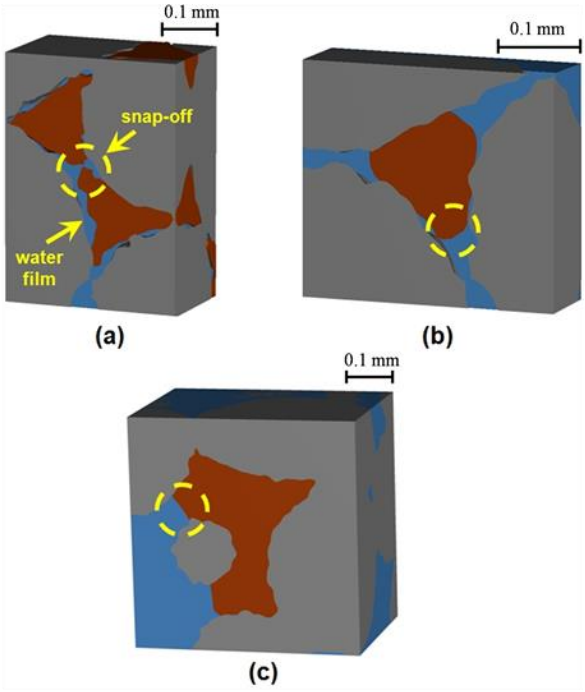


Fig 2.8-(a) moment at which snap-off occurs, (b) trapped oil in a water-wet porous medium, (c) trapped oil in an oil-wet porous medium (Setiawan et al., 2014)

2.5.1 Strand Theory

Sunde and his colleagues (2012) hypothesized that reservoir systems will self-organize to the form that is least resistive to the injected fluids. Instead of snapping off into blobs, the fluids in the system will automatically arrange itself to a profile in which friction is minimized. Due to the system's inherent tendency to minimize the forces at

play, the threshold pressure for snap-off is never reached. Residual oil will redistribute its surrounding water to remain as connected strands from the near injector area to the producer as a complex three-dimensional network. These strands of residual oil remain unproduced because they are trapped under capillary forces in the near producer well area. An illustration of remaining oil under the Strand Theory is presented in Fig 2.9.

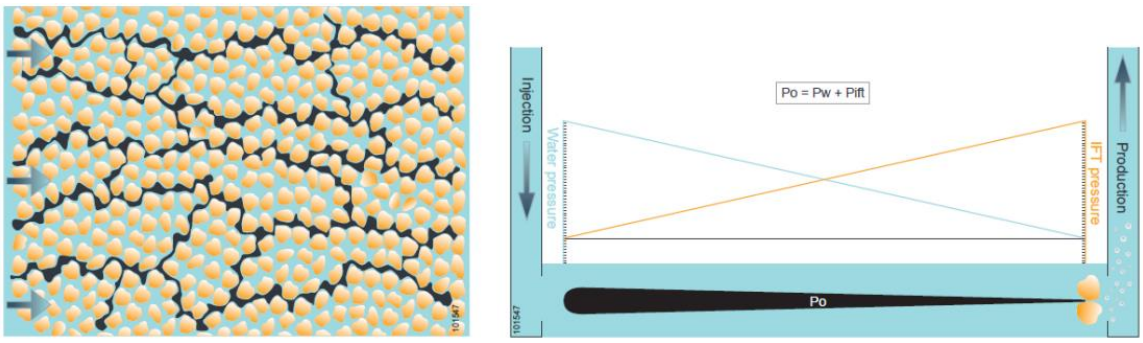


Fig 2.9-(left) Two-dimensional impression of residual oil, (right) fluid pressure relationships (Sunde et al., 2012)

The general orientation of the residual strands is dependent on the forces enacting on the system. The strands are aligned parallel to the direction of flow due to the shear forces of injected water. Additionally, in order for the oil strands to remain stable, the oil pressure (P_o) must equal the sum of the surrounding water pressure (P_w) and pressure created from IFT (P_{ift}). Since pressure decreases from injector to producer wells, the interfacial pressure must be greatest at the producer. Consequently, strands are not uniform in size; the strand diameter must decrease from injector to producer. However, once water flooding stops (P_w is constant throughout the reservoir) the oil strand will redistribute into uniform pore structures. From this model, it is assumed that mixed-wet

reservoirs do not exist and low oil residual saturations in water-wet reservoirs are caused by the beneficial geometry of the residual oil.

This model's explanation for the Field X's rapid response time is that the microbes are reducing the IFT in the near wellbore area. Given enough microbial growth, produced biosurfactants will gradually decrease the IFT. Since oil is connected throughout the entire reservoir, a change in oil pressure at the injector will result in a continuous pulse to the producer. Once the oil pressure can overcome the capillary pressure of the pore near the producer, the oil is immediately produced. Once the nutrient injection stops, biosurfactant production rate slows down. The rapid decrease in oil production is caused by capillary pressure reinstating as the dominant force.

Chapter 3: Experimental Approach

This chapter introduces the materials, equipment set up and experimental methodology used for this study.

A series of experiments were conducted to help determine the applicability of MEOR processes for various system salinities. All steps and measurements were conducted at room temperature of approximately 26 °C. Eleven total coreflood experiments were conducted, three computed tomography (CT) and eight microbial tests. The general experimental methodology is presented in Section 3.3. Results from this study are discussed in Chapter 4.

3.1 MATERIALS

3.1.1 Core

Several core samples were drilled out of large Bentheimer Sandstone outcrop blocks. These cylindrical cores were approximately 2 inches in diameter and 12 inches in length. The brine permeability for these cores ranged from 1.3 to 1.8 Darcy and had a porosity of approximately 24 %.

3.1.2 Hydrocarbon Phase

Crude oil samples obtained from a field were used throughout this study. Special measures were taken to ensure all crude samples were produced anaerobically from the wellhead and preserved in an anaerobic state. The light oil had a viscosity of about 6 cp. The favorable mobility ratio between this oil and the injection brine allowed the waterflood to reach residual saturation quickly. All post-waterflood oil production was attributed to the microbes' effects on the system.

In addition to crude, a pure alkane hydrocarbon was used in one of the CT experiments. The tetradecane, $C_{14}H_{30}$, used in this coreflood had a measured viscosity of 2.2 cp.

3.1.3 Formation and Injection Brine

Each experiments' formation and injection brine was comprised of 1 to 5 wt% Sodium Chloride (NaCl). Brines used in the initial core floods contained an additional 0.1 wt% Sodium Dithionite ($Na_2S_2O_4$) as a reducing agent. However, reducing agents have the possibility to generate toxins that inhibit microbial growth (Fukushima, 2001). Thus, all core reduction components were removed from latter experiments.

Additionally, these aqueous solutions were filtered through a 0.45 μm filter paper for the removal of unwanted bacteria and the prevention of pore plugging. Furthermore, to limit hydrocarbon exposure to oxygen, these solutions were bubbled with Nitrogen or Argon gas for a minimum of 10 minutes per 100 mL solution.

3.1.4 Reduction Solution

The reduction step was conducted through injecting two reduction solutions. The first reduction solution contains 1 wt% NaCl, 1 wt% Sodium Bicarbonate ($NaHCO_3$), and 0.25 wt% Tetrasodium Ethylenediaminetetraacetate (Na_4EDTA). After degassing with Argon gas, 0.25 wt% Sodium Dithionite was added to the solution. The second reduction solution was comprised of the same components as the first, but Na_4EDTA is excluded. When a reduction step was taken, 0.25 wt% Sodium Dithionite was added to all ensuing injection brines to keep both brine and core in a low oxidation-reduction potential (ORP) state. Typical values of low ORP in a core are approximately -600 mV.

3.1.5 Microbial Inoculant

As mentioned in Chapter 2, salt concentration and hydrocarbon phase have strong effects on defining the diversity of a bacterial community. In general, as environment salinity increases, fewer species of microbes are capable of surviving. To maximize the compatibility between bacteria and its surroundings, separate cultures of microbes were grown and specially tailored for each experiment's fluids.

The objective of this study is to observe the oil-producing effects of a mixed and diverse microbial population of both aerobic and anaerobic microbes. Ideally, new bacterial samples are obtained for each experiment; however, costs of each coreflood would be extremely high. Instead, a few base cultures were obtained from reservoirs and is grown in the lab. Two methods can be used to develop base cultures into suitable microbial inoculants for corefloods.

The first method was to breed cultures in a static environment known as batch cultures. Reservoir microbes and filtered brine with a target salinity are placed into a glass septa bottle. A hydrocarbon phase, such as crude oil, is then added to serve as their carbon food source. Since these cultures contain a mixture of both aerobic and anaerobic microbes, respiratory gases must be supplied to the closed container. Nitrate-laden brine is introduced to the septa bottle to stimulate Nitrate Reducing Bacteria (NRB) growth, while Oxygen was supplied by injecting ambient air for the anaerobic bacteria. All fluids were filtered through a 0.45 micron filter before being introduced to a closed system. These cultures were incubated in a 35℃ oven and closely monitored for nutrient consumption. Although microbes in a batch culture initially reproduce rapidly, the exponential growth cannot be sustained; the nutrients within the system are eventually all consumed and the accumulation of waste products hinders growth (Tankeshwar, 2016). Fig 3.1 shows an example of a batch culture inoculum grown in a glass septa bottle.

Fig 3.1-Batch Culture Inoculum Grown in Glass Septa Bottle (Satyan, 2008)

The second method for preparing the core inoculum is to grow the microbes in a dynamic system. In this type of system, microbes must resist the shear forces induced by the flowing water in order to maintain a stable grow. Initially when a flowing system's quantity of microbes is low, there is adequate space for individual strains to adhere to the solid surface. As bacteria reproduce, available solid surfaces become limited, thus forcing cells to stick to one another and form biofilm to prevent from being washed away. When removed from the biofilm, it can be expected that these microbes will repeat the growth pattern and quickly form biofilm in a different environment (Bester et al., 2005). Using continuous flow cultures in coreflood experiments can expedite the oil releasing process.

Filtered brine and then oil are injected into a 1 ft long glass bead pack in a cylindrical column at room temperature. A bacterial culture was then introduced to the system followed by a continuous flow of nutrient-laden brine. The bacteria are continuously stimulated until signs of adequate nutrient consumption are present. These

microbes are then removed from the column and inoculated into the experimental core. Fig 3.2 shows the dynamic system used to grow an inoculum in a column.

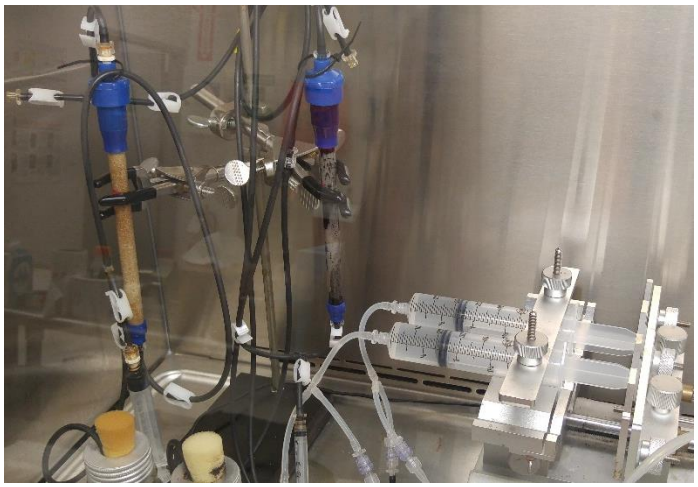


Fig 3.2-Microbial Inoculum Grown in Column

3.1.6 Nutrient Brine

Commercially prepared nutrient brines were used throughout this study. These solutions have the same salinity as the injection brine used in preceding steps and are filtered to minimize the introduction of unwanted bacteria. As mentioned in Chapter 2, the energy efficiency is greatest for aerobic and NRB. These target groups of microbes are stimulated only through the nutrient brine. Thus, these nutrient brines are aerobic and contain sufficient amounts of Nitrate ions as well as other components to stimulate bacterial growth.

3.1.7 Sodium Acetate Solution

A separate solution containing 1 wt% of Sodium Acetate (CH_3COONa) was also prepared for the nutrient injection step. Trace amounts of CH_3COONa can help boost the metabolism of microbes and accelerate their growth.

The objective of the experiments is to stimulate and maintain microbial growth in a core rather than continuously introducing new bacteria to a core. Confining microbial growth to areas only within the core requires a special configuration for fluid injection. Nutrient brine may be kept in an accumulator for several days at a time; any exposure to organic compounds, such as Sodium Acetate, would result in unwanted bacterial growth in the brine accumulator. Thus, Sodium Acetate was injected from a separate pump and into the core via a port downstream of the nutrient brine.

