Surfactants in Enhanced Oil Recovery

by

Koh Pei Ling

Dissertation

Submitted to **Prof. Syed Sakhawat Shah**
Chemical Engineering Programme
as Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Chemical Engineering)

July 2005

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Surfactants in Enhanced Oil Recovery

By

Koh Pei Ling

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Prof. Syed Sakhawat Shah)

Universiti Teknologi PETRONAS
Tronoh, Perak
July 2005

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

KOH PEI LING

ABSTRACT

Petroleum provides the main energy supply to the world. Within the past 30 years, crude oil price has been increasing due to the ever-increasing demand for more energy resources. This has given way to recover more oil from existing resources as primary and secondary recovery can only recover one-third of the Original-Oil-in-Place (OOIP). Enhanced oil recovery (EOR) implies oil recovery beyond the conventional recovery stages of primary or secondary recovery.

The title of this report is Surfactants in Enhanced Oil Recovery, the main objective of the project is to evaluate commercially available surfactant products for their potential as wettability modifier and interfacial tension reducer by performing spontaneous imbibition test on cores. Other objectives include literature review on current EOR initiatives and opportunities in Malaysia and design of spontaneous imbibition cell. A total of 8 preliminary screening tests and 6 second stage test has been conducted to screen 6 commercially available surfactants. The experimental work done has proven that certain surfactants can increase the recovery of oil by altering the wettability from water wet to oil. With the addition of alkali, the recovery factor is higher. Recommendations for future work include conducting the experiments at real reservoir temperature for higher accuracy results and using chemical systems with different concentrations of surfactants diluted with different solvent to compare the best system for highest recovery of oil.

The first part of the report gives the background studies of the project with a brief overview of Malaysia oil and gas industry and EOR status in Malaysia. First part also includes problem statement and objectives of the project. Second part of the report detailed on the literature review on mechanisms involve in chemical EOR and chemistry of surfactants as a potential wettability modifier and interfacial tension reducer. Third part of the report focus on the experimental work, the experimental procedure, equipments and chemicals used, design of imbibition cell and discussions of the results obtained. The recommendations and conclusions are made in the last part of the report.

ACKNOWLEDGEMENT

This project would have been impossible if not been for the help, support and advice from a number of people. Thus, I would like to take this opportunity to express my profound thanks and gratitiude to each and every one of them.

I thank my supervisor, Prof. Dr. Syed Sakhawat Shah for agreeing to supervise my final year project. Thanks to his constant guidance and advice, the project is able to amount to success. Equal thanks to Final Year Project Committee whom have gave us support and guidance while undergoing the experimental work and report writting.

Special thanks to Middle East and Asia Client Support Laboratory (MEA CSL), Schlumberger Oilfield Servies for giving me this opportunity to carry out my experimental work , with the guidance of all the staff, and experiences gained during my internship with Schlumberger, I have managed to run the experiments smoothly. Special gratitude to Dr. Mathew Samuel, MEA CSL manager and Dr. Mohan Panga, CSL Engineer for allowing me to use the resources in CSL and supporting me technically.

Special gratitude to Mr. Nadeem, Ph.D student of Chemical Engineering , for helping me in reviewing my reports and presentation slides and supporting me technically.Thanks to all the technicians in Chemical Enginering Department, especially Mr. Zaaba and Mr. Jalani for provinding me the aparatus and chemicals that is needed for experiments.

Lastly, my appreciation goes to all my friends and family who contributed their time and energy in supporting me. All your contributions are highly regarded and would be remembered.

Table of Content

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

The current energy crisis has been precipitated by the limited availability of oil reserves and the accelerating demand of its products such as natural gas, liquefied petroleum gases, gasoline, and heavier constituents that fins outlet as Diesel fuel, lubricating oils, waxes and others. The recent rise of oil price to USD 69[1] per barrel and ever increasing demand of more energy resources has given way to recover more oil from the existing resources as primary and secondary recovery can only recover one-third of Original-Oil-in-Place (OOIP). Enhanced Oil Recovery (EOR) implies oil recovery beyond the conventional recovery stages of primary or secondary recovery which include natural drive, waterflood, and gas injection. This chapter introduces petroleum industry as a whole with focus on oil and gas industry in Malaysia and the initiatives and potential of Malaysian oilfield to implement EOR.

1.1 BACKGROUND STUDIES

Figure 1 schematically shows a view of petroleum reservoir. In a petroleum reservoir, the structure of oil and gas trap differs from one well to the other. There are different types of rocks with different properties. The basic requirements must be fulfilled to accumulate oil and gas in a commercially exploitable reservoir. First, the reservoir rock must possess sufficient void space, call porosity to contain the oil and gas. Secondly, there must be adequate connectivity, or permeability of the pore spaces to allow transportation of the fluids over large distance under reasonable gradients of pressure. Third, a sufficient quantity of hydrocarbon must be accumulated intro a trap of impervious cap rock which prevents upward migration of the oil and gas from the source beds, forming a petroleum reservoir. Reservoir rock are usually sedimentary rocks, example of sedimentary rocks are sandstone (quartz), limestone (calcium carbonate) and dolomite (magnesium calcium carbonate).

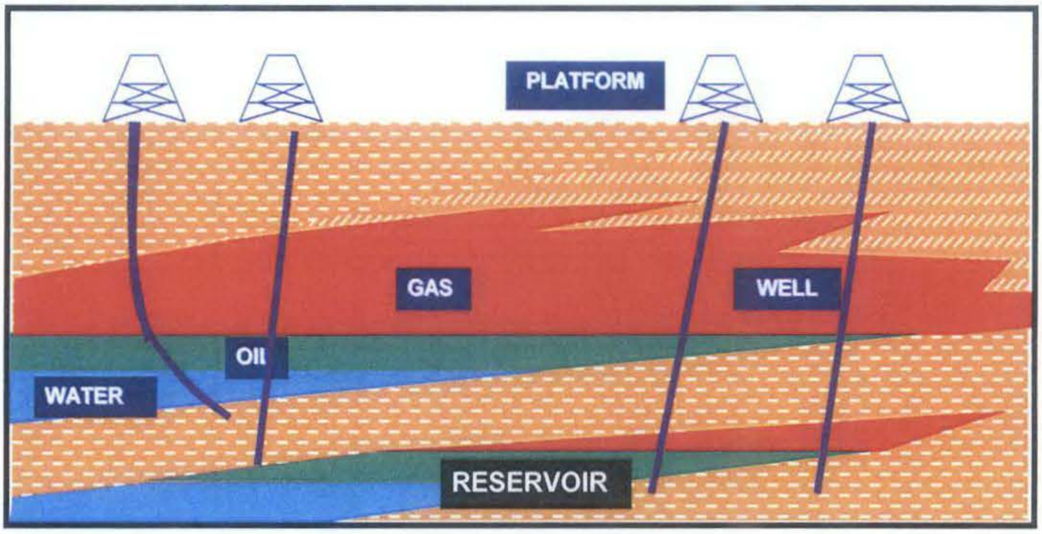


Figure 1. Schematic diagram of an oil and gas reservoir.