3.1.8 Glycerol

After MEOR processes, a high viscosity glycerol and brine solution was sometimes injected into the core. A large contrast between the oil and displacing fluid viscosities would result in an extremely favorable mobility ratio. For this study, a glycerol solution with a viscosity of about 50 cp was used to quantify any remaining unswept oil left in the core.

3.2 EXPERIMENTAL SET UP

An ISCO syringe pump was used to regulate all liquid flow rates. The pump feeds a 1.5 % Sodium Sulfite (Na_2SO_3) brine into a stainless-steel accumulator. As the pump fluid enters one end of the metal accumulator, the piston within displaces waterflood brine or nutrient brine out of the other end and into the core. Piston displacement is critical to microbial coreflood experiments as contact of nutrient brine with other fluids can result in contamination. Flow lines are hydraulically connected to a pressure transducer immediately before and after the core. Experimental effluents were collected in either a fractional collector or an oil trap.

Corefloods performed within the CT scanner require a special set up. After leak tests have been conducted, the epoxy-sealed core was mounted into a vertical lift system. Since the CT scanner can only scan one plane at a time, the hoist raises and lowers the core in order to get measurements for the entire length of the core. Scans of the entire core were performed at various stages throughout the experiment, namely when the core was evacuated, after imbibing with water, after oil injection and throughout the waterflooding step. Fig 3.3 shows the schematics of a CT coreflood experiment.

For microbial experiments, a separate medical syringe pump was connected between the accumulator and core for the injection of Sodium Acetate. Additionally, a backpressure regulator was added to latter experiments to prevent gas from volatilizing out of the oil phase within the rock. The experimental setup that was used for the microbial corefloods is shown schematically in Fig. 3.4.

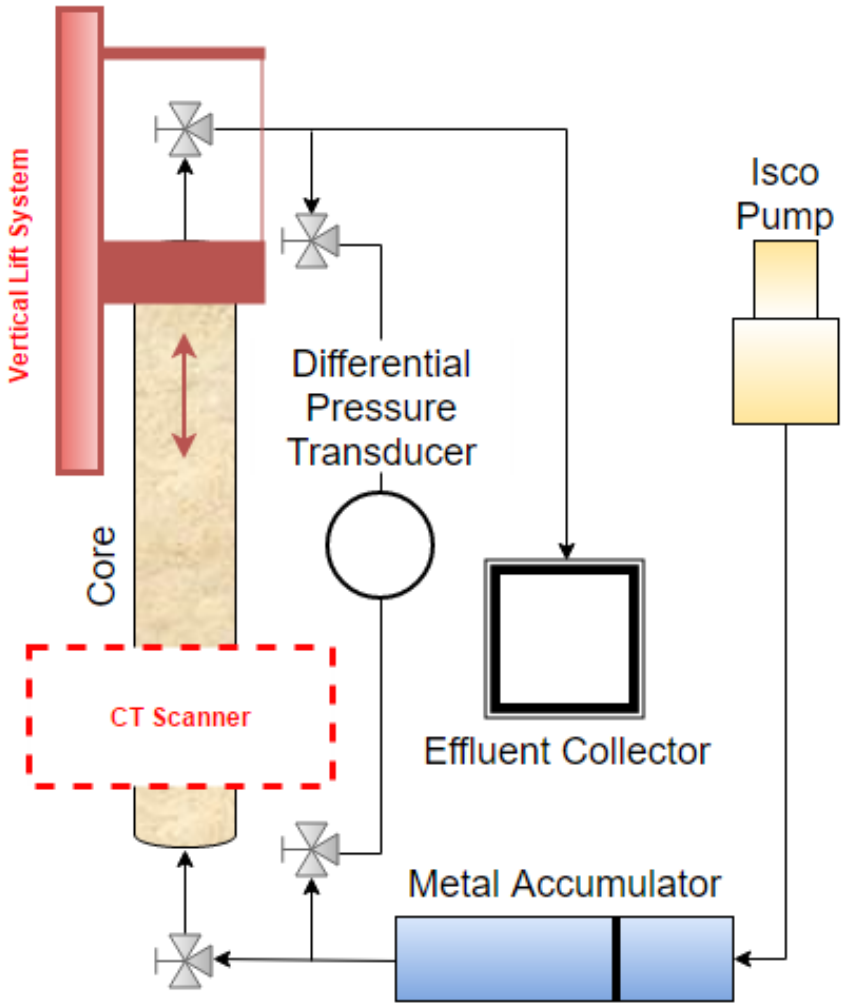


Fig 3.3 Schematic of CT experimental setup

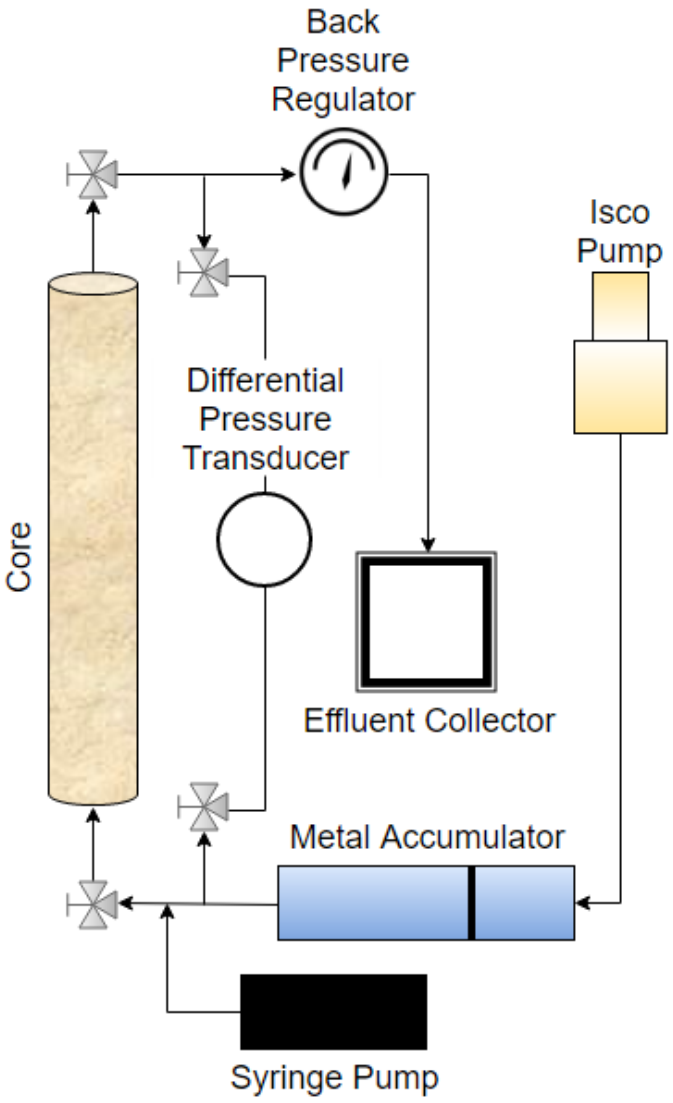


Fig 3.4 Schematic of microbial experimental setup

3.3 METHODOLOGY

3.3.1 Core Preparation

Each sandstone core was sealed in a polycarbonate tube. First, caliper measurements were taken to obtain accurate dimensions of the core. After determining the bulk volume, a quick-drying 5-min epoxy was used to attach polycarbonate end caps to each of the core's circular face. Due to the rock's high permeability, slower drying epoxy solutions can seep further into the core before solidifying. Thus, for high permeability cores, such as Bentheimer, a layer of a quick drying epoxy glue was applied to the entire lateral surface of the core to isolate interior pores from future slower drying epoxy.

A layer of vacuum grease was then applied to the bottom injection face and was allowed to enter a few centimeters into the annulus between the core and a polycarbonate tube. This enacts as a seal to keep slow drying epoxy solutions from leaking out the bottom. Next, a mixture of 2:1 ratio of Epon 828 resin and Versamid 140 hardener was poured into the annulus and left to dry overnight.

Steel ports, tubing, fittings, and valves were used in appropriate locations to minimize system exposure to oxygen. The core was then pressurized with air to 60 psi and submerged in a water bath. This leak test was conducted to ensure the integrity of the epoxy seal and ports. Fig 3.5 shows a finished core encased in epoxy with metal inlet and outlet valves.

Fig 3.5 Epoxy Sealed Bentheimer Core

3.3.2 Air Permeability

A preliminary screening of each core can be conducted through an air permeability test. The steady-state fluid flow rate was recorded for various air injection pressures. These measurements along with core dimensions can be used in Darcy's Law to calculate the rock's permeability to air.

$$q = -\frac{kA(P_o^2 - P_i^2)}{2\mu P_o} \tag{3.2}$$

where q is the air flow rate, k is the permeability, A is the cross-sectional area of the core, P_o and P_i are the air outlet and inlet pressure respectively, and μ is the air viscosity. Abnormally high results may show signs of fractures hidden within the core, while lower than expected permeability measurements may indicate the possibilities of plugged pores or high heterogeneity.

3.3.3 Brine Saturation

After rock screenings were completed, pore volume measurements were conducted by saturating the core with brine. One end of a core was connected to a vacuum pump and evacuated for a minimum of three hours. The core system was then disconnected from any external apparatuses. The initial weights of the core and brine bottle were recorded. The brine bottle was then connected to the inlet port and allowed to imbibe into the core. After an equilibrium was reached, the final weights of the core and brine bottle were measured. Since the flow lines, injection ports, end caps, and valves did not contribute to the rock's pore volume, the dead volume was calculated.

$$V_p = \frac{W_B - W_A}{\rho_w} - V_{dead} \tag{3.3}$$

where V_p is the core's pore volume, W_B and W_A are the core system's weight before and after brine saturation, ρ_w is the water density, and V_{dead} is the dead volume that does not contribute to the core's void space.

3.3.4 Core Reduction

The first reduction solution was injected at 5 PV/day until the effluent iron concentration decreased to a steady state level (e.g. below 10 ppm) and ORP becomes the same as injected solution. Afterwards, the second reduction solution was injected into the core at the same rate until the pH of the effluent matches that of the influent. Both reduction solutions were vacuum loaded into a polycarbonate accumulator and injected by a mineral oil drive.

3.3.5 Tracer Test

A tracer tests was conducted to assess a core's porosity and heterogeneity. A brine with higher or lower salinity is injected into the core at a constant rate until effluent salinity is equivalent to tracer brine salinity. Effluent water was fraction collected into plastic centrifuge tubes. The area under the plot of normalized salinity versus volume injected gives an approximate measurement of the volume of water in the core. Tracer tests conducted prior to oil injection gave estimations of the core's pore volume.

3.3.6 Brine Permeability Test

Formation brine was injected into the core at flow rates ranging from 15 mL/min to 30 mL/min. Steady state pressure drops were recorded and used in Darcy's Law to calculate the core's permeability to brine.

$$q = -\frac{kA\Delta P}{\mu L} \tag{3.4}$$

where q is the brine injection rate, k is the permeability, A is the cross-sectional area of the core, ΔP is the pressure drop, μ is the brine viscosity, and L is the length of the core.

3.3.7 Oil Saturation

When handling the crude oil, all associated fittings and equipment were leak tested to ensure minimal hydrocarbon exposure to oxygen. Containers holding liquids were initially connected to a vacuum gauge and evacuated. After reaching a steady level of low pressure, the system is closed off. Any changes in the pressure gauge will indicate

an imperfect seal. For all tubular connections, visual leak checks were performed by pressurizing all segments of the experimental set up with water/gas. A fully sealed apparatus will have no fluids escaping between the connections.

After all brine measurements were complete, a hydrocarbon phase in an anaerobic state was flooded into the core. First, a spun-aluminum container was vacuum pumped for an hour. Next, an argon drive was used to push the crude oil was through an inline filter into the evacuated metal vessel. The oil is filtered through a 1.2 μm filter to remove any suspended sands and particulates that may plug the core.

This system was then connected to the inlet port of the core and pressurized with argon gas. Oil flowed into the core at a constant pressure until brine effluent cut reached below 1 %. Produced water was collected into volumetric burets and used to calculate the initial oil saturation through the following equation.

$$S_{oi} = \frac{V_w}{V_P} \tag{3.5}$$

where S_{oi} is the initial oil saturation, V_w is the total volume of water collected during this step, and V_P is pore volume. Steady-state oil flow rate and core differential pressure were recorded for measuring oil end-point relative permeability.

3.3.8 Waterflood

Once the initial saturation of oil and water has been established, anaerobic injection brine was flooded into the core at a constant flow rate of 1 to 5 pore volumes per day. All oil produced from the core was fraction collected into graduated glass test tubes. The core's steady-state differential pressure was recorded and used for relative

permeability calculations. Residual oil saturation to waterflood, S_{orw}, was determined from the effluent volume levels.

3.3.9 Microbial Inoculation

Although reservoirs have thriving populations of indigenous bacteria, cores used in this study do not have nearly as much microbial activity. Thus, for all microbial coreflood experiments, a lab grown culture that replicates a bacterial population found in the field was introduced to the core to start the MEOR recovery process.

A brine solution containing microbes was first loaded into a sterile syringe. It is then connected to a syringe pump and the solution is injected into the core at the same constant flow rate as used in the waterflood step.

3.3.10 Nutrient Injection

Immediately following the microbe solution, a continuous source of nutrient is required to support the growth of microbes. The nutrient brine with the desired salinity is loaded into one end of a metal accumulator. A 1.5% Sodium Sulfite solution is used to push the accumulator's piston and displace nutrient brine into the core. In addition to nutrients, a separate syringe pump is used to inject 1 ppm/day of Sodium Acetate into the core. Sodium Acetate was injected separately to minimize unwanted growth in the metal accumulator that holds the nutrient brine.

A population of microbes can take several days to reach its maximum potential, thus, nutrient injection was carried out for 3 – 4 weeks. All effluents were collected into an oil trap and oil levels were recorded periodically.

Chapter 4: Experimental Results and Analysis

This chapter presents the results of the three CT and the eight microbial experiments performed throughout this study.

The physical properties of each core are divided into Tables 4.1 and 4.3. All experiments were performed in Bentheimer sandstone cores at room temperature. These cores all had relatively the same high permeability (1250 mD to 1880 mD) and porosity (21 to 25 %). All crude oil used throughout the entire study was produced from the same field and had a typical viscosity of 6 cp. The tetradecane used in one of the CT experiments had a viscosity of about 3 cp.

The chapter is divided into two sections. In section 4.1, results from the CT experiments are presented. The objective of these experiments was to visualize the connectivity of the residual oil phase using a medical CT scanner. One coreflood was performed with a pure alkane hydrocarbon phase and two corefloods utilized the light crude oil. CT experiment oil saturations are listed in Table 4.2.

Section 4.2 discusses the experimental results from stimulating microbes. All microbial inoculations and nutrient brines were prepared by team members of Glori Energy. The performance data for the microbial corefloods are summarized in Table 4.4.

Table 4.1 Physical data for CT coreflood experiments

Coreflood number	CT1	CT2	CT3
Diameter, cm	5.1	5.0	5.0
Length, cm	29.6	29.9	30.3
Area, cm^2	20.5	19.6	19.6
Bulk Volume, cm^3	607	585	593
Pore Volume, cm^3	139	136	131
Porosity, %	23	23	22
Permeability, md	1508	1564	1251

Table 4.2 Performance data for CT coreflood experiments

Coreflood number	CT1	CT2	CT3
Initial			
Flood Orientation	Vert.	Vert.	Vert.
Brine Salinity, %	3.5	3.5	3.5
Hydrocarbon Phase	Tetradecane	Crude Oil	Crude Oil
$S_{oi,}$ %	69.0	76.68	75.4
Waterflood			
Flow Rate, ft/Day	5	5	5
$S_{orw,}$ %	30.0	25.8	32.3

Table 4.3 Physical data for microbial coreflood experiments

Coreflood number	M1	M2	M3	M4	M5	M6	M7	M8
Diameter, cm	5.1	5.1	5.1	5.1	5.1	5.0	5.0	5.0
Length, cm	30.2	29.8	30.4	30.4	30.4	30.2	30.1	30.3
Area, cm^2	20.8	20.6	20.5	20.5	20.4	19.5	19.5	19.4
Bulk Volume, cm^3	627	614	624	623	620	589	586	588
Pore Volume, cm^3	139	143	159	129	146	136	141	139
Porosity, %	22	23	25	21	24	23	24	24
Permeability, md	1881	1398	1446	1374	1530	1637	1770	1542

Table 4.4 Performance data for microbial coreflood experiments

Coreflood number	M1	M2	M3	M4	M5	M6	M7	M8
Initial								
Flood Orientation	Hor.	Hor.	Vert.	Vert.	Vert.	Vert.	Hor.	Hor.
Brine Salinity, %	2.5	5	2.5	5	1	1	5	5
$S_{oi,}$ %	66.8	71.2	66.9	77.2	76.2	80.7	85.9	82.2
Waterflood								
Flow Rate, ft/Day	1	1	1	1	1	1	1	5
$S_{orw,}$ %	31.6	32.4	34.3	26.3	34.9	35.7	27.0	30.8
Microbial								
Inoculum Condition	Static	Static	Static	Dynamic	Dynamic	Dynamic	Dynamic	Dynamic
Additional Oil, mL	0.10	0.17	1.60	8.62	0.10	0.10	9.10	2.70
% OOIP	0.11	0.17	1.48	8.26	0.09	0.09	7.46	2.30
$S_{orm,}$ %	31.6	32.3	33.3	19.7	34.8	35.7	20.6	28.8

4.1 CT EXPERIMENTS

The objective of these experiments was to test the connectivity of residual oil. Based on the strand theory (Sunde et al., 2012), it is hypothesized that a change in water injection pressure will result in a change in residual oil distribution. Vertical corefloods were conducted inside a CT scanner to visualize the fluid saturation profile.

The length of the core was divided into 1 cm scanning sections. Each core had thirty slices with slice 1 being closest to the outlet and slice 30 being closest to the injection port. However, data near the both ends of the core are not presented because of the interference in CT absorption generated by the plastic end caps.

The fluid rock systems were scanned at various stages of their experiments, more precisely at the end of core evacuation, post water saturation, after hydrocarbon phase injection, throughout the water flood, and at steady state after changes in water injection rate.

The dry core scan is described by:

$$CT_{Dry} = (1 - \phi)CT_R + \phi CT_A \tag{5.1}$$

where CT_{Dry}, CT_{R}, and CT_{A}, are the dry core, rock grain, and air CT numbers.

All subsequent fluid-saturated core scans is described by:

$$CT_M = (1 - \phi)CT_R + \phi(S_w CT_w + S_o CT_o) \tag{5.2}$$

where CT_{M}, CT_{w}, and CT_{o} is the total measured, water, and oil CT numbers respectively.

The CT number of air, water, and oil can be easily measured by scanning the fluid in a large container. Subtracting equation 5.2 from 5.1 yields equation 5.3.

$$\phi = \frac{CT_M - CT_{Dry}}{S_w CT_w + S_o CT_o - CT_A} \tag{5.3}$$

When comparing only the dry core and water-saturated core scans, porosity can be determined by setting oil saturation to zero. After the porosity is determined, a reorganization of equation 5.3 will give the oil saturation profile when comparing oil-filled cores with the dry core.

$$S_o = \frac{CT_M - CT_{Dry} + CT_A\phi - CT_w\phi}{\phi(CT_o - CT_w)} \tag{5.4}$$

Calculations from equations 5.3 and 5.4 are repeated for each point of measured data.

4.1.1 CT Coreflood #1

In the first CT coreflood, tetradecane was used as the hydrocarbon phase. The core was secured vertically into a CT scanner. Following the evacuation of the core, 3.5 % NaCl brine was imbibed into the rock. The difference between the core's dry weight and saturated weight divided by brine density yields a calculated pore volume of 139 mL. The core's brine permeability was then measured to be 1508 md. Next, tetradecane was injected into the core until water production ceased. The same initial saturation brine was then injected into the rock at 5 PV/day for 24 hours. Water is injected into the inlet side (slice 30), the tetradecane is produced at the outlet (slice 1). After an hour of

waterflooding (~0.2 PVI), areas further downstream from the injection port (slice 2 through 20) did not experience a saturation change. After 2 hours (~0.4 PVI) of waterflooding, the injection waterfront reached the outlet and tetradecane saturation decreased throughout the entire core. After 4 hours of waterflooding (~0.8 PVI), the core reached its residual oil saturation; no oil was produced for several pore volumes. Data from Fig 4.1 shows the displacement of tetradecane over time when conducting the waterflood. Water flow rate was then decreased to 3.0, 1.0, and 0.0 ft/day and then increased back up to 5 ft/day. For each flow rate, differential pressure readings stabilized and reached steady state after a few minutes. Steady state oil saturation for each flow rate is shown in Fig 4.2.

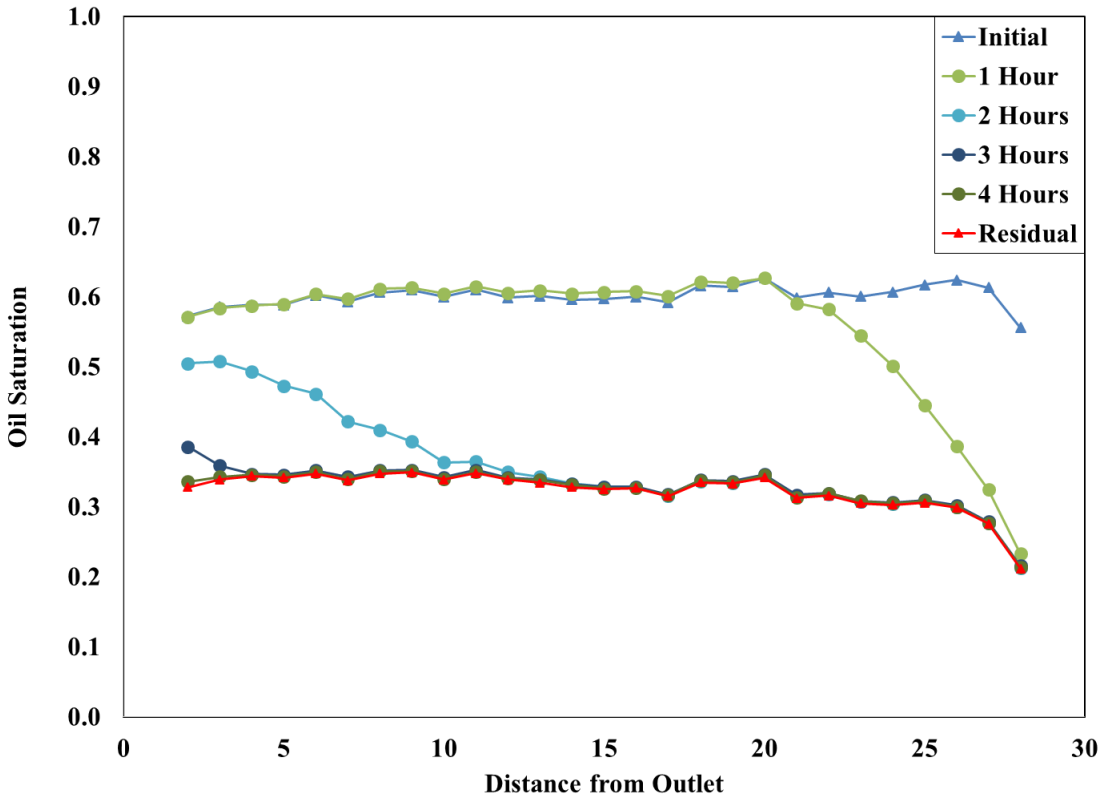


Fig 4.1-Tetradecane saturation during waterflood for CT #1

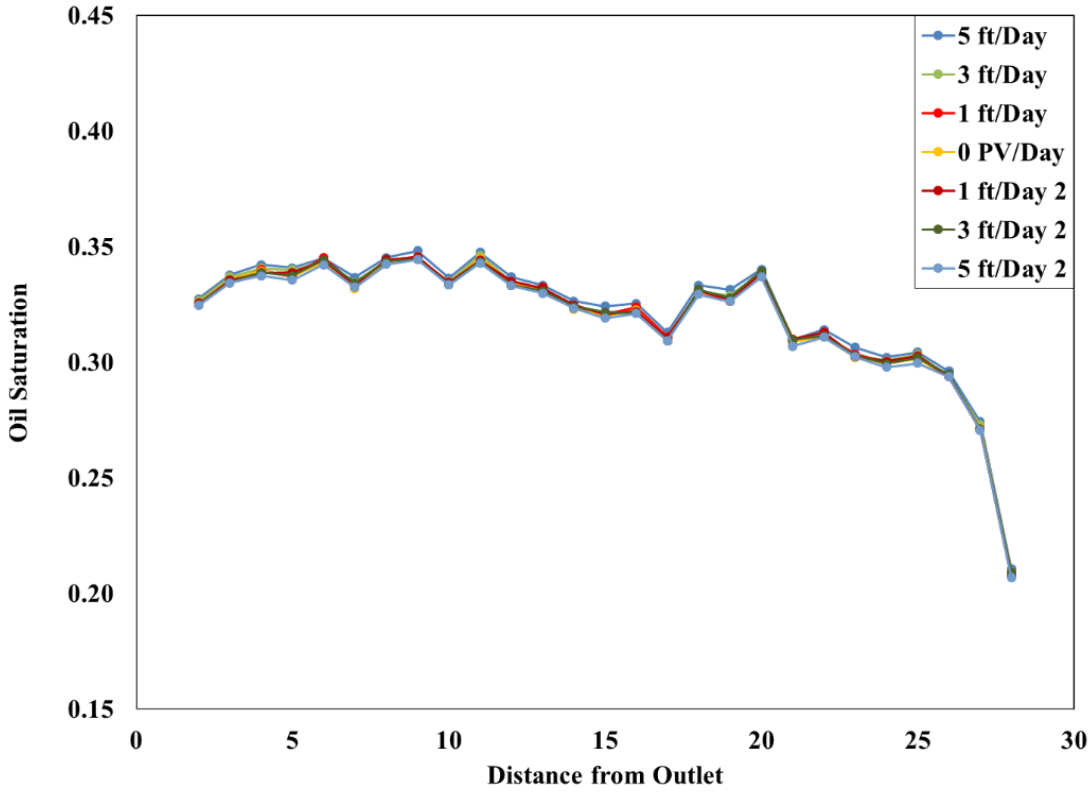


Fig 4.2-Tetradecane saturation with varying flow rates for CT #1

The data collected from the tetradecane indicated minimal changes in oil distribution after reaching residual saturation. Slight deviations in the data are due to the CT scanner's margin of error, which is often affected by the heat of the x-ray tube.