Source: Schlumberger Oilfield Services presentation slides.

Oil can be recovered from the pore spaced of a reservoir rock; usual drive mechanisms include water drive and gas drive. As the hydrocarbon is producing, the pressure difference in the reservoir will decrease and thus decrease in oil productivity.

1.1.1 Overview of Malaysian Oil and Gas History

The earliest officially recorded oil find in Malaysia was made in July 1882 by the British Resident of the Baram district in Sarawak. Today, the Malaysian oil and gas industry has extended to approximately 500,000 sq.km of acreage contained in 52 offshore blocks[2] which are demarcated for exploration and production. Eight major operators currently operate 31 of the Production Sharing Contract (PSC) blocks, carrying out exploration, development and production activities. As of 1st January 2003, the Malaysian oil reserves stand at 3.5 BSTB (Billion Stock Tank Barrel) and cumulative oil production is 4.9

BSTB and oil-in-place of 24.9 BSTB[2]. These figures translate to an average of oil recovery of factor of 34%. This means that there is still substantial amount of petroleum resources in the ground that could potentially be recovered through other means such as EOR.

Since 1994, the Malaysian crude oil reserves have been on the decline (Fig 2). Although exploration activities in Malaysia is still active, and recent discoveries have added more to the national's reserves book, the Malaysian oil and gas upstream activities is already entering a maturing phase (declining pressure and increasing water and gas production) as shown in Figure 3.

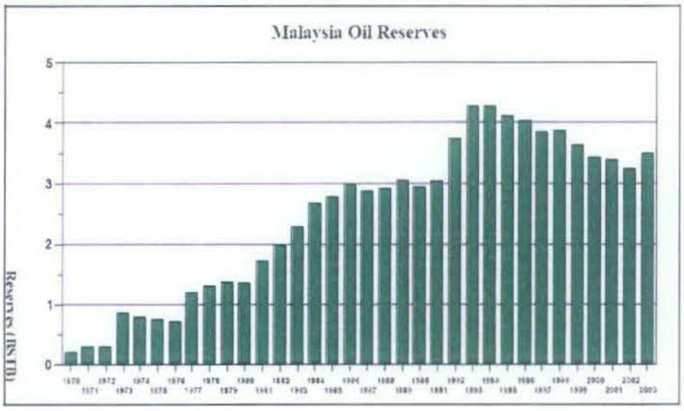


Figure 2. Malaysian reserves trend as of 1.1.2003[2]

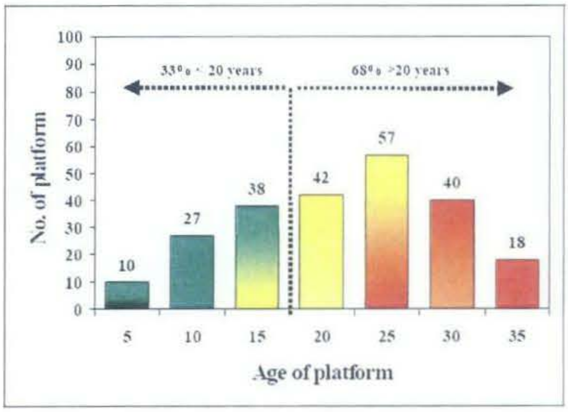


Figure 3. Platform age distribution in Malaysia.[2]

A number of fields are already under secondary recovery (pressure maintenance either by gas or water injection) to supplement the production. PETRONAS as national oil and gas company and Resource Manager have set a target of increasing the recovery factor from existing 34% up to 45%[2].

1.1.2 EOR initiatives and opportunities in Malaysia

The earliest feasibility study for EOR in Malaysia was recorded in 1985[3], with the objective to investigate the technical potential of miscible enriched gas and surfactant flooding in the fields located in Peninsular Malayisa[2]. Since then, there were several feasibility studies conducted by the operators looking at adding reserves to the existing fields.

Screening studies done by PETRONAS in 72 reservoirs identified that 52 reservoirs are technically feasible for the application of new EOR processes[2]. At present the major challenge for offshore EOR in Malaysian oilfields is of high cost of implementation, operating environment, limited detailed assessments, planning and studies in the past and lack of technical expertise. To date, there has been no full-field application of chemical enhanced oil recovery (CEOR) in Malaysia with exception of pilot Water Alternate Gas (WAG) project in Dulang field and Micellar Enhanced Oil Recovery (MEOR) stimulation project in Bokor field. A screening study has identified several key EOR technologies that are most applicable in Malaysian oilfields namely gas injection, chemical injection and microbial[2].

1.1.3 Drawbacks of EOR

Same principles of EOR engineering may not apply to offshore oil fields because offshore wells tend to be highly deviated or extended reach, the distance between them is often greater than between onshore wells. This extends the time between EOR initiation and meaningful results and flattens the recovery response. These effects complicate process control and limit and number EOR techniques that may be applicable. Cost of EOR is also very high and it must be well planned.

1.2 PROBLEM STATEMENT

The oil recovery from an oil wet formation is usually low. Oil production by means of pure pressure reduction may result in an oil recovery less than 20% of OOIP. The objective of this project is to increase the recovery of OOIP by using surfactants than can alter wettability from oil wet to water wet. Additional of additives to the surfactants also will be introduced to further enhance the chemical system.

1.3 OBJECTIVE AND SCOPE OF STUDY

1.3.1. Main Objective

- Increase the recovery of OOIP by using surfactants by experimental approach.

1.3.2 Sub-Objectives

- Literature review on latest EOR status and wettability alteration using surfactants.
- Focus on surfactant flooding to alter wettability.
- Experimental testing plan.
- Equipment set-up to measure wettability alteration and lowering of interfacial tension by designing an imbibition cell using apparatus available in the lab.
- Evaluate commercially surfactant products for their potential as wettability modifier and interfacial tension reducer by performing spontaneous imbibition test on cores.

- Evaluate the performance of chemical system (surfactant+solvent) with addition of alkali that can further enhance the system.

1.4 FEASIBILITY OF THE PROJECT

The study of surfactants for EOR is abundant and wide, and due to limited timeframe, a specific area of study needs to be narrowed down and acknowledged. It is therefore case studies are analyzed and discussed so that a feasible topic can be selected and investigated efficiently and comprehensively. Continuous effort would be stressed on literature research on books and journals, in addition of references from focal persons that are considered expert in this field.