4.1.2 CT Coreflood #2

The second CT coreflood was conducted to confirm the results of the first experiment; however, tetradecane was replaced with the light crude oil. The glass bottle containing the oil is pressurized with argon gas via a needle in the bottle's rubber septa.

The glass bottle is then connected to a vacuum evacuated spun-aluminum container and oil is allowed to flow from the high-pressure bottle into the low-pressure metal container.

The core's pore volume and permeability were 136 mL (23 % porosity) and 1564 md, respectively. After oil injection, waterflood was conducted with 3.5% NaCl brine at 5 ft/day for 24 hours. The oil saturation profile throughout the waterflood is shown in Fig 4.3. However, after the conclusion of the waterflood, residual CT scans detected areas of lower CT density within the core. Due to the low density of the oil, the aforementioned regions translated into a perceived increase in residual oil saturation.

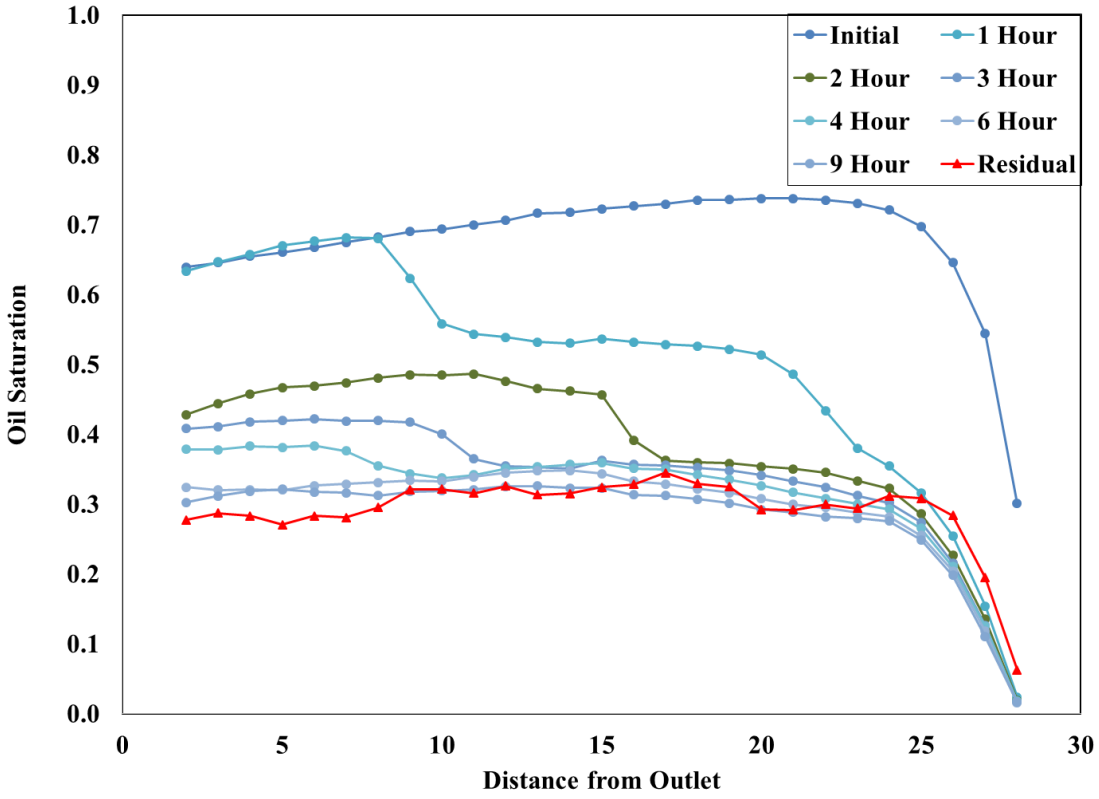
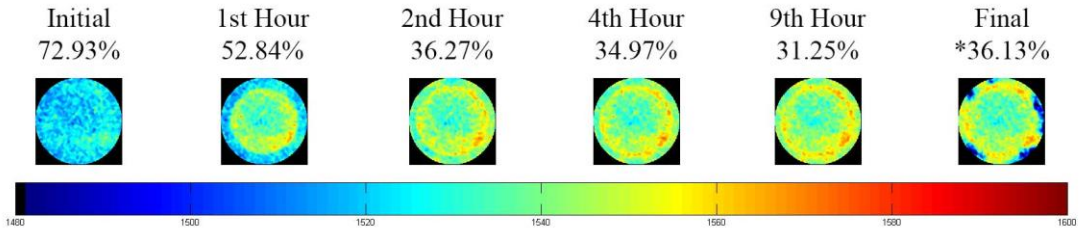


Fig 4.3-Oil saturation during waterflood for CT #2

Fig 4.4 shows the change of scanned CT number in Slice 17 with respect to time along with the resultant oil saturation calculations. For this experiment, the oil had a lower CT number than the injection brine. Since the core initially starts with a high oil saturation, this translates into detecting a low CT number profile. As waterflood continues, denser water displaces the less dense oil and results in an increase in CT number.



*Calculated oil saturation does not represent actual due to abnormally low CT number

Fig 4.4-Scanned CT number profile and calculated oil saturation for CT#2 slice 17

However, after the 9th hour (~1.9 PVI), a decrease in CT number was detected. After 24 hours (5 PVI) of waterflooding, the final CT number profile is shown in Fig 4.4. A superficial increase in calculated oil saturation resulted from the raw CT number data. However, an increase in oil volume within the core is physically impossible since no additional oil was added to the core. Initial guesses for this abnormality was that, although near impossible, gases may have accrued in the fluid accumulator and were accidentally injected into the core.

Interestingly, after water injection stopped, the decrease in CT number continued. With no new fluids entering the core, the only explanation was that light hydrocarbon

components were evolving from the oil as a gas phase. Fig 4.5 shows the skewed oil saturation calculations due to the continual decrease in CT number.

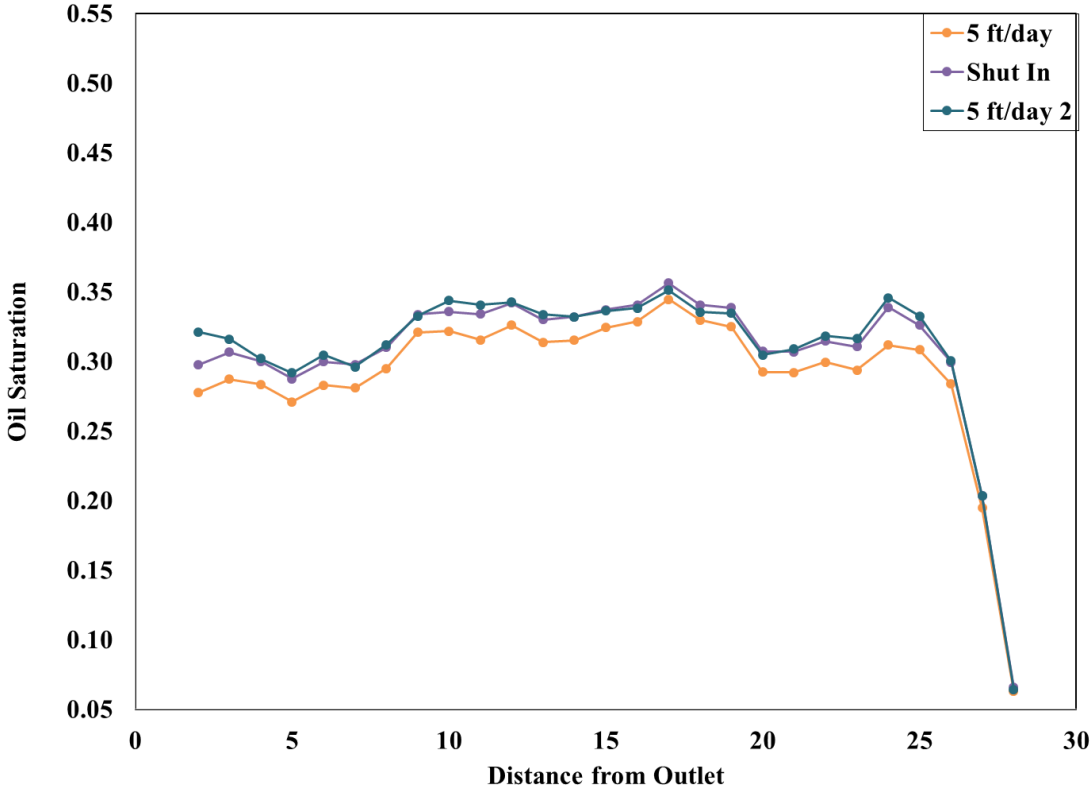


Fig 4.5-Oil saturation increases even after stopping brine injection

4.1.3 CT Coreflood #3

Coreflood #2 was repeated in coreflood #3 with the same procedure given the irregularity described in Section 4.1.2. Extra measures were taken to ensure that no gases were injected into the core; all fittings and connections were leak tested and all liquid accumulators were vacuumed and fully saturated with respective liquids.

The core used in this experiment had a pore volume of 1251 mL (22 % porosity) and permeability of 131 md. Normal results were detected for the first few pore volumes

of water injection; scanned oil saturation decreased monotonically at any given point in the core. However, the data in Fig 4.6 shows an observed increase in oil saturation occurring at the end of the waterflood similar to CT Coreflood #2.

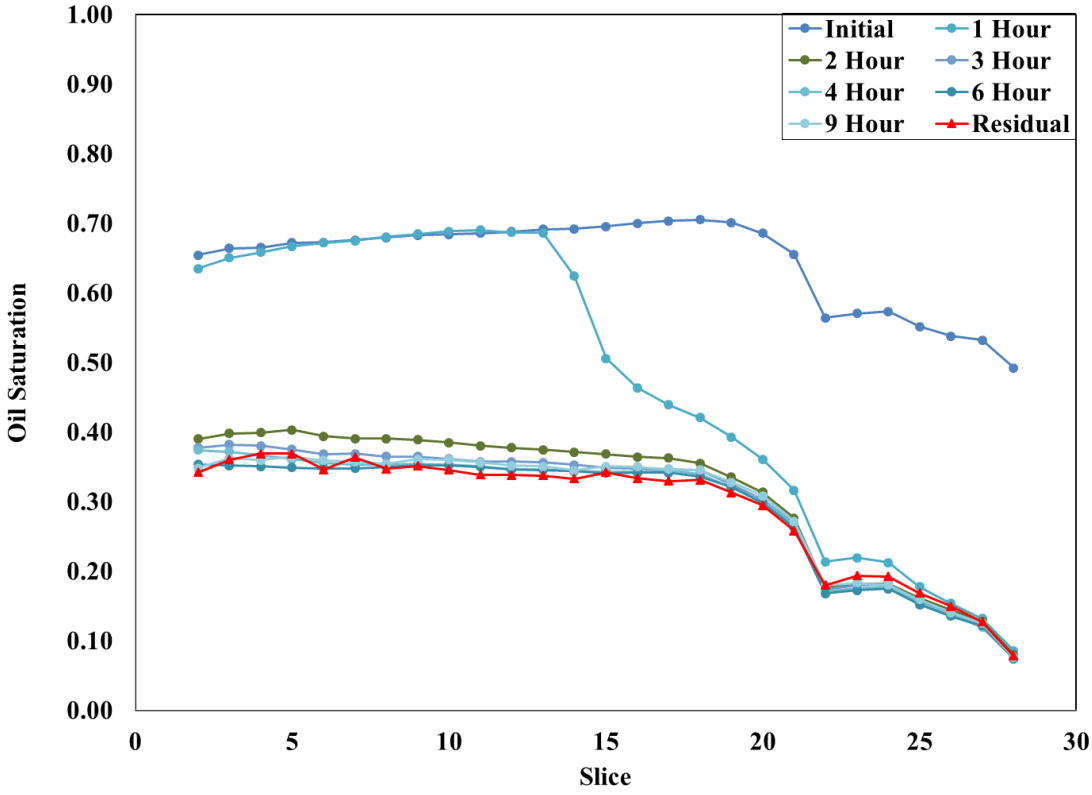
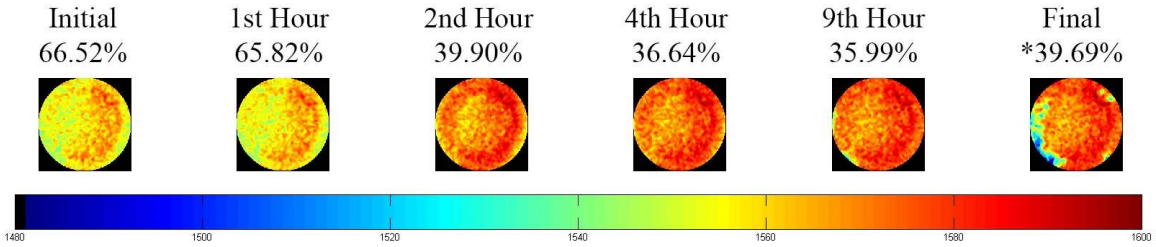