Laboratory studies test to proposed EOR processes in coreflood with samples of reservoir rock and fluids. These small, one-dimensional flow tests in relatively homogeneous media do not always successfully scale up to reservoir dimensions. But if the process fails in the laboratory, it will more likely fail in the field.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 OIL RECOVERY MECHANISM

It is well recognised that the energy consumption per capita and the standard of living of a society are interrelated. Among various sources of energy, fossil fuels or crude oils play an important role in providing the energy supply of the world. It also serves as a raw material for feedstocks in chemical industry. In the view of the worldwide energy crisis, the importance of enhanced oil recovery process has been proposed. There are many methods of EOR as shown in Fig. 4. All employ one or more of three basic mechanisms for improving on water drive alone:

- Increase the mobility of the displacement medium by increasing the viscosity of the water, decreasing the viscosity of the oil, or both.
- Extract the oil with solvent.
- Reduce the interfacial tension between oil and water

Each EOR process is suited to particular types of reservoir. EOR begins with throughout geologic study. Technical rule-of-thumb (Fig. 5) screening criteria are available to aid preliminary evaluation of a reservoir's suitability for EOR

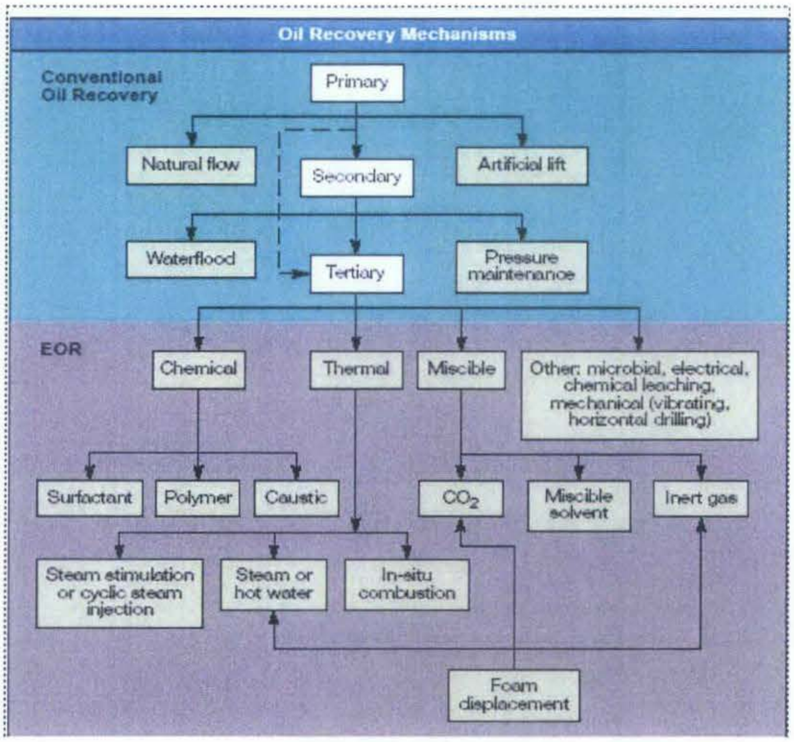
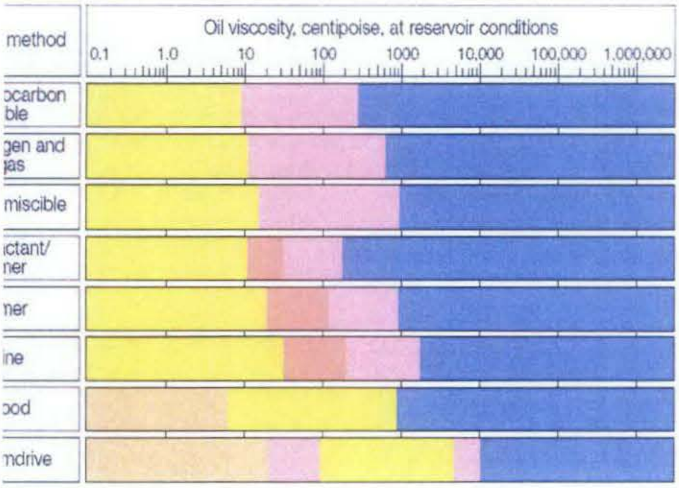
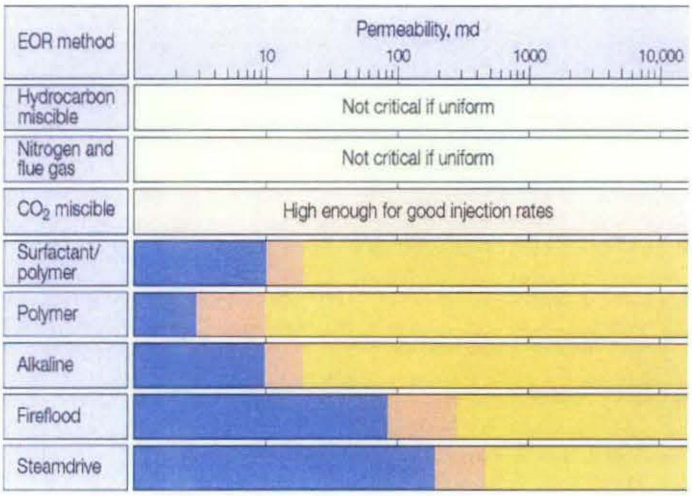


Figure 4. Oil recovery mechanisms (Primary, Secondary and Tertiary)[4].





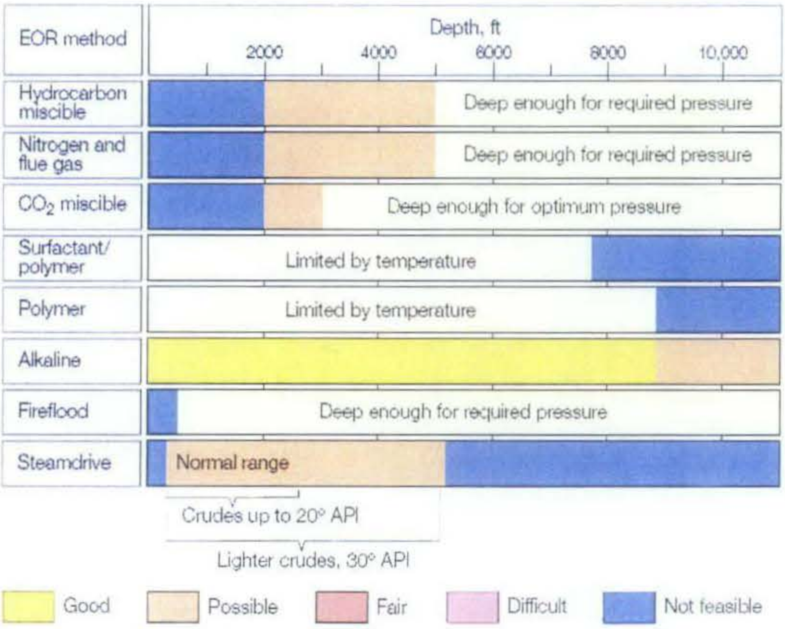


Figure 5. Selection of EOR techniques by oil viscosity, permeability and depth[4].

2.1.1 Primary Oil Recovery

The first stage of hydrocarbon production, in which natural reservoir energy, such as gas drive, water drive or gravity drainage, displaces hydrocarbons from the reservoir, into the wellbore and up to surface is not so good to recover sufficient oil . Initially, the reservoir pressure is considerably higher than the bottom hole pressure inside the wellbore. This high natural differential pressure drives hydrocarbons toward the well and up to surface. However, as the reservoir pressure declines because of production, so does the differential pressure. To reduce the bottom hole pressure or increase the differential pressure to increase hydrocarbon production, it is necessary to implement an artificial lift system, such as a rod pump, an electrical submersible pump or a gas-lift installation. Production using artificial lift is considered as primary recovery. The primary recovery stage reaches its limit either when the reservoir pressure is so low that the production rates are not economical, or when the proportions of gas or water in the production stream are too high. During primary recovery, only a small percentage of OOIP are produced, typically around 10% from oil reservoirs[2, 4, and 5].

2.1.2 Secondary Oil Recovery

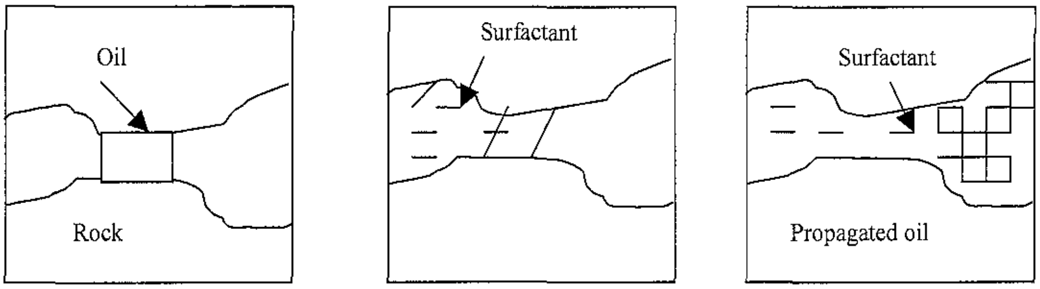
The second stage of hydrocarbon production during which an external fluid such as water or gas is injected into the reservoir through injection wells located in rock that has fluid communication with production wells is known as secondary recovery processes. The purpose of secondary recovery is to maintain reservoir pressure and to displace hydrocarbons toward the wellbore. The most common secondary recovery techniques are gas injection and water flooding. Normally, gas is injected into the gas cap and water is injected into the production zone to sweep oil from the reservoir. A pressure-maintenance program can begin during the primary recovery stage, but it can be graded as a different form or enhanced recovery process. The secondary recovery stage reaches its limit when the injected fluid (water or gas) is produced in considerable amounts from the production wells and the production is no longer economical. The successive use of primary and secondary recovery in an oil reservoir produces about 15 - 40% of the OOIP[2, 4, 5].

2.1.3 Tertiary/Enhanced Oil Recovery

The third stage of hydrocarbon production during which sophisticated techniques that alter the original properties of the oil are used is known as tertiary oil recovery. Enhanced oil recovery can begin after a secondary recovery process or at any time during the productive life of an oil reservoir. Its purpose is not only to restore formation pressure, but also to improve oil displacement or fluid flow in the reservoir. The three major types of enhanced oil recovery operations are chemical flooding (alkaline flooding or micellar-polymer flooding), miscible displacement (carbon dioxide [CO_2] injection or hydrocarbon injection), and thermal recovery (steam flood or in-situ combustion). The optimal application of each type depends on reservoir temperature, pressure, depth, net pay, permeability, residual oil and water saturations, porosity and fluid properties such as oil API gravity and viscosity.

2.2 CHEMICAL FLOODING

Chemical flooding using surfactants is one of the vastly chemical methods used in EOR. This is because by the unique characteristics of surfactants that consists of hydrophilic and hydrophobic properties. Generally, one of the main problems encountered for EOR is that oil is difficult to recover due to its high interfacial tension between the oil and the rock. It is a crucial target in chemical flooding where the ultimate objective is to reduce the interfacial tension or IFT. By applying surfactants, hydrophilic and hydrophobic effects would allow the lowering of the IFT, and presence of a driving fluid would push the oil and later to the production. A diagram would illustrate how the role of surfactant is played in the following page.



1. Oil is initially binded to the rock; high interfacial tension makes is nearly impossible for the oil to be recovered

2. Presence of surfactants would interrupt the intermolecular bind of the oil and rock; leading to reduced interfacial tension

3. Reduced interfacial tension allows propagation of oil, driving fluid would drive the solubilized oil and later to production

Figure 6. Schematic illustration of Surfactants in recovering oil.

Figure 6 shows a simple mechanism of how a surfactant would interact and change the physico-chemical properties of the oil, and later transfers it to the production well. For the surfactants to be fully utilized, effective chemical flooding technique is critical to ensure the success of this method. Surfactant selection is critical because it gradually adsorbs and removes the oil trapped between the rocks. Considerations must be taken as chemical flooding is undeniably expensive, and should the flooding fail, not only it would result poor oil recovery, but incur high losses as well.

Traditional chemical flooding comprises of several phase positions and regions (Fig. 7)[6, 8]; and they are

- Region 1: Residual Oil
- Region 2: Oil Bank
- Region 3: Surfactant
- Region 4: Polymer

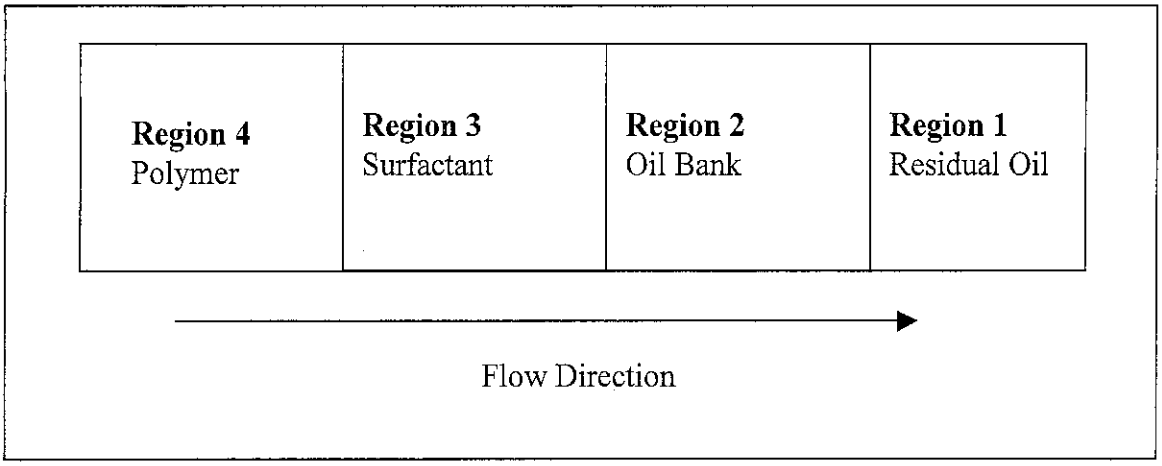


Figure 7. Phase Position in traditional chemical flood[8].

Before injecting the surfactant to the reservoir, initially an oil bank must be formed to give a mobility profile to the surfactant and polymer. This is done by injection of sea water in which sodium chloride is added to provide an adequate salinity. A point of injection is secured in order to form a good oil bank. After the oil bank is formed, the surfactant solution is injected to lower the IFT of the oil. Polymer is later injected to give mobility control to the surfactant, and provides a good displacement of the surfactant solution to prevent any immobilization and trapping that will consequently lead to surfactant losses. Naturally, the polymer slug is followed by a drive water, to displace the polymer and surfactant to the production well.