Fig 4.6-Oil saturation during waterflood for CT #3

Fig 4.7 shows the decrease in CT density specifically for slice 4. The decrease in CT number at a location far from the inlet implies that this phenomenon was not caused by gas injection. Any injected gas would immediately affect the near injection area. An increase in CT density was not detected until after 9 hours of waterflooding (~1.9 PVI). Additionally, the shape by which the CT profile changes suggests that the decrease was

caused by local effects. Based on these two observations, it was made apparent that gases were not being injected, but gases may have evolved out of the oil phase.



*Final calculated oil saturation do not represent actual due to abnormally low CT number

Fig 4.7 Scanned CT number profile and oil saturation for CT#3 slice 4

Further evidence to support this premise is that the CT number decreased even further after water injection pressure reached 0 psi. Fig 4.8 shows the oil saturation change before and after water injection shut in.

Calculations based on the change in CT number indicate a 0.3 % change in the residual oil saturation. Although gas in the core has minimal effects on the overall mass balance, CT scans are sensitive to trace amounts of gas. A direct comparison in oil saturation between each waterflood rate could not be concluded.

A potential solution to this issue is to attach a backpressure regulator at the effluent end of the core. This will increase the overall pressures within the core and may keep the dissolved gases from escaping from the liquid hydrocarbon phase.

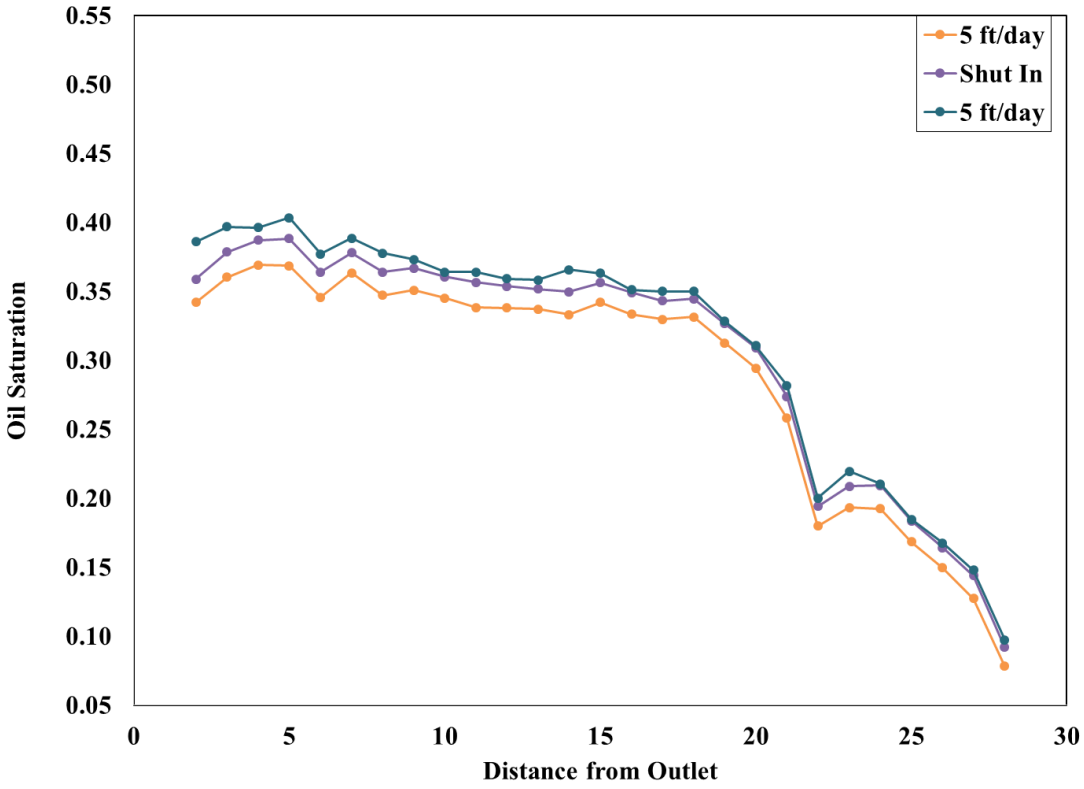


Fig 4.8-Oil saturation with varying flow rates for CT #3

4.2 MICROBIAL EXPERIMENTS

4.2.1 Microbial Coreflood #1

The objective of the microbial corefloods was to observe microbes' ability to reduce residual oil saturation in-situ. The horizontal core was first vacuum evacuated and then flooded with a 2.5 % NaCl brine. The core's pore volume was measured to be 139 mL. After the core was reduced with two reduction solutions described in chapter 3, sodium dithionite was added to the waterflood brine. The solution was used to flush the core and measure the permeability, which was calculated to be 1881 md. Next, crude oil was injected into the core at 50 psi. This pressure was chosen to stay within the equipment's range of safe operations. Initial oil saturation was determined to be 66.8 %. Brine was injected into the core at a flow rate equivalent to 1 ft/day.

After reaching residual oil saturation of 31.6 %, 15 mL of a batch inoculum was introduced into the core. These microbes along with subsequent 2.5 % salinity nutrient brine were injected at 1 ft/day. Throughout the entire 20 pore volumes of nutrient injection, only 0.1 mL of oil was gradually produced. Although Fig 4.9 only shows data up to 13 pore volumes of total injection, no changes in the system were observed for the remaining 12 pore volumes.

No substantial oil mobilizing effects of MEOR were observed with this experiment. Initial hypothesis surmised that the microbes lost activity and were not compatible with the chemical components found in the core environment. Analysis of the effluent samples revealed nitrite concentration unexpectedly dropped to zero, indicating the metabolic process that converts nitrate to nitrite had ceased. This was later attributed to the presence of sodium dithionite, which can be toxic to microbes.

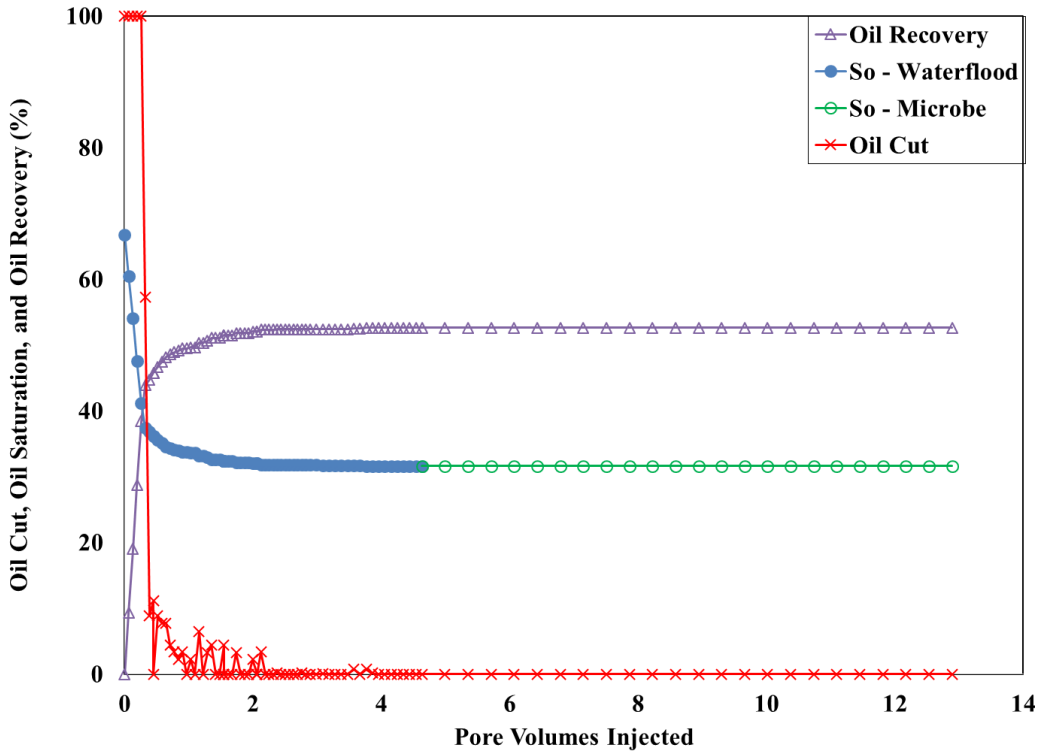


Fig 4.9-Oil recovery for microbial coreflood #1

4.2.2 Microbial Coreflood #2

The objective of the second microbial coreflood was to determine whether the batch culture or injected components used in the first microbial coreflood were defective. In this experiment, all injected chemical components were the same as the first coreflood. However, a higher salinity brine was used along with a different batch of microbes tailored to survive in higher salinity environments. The horizontal core was evacuated and a 5 % NaCl brine was used to measure the pore volume and permeability and those values are 143 mL (23 % porosity) and 1398 md respectively. The core was reduced with solutions of the same concentrations as those used in coreflood #1. The oil was then injected at 50 psi and reached an initial oil saturation of 71.2 %. Waterflood (brine with

5% salinity) ensued at 1 PV/day and produced oil until oil saturation reached 32.3 %. 15 mL of a bottle-grown inoculum suitable for the higher salinity was inoculated into the core at 1 PV/day flow rate. Again, after 10 pore volumes of nutrient injection, only 0.17 mL of oil was retrieved after the introduction of microbes. The results from this coreflood were very similar to that of coreflood #1. Fig 4.10 shows the performance data for coreflood #2.

A review of the chemical components present in this experiment revealed that some researchers have indicated the chemical reactions from sodium dithionite may result in products toxic to microbes (Fukushima, 2001). Thus, core reduction of iron and the use of sodium dithionite were removed from all future experiments.

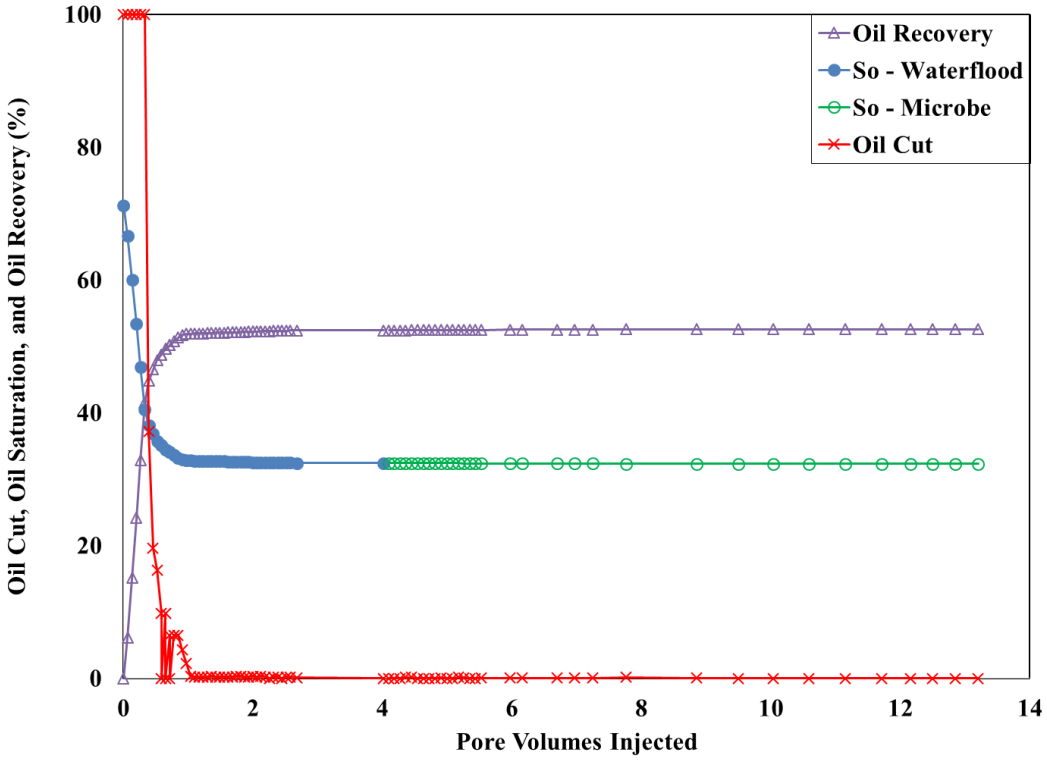


Fig 4.10-Oil recovery for microbial coreflood #2

4.2.3 Microbial Coreflood #3

A revised methodology was implemented in coreflood #3; this was the first test in which all reduction agents were removed. Additionally, the core was flooded in the vertical direction to implement a gravity-stabilized waterflood.