Nevertheless, traditional chemical flooding methods is marginally economical and effective; improvements are required in order to be efficient and more economical. Technical risk was high and traditional chemical flooding methods are subject to several problems, where they are:

- Difficulty of handling the flow of three liquid phases through an inhomogeneous porous medium
- Surfactant losses due to reservoir conditions: low capillary forces, fingering, and misbehaviour of phase gradient
- Retention of surfactants, precipitation, and phase trapping

The goal of chemical flooding technology nowadays is to design a simpler chemical flooding technique that can recover additional oil in a cost-effective manner. Following criteria of a simpler chemical flooding applies:

- Chemicals used are only surfactant and polymer
- Low surfactant concentration
- No imposed salinity or other phase gradients
- Surfactant and polymers used must be stable

This type of proposed chemical flooding is termed Low Tension Polymer Water Flood, LTPWF, or Low Surfactant Concentration Enhanced Water Flood. A schematic illustration of the proposed flooding is as shown in Fig. 8.

The caustic or alkali flooding process relies on a chemical reaction between the caustic and organic acids in the crude oil to produce in-situ surfactants that lower interfacial tension between water and oil. Other mechanisms that may enhance recovery are changing rock from oil-wet to water-wet, which lower interfacial tension, and emulsification, which lowers viscosity. Caustics can react strongly with the reservoir rocks to the detriment of the process.

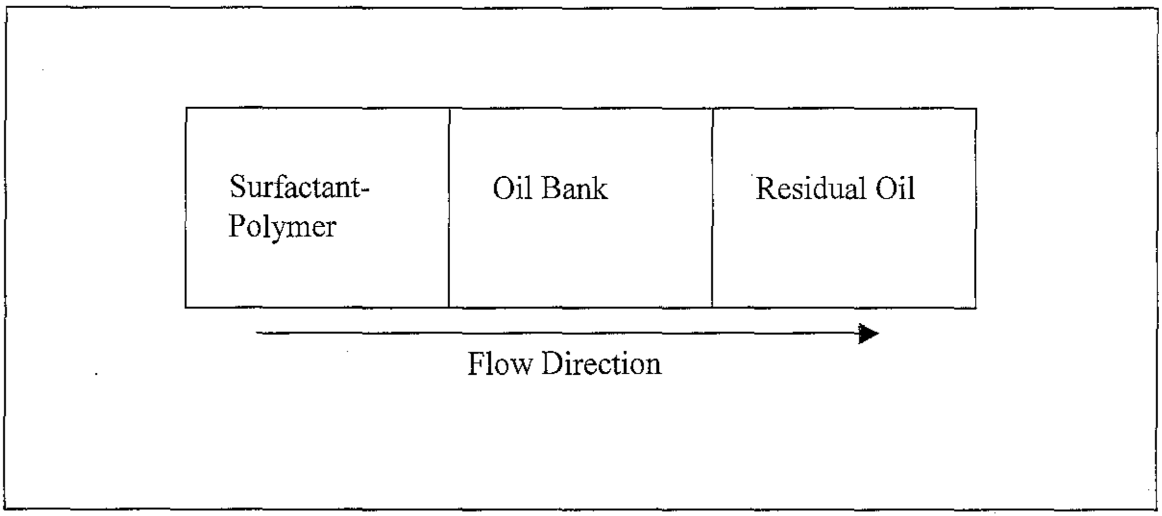


Figure 8. Schematic illustration of a LTPWF.

2.3 SURFACTANTS

A surfactant (surface active agent) is a molecule that when added at a low concentration changes the properties of the liquid at a surface or interface. The general structure of a surfactant includes a hydrophilic portion and a hydrophobic portion as shown in Fig. 9. The hydrophilic end is water-soluble and usually a polar or ionic group. The hydrophobic end is water insoluble and is usually a long fatty or hydrocarbon chain. This dual functionality hydrophobic and hydrophilic provides the basis for characteristics useful for surface tension modification, emulsification, foaming and cloud point. Surfactants are classified by the different charges on the head groups; there are four types of surfactants: Anionic, Cationic, Nonionic and Amphoteric.

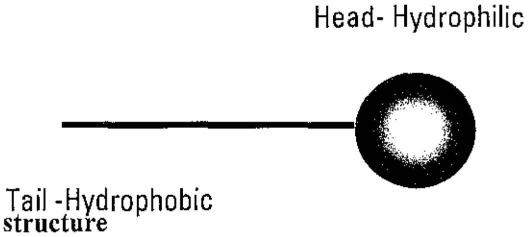


Figure 9. Surfactant's structure

An example of surfactant that is being used in detergents is Sodium Dodecyl Sulphate (SDS) (Fig. 10). SDS an anionic surfactant consists of a head and tail group. The tail group that is the water hating is repelled by water but attracted to the oil. At the same time, the head group that is water loving is attracted to the water molecules. These opposing forces loosen the oil and suspend it in water. SDS enhances clean up of surfaces.

Figure 10. Structure of Sodium Dodecyl Sulphate.

In aqueous solutions dilute concentrations of surfactant act much as normal monomers, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles (Fig. 11), in which the tail groups of the surfactant associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. There are different types of micelles, namely spherical, cylindrical and bilayers. The tendency of different monomers to form different types of micelles depends upon their tail group length, longer tail group tend to form bilayers, while shorter tail group tend to form spherical micelles[7]. The formation of micelles in aqueous solutions is generally viewed as a compromise between the tendency of carbon chain to avoid contacts with water and the desire for polar parts to maintain contact with the aqueous environment. The surfactant concentration at which micelles are formed is known as critical micelle concentration (CMC). The CMC is a property of the surfactant and several other factors

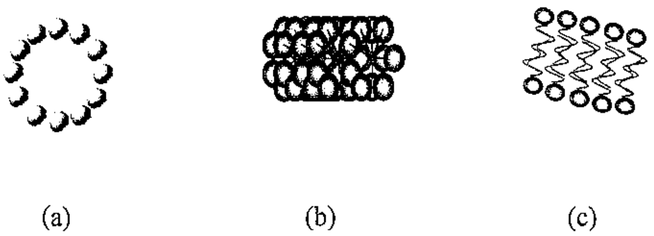


Figure 11. Different types of micelle (a) Spherical (b) Cylindrical (c) Bilayer.

2.4 SURFACTANTS INDUCED WETTABILITY ALTERATION

Surfactants provide a tool that can transform the wettability of the porous rock. Wettability alteration of porous reservoir rock with surfactant is one means to improve the flow and distribution of fluids in a reservoir. A number of factors affect the interaction of surfactant with the solid surface of porous rock and consequently affect wettability:

Description of surfactant has been discussed earlier. Surfactants are generally classified according to their hydrophilic head group. Common classifications are:

1. Anionic- negative charge
2. Cationic-positive charge
3. Amphoteric-charge changes with pH
4. Nonionic-no charge

The dual nature of surfactants produces a strong affinity for interfaces between immiscible fluids such as gas and water or fluid/solid surface. The surfactant by absorbing a fluid/solid interface reduces interfacial tension and modifies the ability of water or oil to wet the solid surface. A surfactant that orients itself on a surface such that the surfactant molecules have the hydrophobic tail groups away from the surface or along the surface will decrease water wetting and increase oil wetting. The orientation of a surfactant with the head group away from the surface can make the surface more water wet.

Studies done by Seethepali et. al.[11] proved that anionic surfactants can change the wettability of calcite surface to intermediate/water-wet conditions as well or better than cationic surfactant t DTAB with crude oil, adsorption of the sulphonate surfactants can be suppressed significantly by the addition of the alkali.

2.5 CRITICAL MICELLE CONCENTRATION

It is well known that physical/chemical properties of surfactant vary significantly above and below a specific surfactant concentration, the CMC value. Below CMC value, the physical/chemical of ionic surfactants like SDS resembles a strong electrolyte. Above the CMC value, these properties change dramatically, indicating another process is taking place. Figure 12 shows the adsorption of surfactant changes below and above CMC point. The CMC is of interest because at concentrations above the value the adsorption of surfactant onto reservoir rock surfaces increases very little. That is, the CMC represents the solutions concentration of surfactant from which nearly maximum adsorption occurs. Typical CMC values for low electrolytes concentration at room temperature are[8]:

Anionic ⇒ 10^{-3}-10^{-2} M (for SDS: 0. 0256-0/256 wt %)
Cationic ⇒ 10^{-3}-10^{--1} M
Amphoteric ⇒ 10^{-3}-10^{-1} M
Nonionic ⇒ 10^{-5}-10^{-4} M

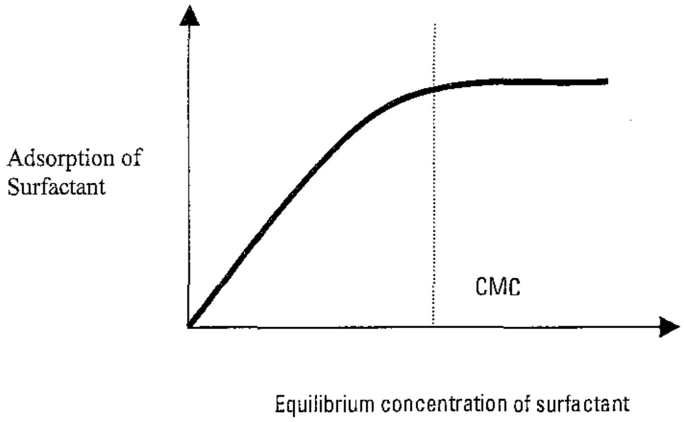


Figure 12. Typical ionic surfactant adsorption isotherm.[8]

2.6 SWEEP DISPLACEMENT EFFICIENCY BY SURFACTANTS

The effectiveness of a water flood or EOR project can be described in terms of sweep and displacement efficiencies. Sweep efficiency is a ratio of the pore volumes that are contacted by the injected fluid to the total reservoir pore volume. Both horizontal and vertical sweep efficiencies can be computed. Sweep efficiency is strongly influenced by the mobility ratio, the ratio of the driving fluid viscosity to the oil viscosity being displaced[12]. Mobility ratios close to 1 are most efficient because mobility is almost equal to permeability/viscosity. Displacement efficiency is ratio of the volume of oil that is swept by the process to the volume of oil in place before the process.

2.7 CAPILLARY FORCES

To improve recovery factor and increase sweep efficiency, it is necessary to remove the trapped crude oil being trapped in the porous spaces because of capillary forces. Capillary number represents the ratio of viscous forces to capillary forces as shown below:

$$N_C = \frac{k\Delta P}{L\sigma\cos\theta} \qquad [1]$$

Where

N_c = Capillary number

K = permeability

P= differential pressure

L=Length

σ = interfacial tension

cos θ= Contact angle (measurement of wettability)

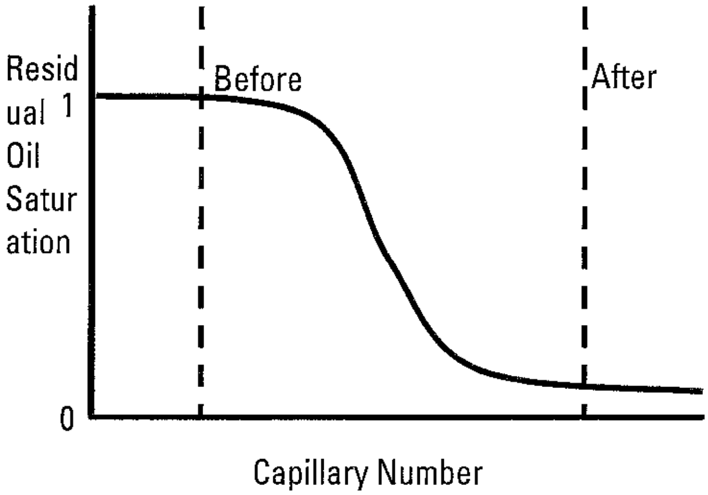


Figure 13. Residual oil saturation vs. capillary number, as capillary number increases, residual saturation decreases.

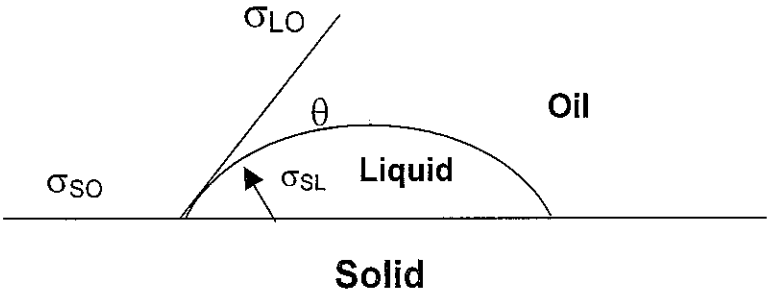
At the end of water flooding, the capillary number is around 10^{-6} and this number has to be increase by 3 - 4 orders of magnitude for EOR in order to decrease residual oil saturation near to zero[9]. The role of surfactant is to produce ultra low interfacial tension at the oil/surfactant interface to mobilise the trapped oil.

Another property that can be change by surfactant is wettability. Details about surfactant and how surfactant can help in wettability alteration will be discussed in the next section.

2.8 WETTABILITY

Wettability is defined as the ability of one fluid to spread on to a solid surface in the presence of other immiscible fluid. When two fluids, mutually immiscible with each other, both contact a solid surface, the less wetting fluid will retreat from contact with the solid while the stronger wetting fluid will be attracted to the surface. At the point of intersection between the two fluid phases and the solid surface, a contact angle is produced (see Fig. 14)

Figure 14. Contact angle measurement.