The core was first vacuum evacuated and 2.5 % NaCl brine was spontaneously imbibed into the core. From this, pore volume was estimated to be 159 mL (25 % porosity). The brine permeability was then measured to be 1446 md. Next, oil was injected (about 400 mL) into the core until steady state was reached and the initial oil saturation was measured to be 66.9 %. All ensuing aqueous solutions were injected at 1 ft/day. The vertical core was flooded from the bottom to the top with 2.5 % NaCl brine. The oil saturation after the waterflood was 34.3 %.

Next, 1.0 pore volume of an inoculum grown in a static environment was injected into the core. Over 15 pore volumes of nutrient injection, a continuous slow production of oil was observed. Maximum oil cut for this step never exceeded 0.2 %. In summary, 1.48 % of OOIP (1.6 mL or 3 % of oil remaining) was produced. Data from this coreflood is shown in Fig 4.11. Microbial coreflood #3 was marked as the first successful experiment on exhibiting the microbes' effect on the residual oil.

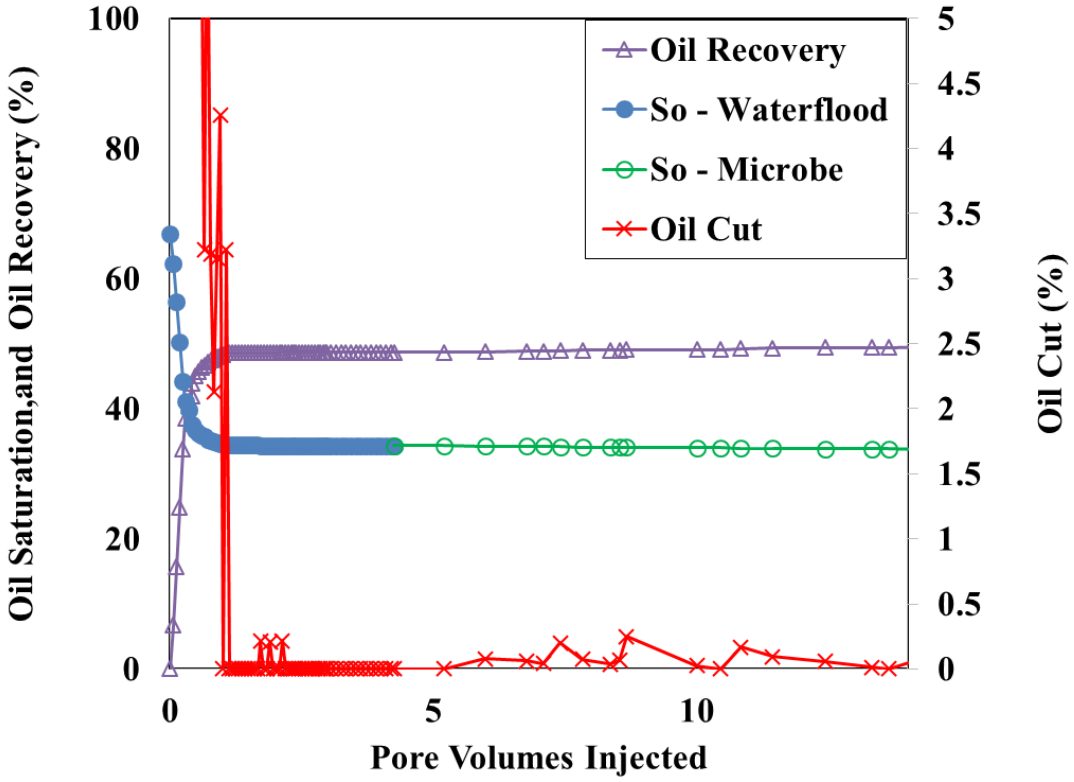


Fig 4.11-Oil recovery for microbial coreflood #3

4.2.4 Microbial Coreflood #4

The objective of microbial coreflood #4 was to assess the benefits of utilizing an inoculum grown in a dynamic environment. This culture was grown in a sandpack with a constant flow of nutrients. The experiment was conducted with 5% salinity aqueous solutions. The pore volume of this core was measured to be 129 mL (21 % porosity). Brine permeability was 1374 md. Initial oil saturation was 77.2 %.

In most of the core flood experiments, waterflood continued until oil recovered ceased for at least 1.0 PV. However, due to the microbe delivery schedule and life/death sensitivity of the inoculum, the microbes were injected into the core before reaching a

whole PV of no additional oil recovery. Oil saturation at the beginning of microbe inoculation was 26.3 %. After 50 mL (0.38 PV) of microbe injection, oil was collected in the oil trap. Nutrient injection continued until no additional oil was recovered for more than 3.0 pore volumes. Figure 4.12 shows the production over the course of the microbial introduction and stimulation. An additional 8.26 % of OOIP (8.62 mL or 25 % of remaining oil) was produced.

The production in oil for coreflood #4 was very different from previous experiments. Not only was the oil released very quickly, but also a substantially larger amount of oil was produced.

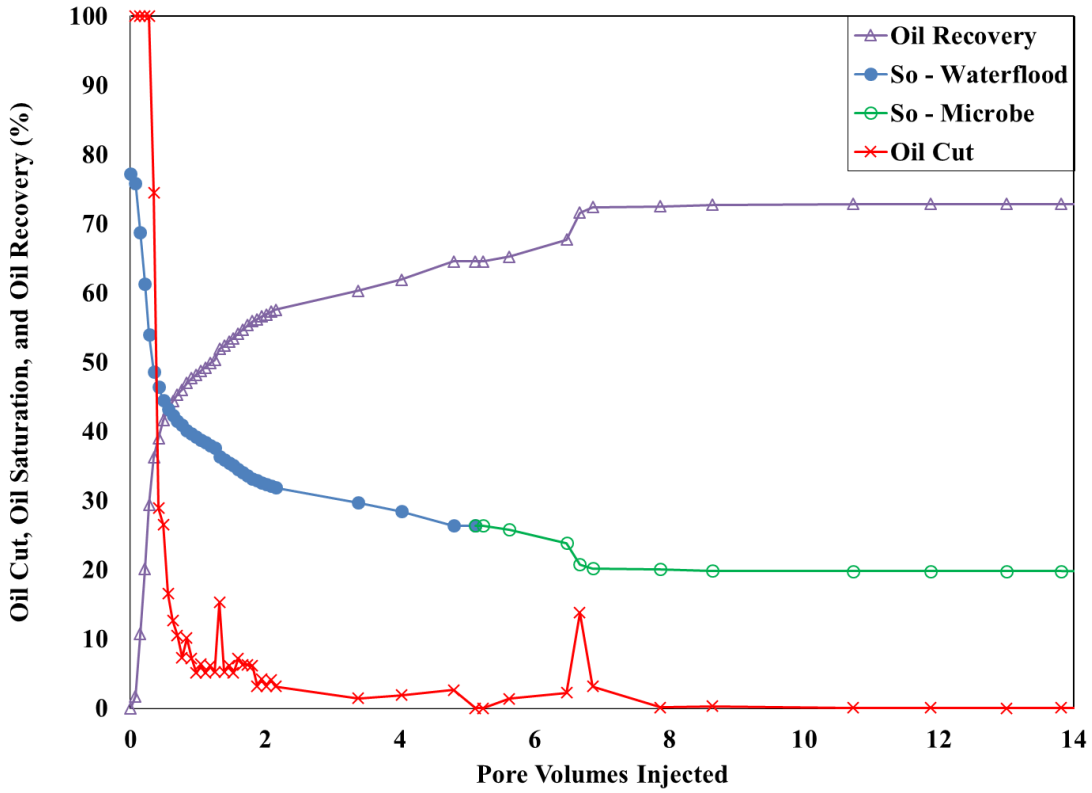


Fig 4.12-Oil recovery for microbial coreflood #4

4.2.5 Microbial Coreflood #5

This experiment was conducted to confirm the residual oil reduction effects of MEOR in a low salinity environment. The core's pore volume was 146 mL (24 % porosity) and its permeability was 1530 md. Oil flood was conducted at 60 psi and oil saturation reached 76.2 %. A 1 % NaCl brine solution was used during waterflooding and brought the oil saturation to 34.9 %.

Microbes were cultivated in a flowing sandpack column and inoculated into the core. After one pore volume of the inoculation, nutrient brine was injected into the core at 1 ft/day for several pore volumes. Data in Fig 4.13 shows that oil recovery from a microbial stimulation was minimal (0.1 mL).

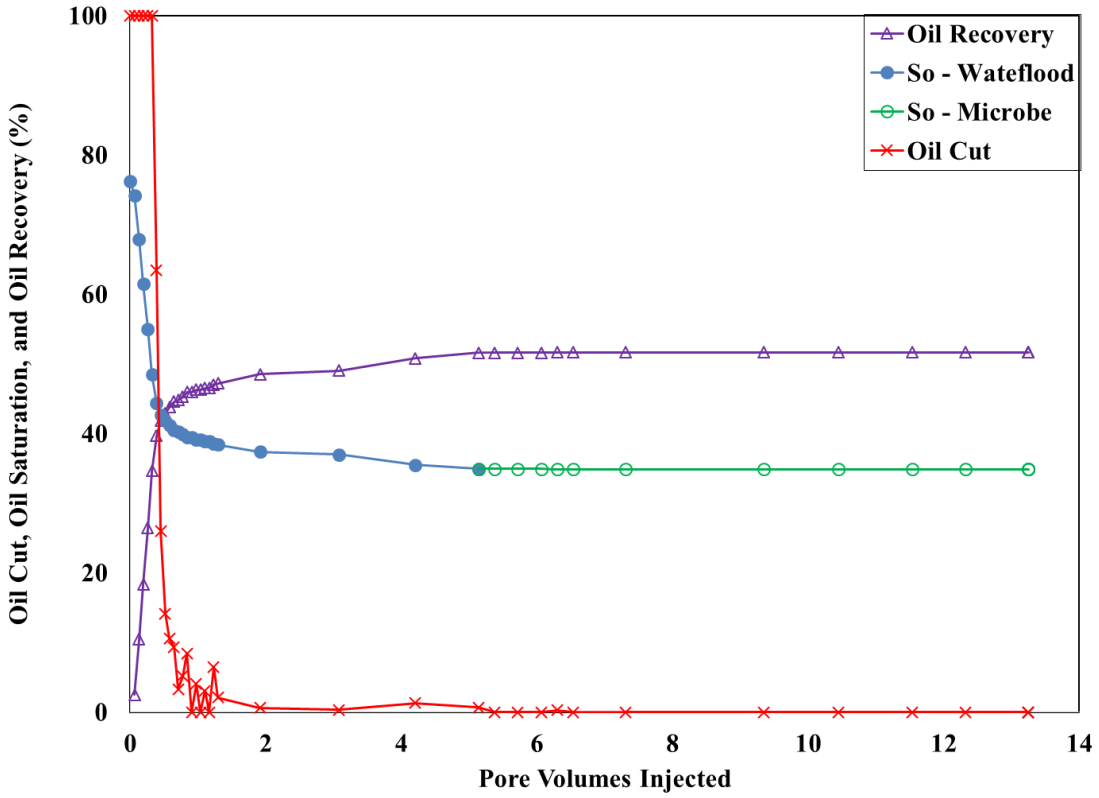


Fig 4.13-Oil recovery for microbial coreflood #5

4.2.6 Microbial Coreflood #6

The objective of this coreflood was to repeat coreflood #5 and confirm the lack of additional oil production was not an outlier (we had anticipated that the low salinity would result in a successful flood). The core used in this experiment had a pore volume of 136 mL (23 % porosity) and a brine permeability of 1637 md. Waterflood reduced initial oil saturation of 80.7 % down to 35.7 %.

The core was then injected with another inoculum grown in a flowing sandpack column. Nutrient injection lasted for 8 pore volumes, but there was no response in additional oil production. The same negligible change in the remaining oil profile (0.1 mL) is shown in Fig 4.14.

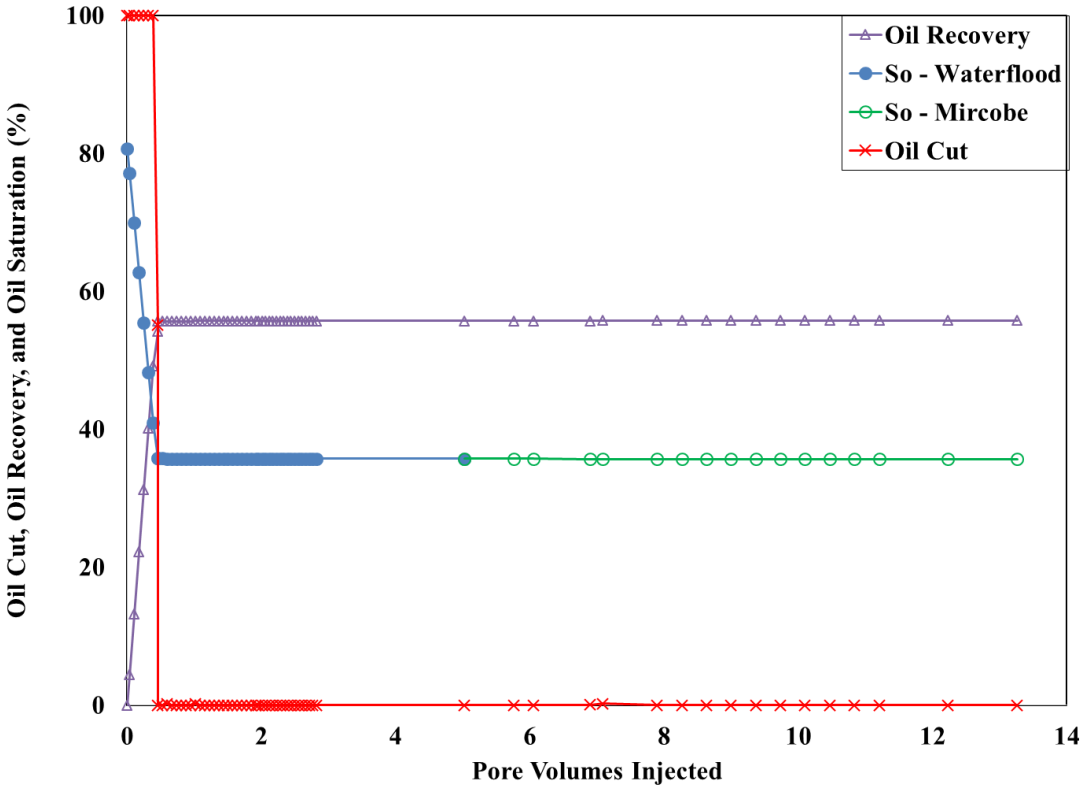


Fig 4.14-Oil recovery for microbial coreflood #6

4.2.7 Microbial Coreflood #7

This experiment was a repeat of coreflood #4, except the flood orientation switched to the horizontal orientation in hopes of using gravitational forces to create unswept oil near the top of the core. However, post-waterflood oil saturation of this coreflood was similar to that of the vertical flood orientation used in coreflood #4. The minimal density difference between the oil and water along with the Bentheimer core's homogeneity resulted in the waterflood reaching residual saturation.

This coreflood followed similar methodologies used in coreflood #4. The core was evacuated then saturated with 5 % NaCl brine. Pore volume and permeability were measured to be 141 mL (24 % porosity) and 1770 md respectively. Crude oil was then flooded into the core at 60 psi until water cut was less than 1 %. Initial oil saturation was determined to be 85.9 %. The ensuing waterflood was conducted at 1 ft/day. After water breakthrough, the oil cut reduced and maintained near 4 % for a pore volume. Oil saturation after the waterflood was 27.0 % (compared to 26.3 % in coreflood #4).

Although it is impossible to reproduce the exact microbe population used in coreflood #4, the inoculation was grown from the same base culture and in a similar dynamic environment. 1.0 pore volume of this microbe solution was inoculated into the core. After approximately 10 mL (0.07 PV) injection of the inoculation, additional oil production was observed at the outlet. Immediately following the microbes was a 5 % nutrient brine and trace amounts of sodium acetate.

Additional oil production in coreflood #7 was very similar in behavior to that of coreflood #4. Within 0.5 PV of the microbial inoculation, additional oil was produced and continued for another 4.5 pore volumes. In total, 7.46 % of OOIP (23 % of remaining oil) was produced from the effects of the introduced microbes. Data from microbial coreflood #7 is plotted in Fig 4.15.

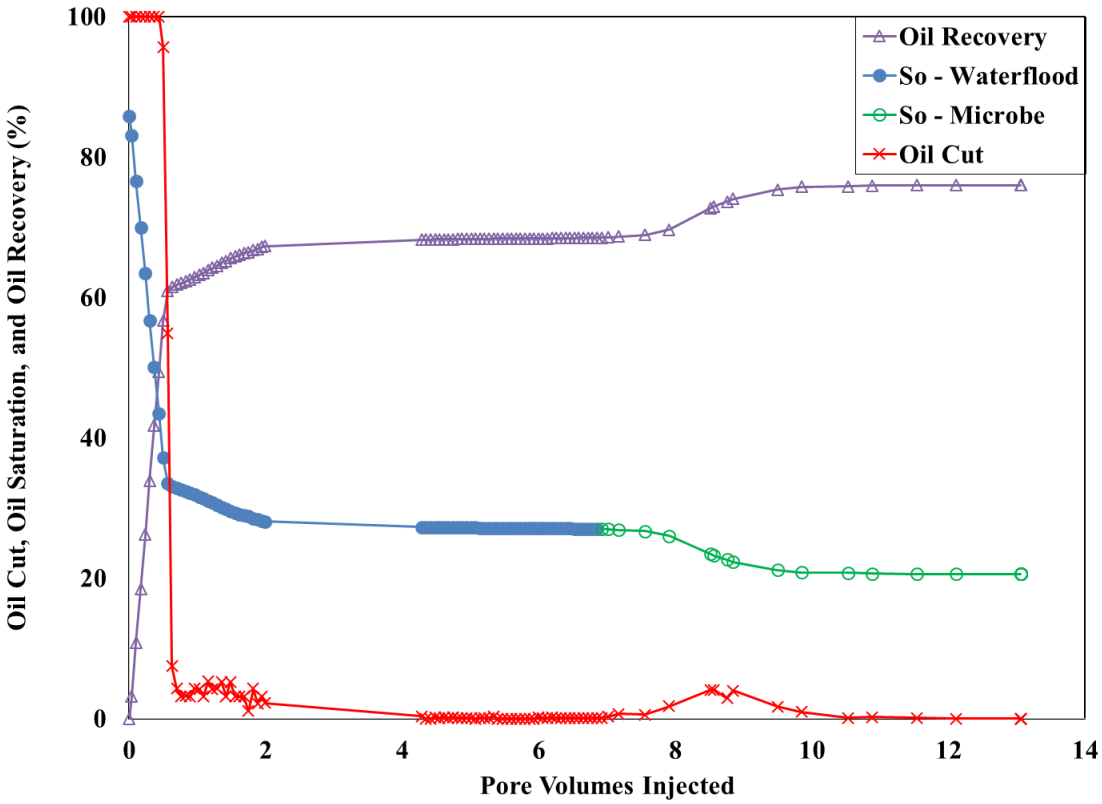


Fig 4.15-Oil recovery for microbial coreflood #7

4.2.8 Microbial Coreflood #8

The final experiment for this study was conducted with the same fluids as coreflood #7; however, waterflood rate was increased to 5 ft/day. The objective of this coreflood was to determine if the waterflood rate would have an impact on the performance of subsequent microbes.

This experiment was also conducted in the horizontal orientation. The core was first saturated with the same 5 % NaCl brine used in microbial coreflood #7 and the pore volume was measured to be 139 mL (24 % porosity). The water permeability was measured to be 1542 md. The core was then flooded with the same oil and reached an

initial oil saturation of 82.1 %. The core then underwent waterflooding at 5 ft/day until no oil was produced. The oil saturation after the waterflood was 30.8 %.

Next, the same inoculation was injected into the core at a reduced rate of 1.0 ft/day. In less than 10 mL (0.07 PV), additional oil was collected in the retriever (similar to coreflood #7). After about 1.0 pore volume of inoculant, the same 5 % salinity nutrient brine was used to stimulate growth. Nutrient flow rate was set at 1 PV/day. The data in Fig 4.16 indicates that oil cut remained around 1 % for ~3.0 pore volumes of nutrient injection. Cumulatively, the microbes produced an additional 2.3 % of the OOIP (6% of remaining oil), which was significantly less than coreflood #7, but still a successful flood.

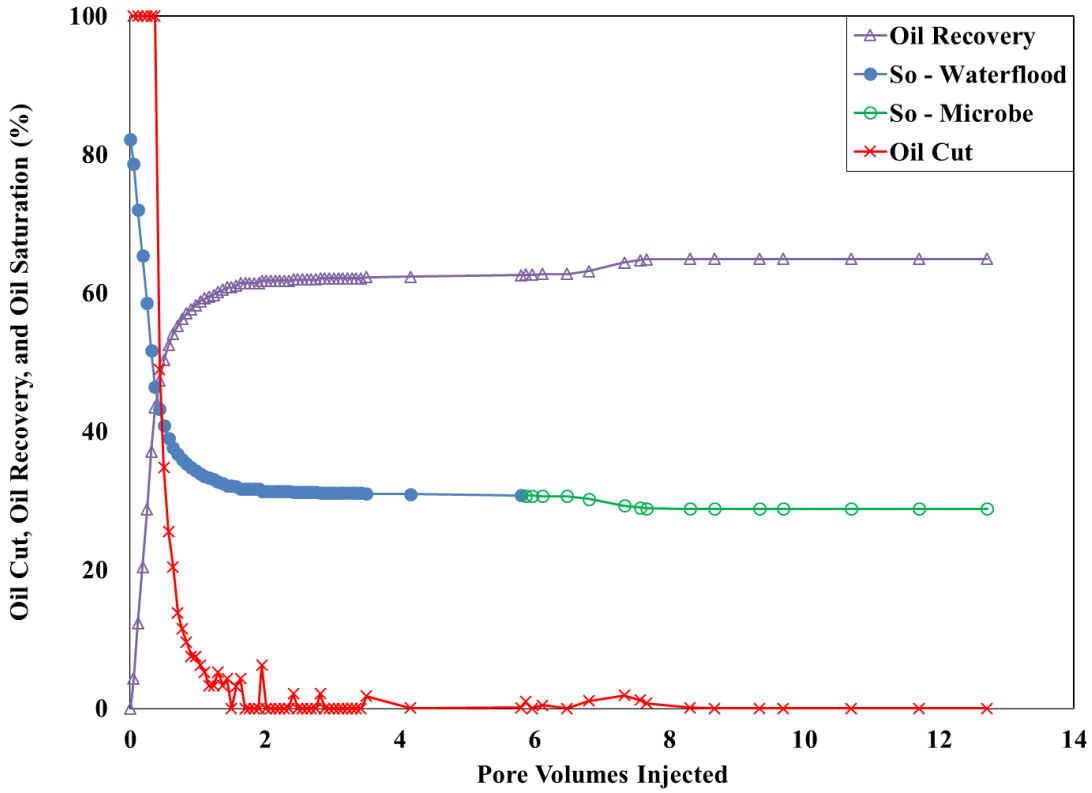


Fig 4.16-Oil recovery for microbial coreflood #8

From this experiment, it seems that the increase in waterflood flow rate drastically affected the residual oil. Firstly, the higher water flow rate left more oil in the core; the remaining oil saturation was 30.8 % in coreflood #8 compared to 27.0 % in coreflood #7. Secondly, not as much oil was recovered from coreflood #8 (2.7 mL) compared to coreflood #7 (9.1 mL). It could be that higher flood rates can induce enough forces to snap oil into disconnected blobs.

Fig 4.17 shows the injection brine flow path in a water-wet porous medium when the oil remains intact. The water must push the hydrocarbon out of the pore in order to continue flowing to the outlet.