The three-phase contact angle that forms is the result of the equilibrium of the three interfacial tensions. Young's denotes the equilibrium relationship.

$$\sigma_{SO} - \sigma_{SL} = \sigma_{LO} \cos\theta \qquad [2]$$

σ_{SO} is the interfacial tension between a solid and oil. σ_{SL} is the interfacial tension between a solid and water and σ_{SL} is the interfacial tension between the solid and water. When the contact angle is less than 70 deg, the surface is referred to as being water-wet, when it is greater than 115 deg, the surface is considered to be oil-wet, and the intermediate range from 70 to 115 deg is considered as intermediate wet (see Fig. 15).

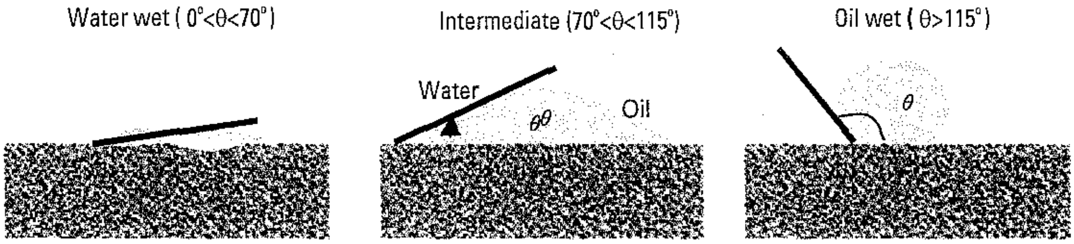


Figure 15. Schematic of different contact angles, yellow represents oil while blue represents water.

To reduce capillary pressure for removal of residual oil saturation, the contact angle of oil with the reservoir rock should be made close to or greater than 90°. Thus, the wettability of the rock has to be altered from oil wet to intermediate wet or water wetting conditions as shown in Fig. 16.

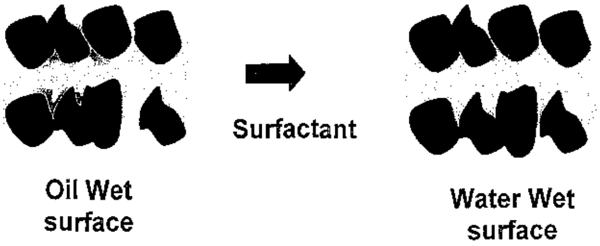


Figure 16. Schematic of oil wet surface being altered to water by surfactant.

Studies done by Mohanty[13] (2004) shows that diluted surfactant recovers about 55% of oil in 150 days by imbibition driven by wettability alteration. Similar results obtained by Babadagli[14], his studies show that addition of surfactants yields higher ultimate recovery and faster recovery rate.

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 PROCEDURE IDENTIFICATION

For the detail study conducted, several procedures are identified and structured into several key points;

3.1.1 Preliminary Literature Review and Data Gathering

- All books describing Surfactants and Enhanced Oil Recovery are gathered by continuous retrieval from information resource center.
- Websites and online information involving surfactants are also gathered via internet. Journals and case studies are also gathered by this media; however most of the information is collected from the resource center.
- Information gathered are rearranged and revised in accordance to the relevance of the project. All information that is gathered is discussed with the selected supervisor.
- Guidance from Schlumberger Client Support Laboratory managers and engineers.

3.1.2 Identifying and Development of Detail Study

- After thorough study of the basic fundamentals of surfactants, case studies are gathered and collected for analysis.
- Analyses of the case studies are presented and discussed with the selected supervisor to provide more comprehensive approach.
- Based on discussion with the supervisor, a specific case study would be identified and secured as a detail study.
- Acquisition on the detail study topic information is enhanced by comprehensive explanation by focal individual or specialists. It is likely that these specialists are referred from Schlumberger Client Support Laboratory Engineers.
- Briefing and references from focal individuals and specialists are conducted to provide more detail approach to the detail study. Experimental or modelling results are gathered as a part of verification or interpretation that is to be forwarded in the results and discussion.

3.1.3 Data Analysis and Comparison

- Analyses from the data acquisition such as experimental results are checked together along with the governing theory of the fundamentals of surfactants.
- If possible, comparison of the results from different case studies is conducted and interpreted based on theoretical understanding.

3.1.4 Preparation of Report

- After all the data including the results and discussions are acquired, a report would be written and produced as the part of the requirement of the final year project. In addition, the report serves as a function as a reference for future part of study.

3.2 TOOLS REQUIRED

Tools required for experiments include core-flooding equipment, tools to measure gas permeability and porosity, tools to measure viscosity and specific gravity and oven.

Main apparatus to run spontaneous imbibition tests is imbibition cell, due to limitation of time and resources, the cell were built using apparatus available in the laboratory.

Spontaneous imbibition is a process in which a wetting phase displaces a non-wetting phase in a porous medium. For example, if the core is water wet and oil is the non-wetting phase then upon contact of oil saturated core with water the water imbibes into the core displacing the oil. Thus wettability can be determined by observing the amount of water that imbibes into the core. Figure 17 shows a schematic of an imbibition cell. Parameters that need to be measured are the volume of oil being displaced by reading the gradation with time.

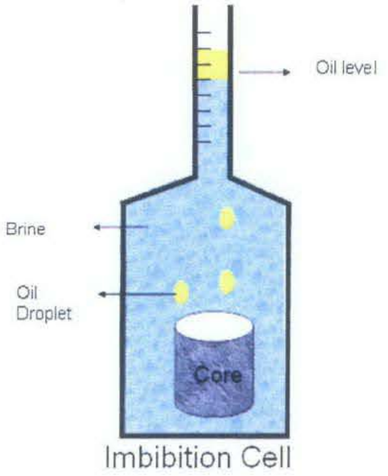
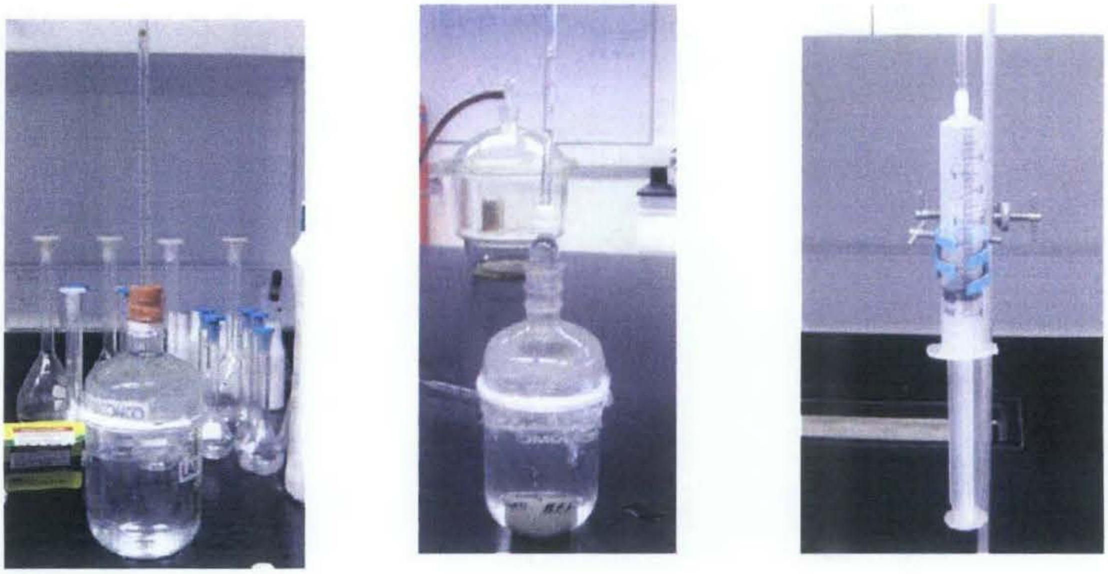


Figure 17. Schematic diagram of a imbibition cell.