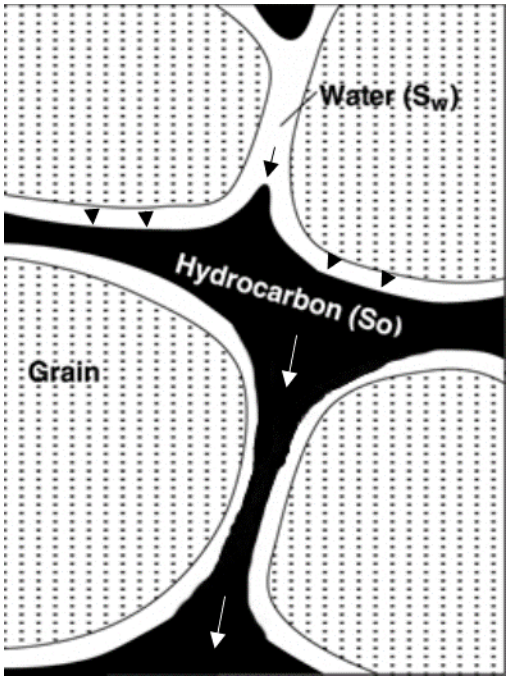


Fig 4.17-Connected oil in water-wet medium,
black and white arrows indicate water and oil flow paths respectively

Isolated oil is surrounded by water in a water-wet porous medium. This phenomenon allows water to bypass oil in a pore space more easily. Fig 4.18 illustrates the bypass of oil when the oil is disconnected.

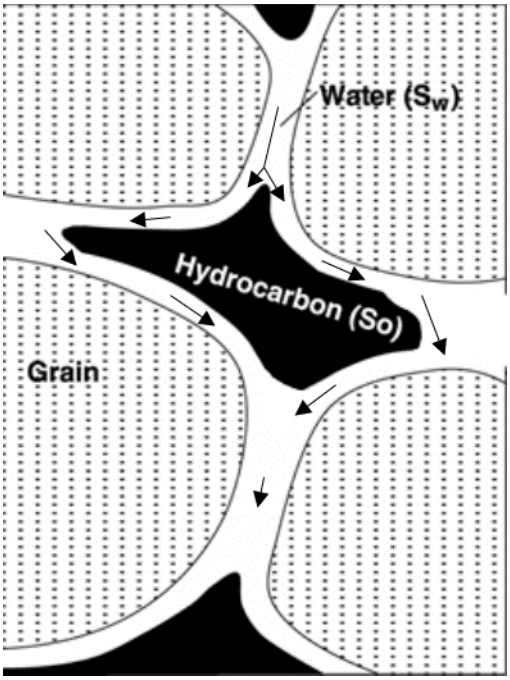


**Fig 4.18-Disconnected oil in water-wet medium,
black arrows indicate water flowing past the isolated oil**

4.2.9 Analysis of the Results

The oil-mobilizing potential of stimulating subsurface microorganisms was demonstrated in each microbial coreflood. Each coreflood produced additional oil after the inoculation of microbes.

Although the earliest experiments had limited success, revisions made to the experimental approach resulted in better oil recovery in later experiments.

Underperformance from early experiments could be a consequence from the toxic effects of reducing agents. The first two microbial corefloods did not result in significant oil production, which may be connected to the observed discontinuity of nitrite in the effluent samples. NRB are able to carry out their metabolic processes by converting nitrate to nitrite; thus, a good indicator of microbial activity is the level of nitrite in the effluent. In these corefloods, nitrate levels remained high because of the continuous injection of nitrate-laden nutrients. However, effluent nitrite levels suddenly disappeared, indicating a cease in the metabolic conversion. Thus, subsequent corefloods conducted were performed in the absence of sodium dithionite. The continual effluent nitrite levels displayed in the later corefloods indicate a much better response in microbial metabolic activity. Additionally corefloods conducted with sodium dithionite had a maximum additional oil recovery of just 0.17 mL. Whereas, corefloods conducted in absence of reducing agents had a maximum additional oil recovery of 9.1 mL.

From the results of this study, it is inferred that inoculums cultivated in a dynamic system outperform those grown in a static bottle. A dynamic system forces microbes to form biofilm and resist shear forces of the continuous fluid flow. Not only do these microbes have a tendency to create more biofilm when introduced to a new environment, this trait may be passed onto their offspring (Bester et al., 2005). Microbial coreflood #4 utilized column-grown microbes showed better responses than coreflood #3 that used batch microbes grown in a septa bottle (8.62 mL vs 1.6 mL oil recovery). Thus, ensuing corefloods were inoculated with microbes grown in a dynamic system.

After the above-mentioned improvements were made to the methodology, corefloods #4 through #8 used the same finalized procedure.

Experiments conducted with 5 % salinity brines have shown the biggest tertiary oil recovery of all corefloods performed in this study. Coreflood #4 and coreflood #7

produced almost exactly the same response; additional oil was produced in less than half of a pore volume of microbe injection and at least 7 % of the OOIP was produced from the effects of microbe stimulation.

Interestingly, the performance difference between microbial coreflood #7 and #8 may have been the caused by a possible different distribution of residual oil. A hypothesis to explain this observation is that the lower waterflood flow rate in coreflood #7 may have kept most of the oil connected, whereas the faster waterflood flow rate in coreflood #8 may have induced the higher forces necessary to snap oil into separated ganglia. As a result, capillary forces may be greater in coreflood #8, necessitating higher local capillary numbers to release these separated oil from capillary trapping. Given only a change in waterflood flow rate, the residual oil saturation was 27.0 % in coreflood #7 (1 PV/day waterflood rate) and 30.8 % .in coreflood #8 (5 PV/day waterflood rate). The higher waterflood forces in coreflood #8 may have separated the oil ganglia made it more difficult to produce the oil. Furthermore, the difference between the 9.1 mL of residual oil produced from coreflood #7 compared to only 2.7 mL from coreflood #8 may show additional signs of oil snap-off.

Nonetheless, in these 5 % salinity corefloods, microbes lowered the oil saturation left after a waterflood. All three experiments consistently showed quick productions in oil and greater than 2 % OOIP additional recovery.

Although the oil production was significant in 5 % salinity corefloods, similar effects were not observed when translating to a 1 % salinity system. Further research should be conducted in order to identify the reasons behind this discrepancy.

Chapter 5: Conclusions and Future Work

5.1 Conclusions

EOR processes are often uneconomical to implement in the field, leaving large amounts of unproduced oil. However, MEOR treatments serve as a cheap method to produce additional oil. The objective of this study was to evaluate the connectivity of residual oil and the viability of inorganically stimulating microbes to release the capillary bound oil.

The high permeability Bentheimer sandstone cores exhibited minimal heterogeneity. Additionally, a low viscosity hydrocarbon phase was used throughout this study. The favorable mobility ratio between the oil and water resulted in a high macroscopic sweep efficiency. Displacement of oil was near uniform across the core making this an ideal system for testing effects on residual oil trapped by capillary forces. Changes to the systems implemented after the waterfloods are assumed to affect capillary bound oil only.

Although minimal changes were observed in CT coreflood #1, the results do not necessarily disprove the existence of a connected residual phase like that of strand theory. From a macroscopic view, distribution of residual tetradecane did not change with varying water injection rates. However, possible changes at the pore level could not be detected. Changes at such a small scale may necessitate the use of a CT scanner with a higher resolution. Furthermore, the high water flow rate implemented in the CT experiments may have induced forces above the snap-off threshold pressure necessary to separate the oil ganglia.

The decrease in scanned CT number detected in CT corefloods #2 and #3 indicated the presence of a phase less dense than water. Accidental gas injection was initially guessed to be the cause, but later it was determined that the oil had trace amounts

of dissolved gases. Although the gas resulted in a 0.3% change in saturation, no additional oil was produced. However, gas presence detected in the CT scans rendered the data incomparable to one another.

The work in this thesis presents a viable method for conducting dynamic corefloods with live microorganisms. More importantly, the ability of microbes to release capillary trapped oil was demonstrated in all microbial experiments.

The primary focus of the microbial experiments was to stimulate NRB with inorganic nutrients. The additional nitrate concentration within the nutrient brines accelerated the growth of biofilms. Microorganisms in biofilms formed on the oil and water interface have the possibility to constrict pore throats and divert fluid flow, thus increasing pressure for other pores. Additionally, these microbes may produce biosurfactants to lower the oil and water IFT. Although it is unclear which mechanism acts as the dominant force, additional oil recovery was observed after every inoculation. However, the magnitude of effect varied across the study.

Sodium dithionite was shown to hinder the microbial metabolic process in microbial corefloods #1 and #2. The sudden loss of nitrite within the effluent samples indicated a decrease in microbial activity. Latter corefloods conducted in the absence of reducing agents showed a sustained metabolic conversion of nitrate to nitrite.

The uses of dynamically grown microbes have generally resulted in greater oil recovery. Microbes subjected to a constant fluid flow can resist the fluid shear forces and form biofilm. When inoculated into a new medium, these microbes have a higher probability of forming biofilm. Not only does this growing method act as an artificial selection, these microbes are hypothesized to serve as a better representation of bacteria found in a flowing reservoir.

Microbial coreflood #5 and #6 recovered miniscule amounts of oil compared to corefloods #3, #4, #7, and #8. The discrepancy in performance may be caused by the magnitude of increase in capillary number. From the capillary desaturation curve, higher capillary numbers result in more residual oil production.

5.2 FUTURE WORK

Revisiting and accounting for the causes of the observed low additional oil production in the 1 % salinity microbial experiments is the primary task. The "finalized" experimental approach may not be the best. Every group of reservoir consists of different microbe species that can behave very differently; some groups have a high concentration of microbes that are able to produce biosurfactants while others do not. Thus, an additional screening process may be needed to test whether the target microbe population actually has members with the ability to change the forces of an oil-water-rock system. Other improvements, such as controlling experimental temperature or using oil recently produced from the field (less degraded quality), may allow for a consistent increase in capillary number across all microbial coreflood attempts.

All experiments presented in this research were performed using a light hydrocarbon phase (about 6 cp) in high permeability and homogenous Bentheimer sandstone cores. Due to the favorable mobility ratio, the waterflood processes quickly flushed the cores to their residual oil profiles. Although these systems were ideal for testing improvements in microscopic sweep efficiency, they could not quantify MEOR effects on macroscopic sweep efficiency.

Utilizing a higher viscosity oil would result in unswept oil. Microbes can be inoculated after a low oil cut is reached. Any increases in oil cut will portray MEOR effects on improving macroscopic sweep efficiency.

Similarly, more corefloods can be conducted with heterogeneous cores. In rocks such as Berea sandstone, water will preferentially channel into higher permeability zones, leaving unswept oil in lower permeability zones. Special attention is needed when experimenting with microbes in heterogeneous cores; if the permeability is too low, microbes may not have access to enough nutrients for growth.

Macroscopic sweep efficiency can be tested even further through experimenting with fractured cores (one streak of extremely high permeability) or with a composite medium consisting of two different rocks (one zone of high permeability and one zone of low permeability). In these type of experiments, waterflooding would leave a large amount of oil in the low permeability zones. Since microbes are injected via a water phase, they would reside and grow in the high permeability zone. As the microbes reproduce, it is possible for biofilm to form and begin to plug the high permeability zone. Subsequent water injection would therefore be forced into the low permeability zones and displace the resident oil.

In this study, it is assumed that hydrocarbon exposure to oxygen will change the flowing properties of the oil, making it more likely stick to the rock. In oilfield reservoirs, the limited amount of oxygen does not significantly affect the oil properties. However, when conducting laboratory experiments, the oxygen to hydrocarbon ratio is extremely large. The crude oils used in this study were maintained in an anaerobic state; nonetheless, the issue of oil oxidation should be further researched.

Given adequate amount of time and preparation, microbial experiments can also be performed in a CT scanner. Microbial corefloods conducted in this study quantify the

total amount of tertiary oil produced; however, these experiments provide information on the locality and distribution of the mobilized oil. The implementation of a CT scanner would not only visualize the oil-producing mechanisms of the microbes but also provide insight on the connectivity of the residual oil phase.

Although more coreflood experiments should be performed with varying oil, water, and rock properties, there are other forms of research that can reveal the influences of MEOR on the residual oil phase. Coreflood experiments are only capable of measuring overall changes in the system. The exact mechanism by which microbes change the oil and water system can only be surmised and not firmly established. Microfluidic experiments can allow for a visualization of a two-dimensional displacement profile in glass slides etched with a customized pattern. In these experiments, bacterial growth and its influence on mobilizing oil can be monitored and recorded under a microscope.

Alternatively, pore network models could provide useful knowledge for improving MEOR projects. Currently, there is not a model that accurately represents the effects of microbial growth in an oil reservoir. Biological models can be combined with traditional numerical models to predict bacterial migration, biofilm growth, metabolic byproduct interactions and the resulting effects on residual oil. These studies can help quantify the manipulation of forces created from microbial stimulation.

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