Three cells has been design as shown in figure below. The main problem with Cell A and Cell B is leaking problem and oil were trapped in the cell as it can moved up to the burette. Cell C solved both problems, by using Cell C, the piston can be pushed slightly to move the oil. The advantage of Cell C also is cheaper and easiest to construct however Cell C capacity is smaller as compared to Cell A and d Cell B. Cell C were chosen to further with imbibition testing.



(a) (b) (c)

Figure 18. Design of imbibition cell (a) Cell A (b) Cell B (c) Cell C.

3.3 PROJECT WORK

The following experimental procedures were carried out in UTP Chemical Engineering laboratory (Building 4) and Schlumberger Client Support Laboratory located in Kuala Lumpur.

3.3.1 Sample and Chemical Identification

Sample Identification

***Oil*:** Diesel (SG=0.8631, viscosity= 8.634 cP), Crude oil (SG=0.9594, viscosity =85.15cP).

***Brine*:** 2 % KCl. (SG=1.021, viscosity=1.06cP)

Surfactants: Sodium Dodecyl Sulphate, N-Cetyl TrimethlyAmmonium Bromide, Dodecyl Benzensulfonic Acid, F103 (Schlumberger), Igepal CO-630, Igepal CO-520 Geropon CYA/DEP (Rhodia Chemical). Specifications of the chemicals are listed in Table 1.

Table 1. Specification of surfactants.

Properties	SDS	CTAB	DBSA	Geropon CYA/DEP	Igepal CO-520	Igepal CO-630	F103
Chemical name	Sodium Dodecyl Sulphate	N-Cetyl N,N,N-Trimethlyammonium Bromide	Dodecyl Benzenesulphonic acid Sodium Salt	Sodium Dodecyl Sulposufinate	N/A	Ethocylated Nonyl-Phenol Branched	N/A
Chemical Company	Merck	Merck	Fluka Chemical	Rhodia	Rhodia	Rhodia	Schlumberger
Chemical formula	$C_{12}H_{20}NaO_4S$	$C_{19}H_{42}BrN$	$C_{18}H_{29}NaO_3S$	N/A	N/A	$(C_2H_4O)_n.^{C15H24O,n=9-10}$	N/A
Character	Anionic	Cationic	Anionic	Anionic	Anionic	Anionic	Anionic
Physical form	White solid	White solid	Flaky solid	Clear viscous liquid	Slightly hazy viscous liquid	Clear viscous liquid	Colourless liquid
pH	N/A	N/A	N/A	6.4	N/A	6-8	5
Flash point	N/A	N/A	N/A	45 deg C	N/A	200 deg F	190 deg F
Surface tension (dyne s/cm)	N/A	N/A	N/A	26	N/A	32	N/A
CMC (%)	N/A	N/A	N/A	0.07	N/A	0.005	N/A

** Specification taken from Material Safety Data Sheets of chemicals provided by supplier, non-specified specification are not given or confidential.*

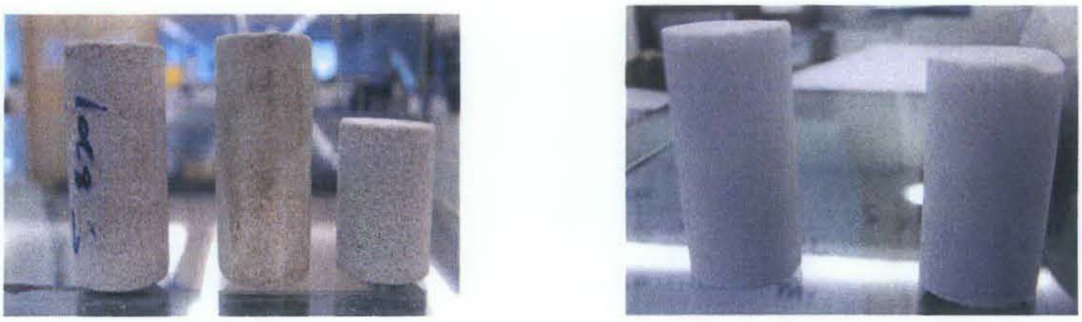
Core: Berea high permeability and middle permeability cores (Fig. 19a) supplied by Schlumberger Client Support Laboratory. Limestone (Fig. 19b) collected from UTP. Properties of core are as shown in Table 2.

Table 2. Specification of cores.

CORE NO.	LENGTH, CM	DIAMETER,CM	PERMEABILITY,MD	POROSITY,%	PORE VOLUME,CM3
1	5.026	2.500	90	19.809	4.886
2	5.180	2.516	74	20.720	5.336
3	4.973	2.500	91	20.800	5.078
4	4.645	2.516	88	21.010	4.851
5*	4.070	2.538	54	26.030	5.359
6*	4.042	2.525	60	24.970	5.044
7**	4.678	2.513	0.02	1.46	N/A
8**	4/589	2.500	0.015	1.36	N/A

*Medium permeability cores

**The permeability and porosity values are too small to proceed with imbibition test.



(a) (b)

Figure 19. Core samples (a) Berea sandstone (b) Local limestone.

Preparation of Chemical Solution

Chemical solutions for imbibition test were prepared with concentration and dilution as shown in Table 3. The dilutions were made using different solvent due to compatibility. Certain surfactants are not compatible with water or salt. The concentration of surfactant is all above CMC value. Viscosity of the solution is measured using capillary viscometer (Fig.20a), specific gravity (SG) of the solution is measured using SG bottle and pH is determined using pH paper. 012 wt% of alkali was added to chemical systems A-D for imbibition test using high pH chemical systems.

Table 3. Specifications of chemical systems.

Chemical system	Surfactant*	Dilution**	SG	Viscosity (cP)	pH
A	0.1 wt% F103	2% KCl + Distilled water	1.018	1.01	6
B	0.1wt % DBSA	2% KCl + 25% Isopropanol alcohol + distilled water	0.9849	2.18	5.5
C	0.1 wt% SDS	Distilled water	1.00	0.975	5.5
D	0.1 wt% N-CTAB	2% KCl + distilled water	1.0261	1.051	6
E	0.1 wt% Geropon CYA/DEP	2% KCl + distilled water	N/A	N/A	N/A
F	0.1 wt% Igepal CO-520	2% KCl + distilled water	N/A	N/A	N/A
G	0.1 wt% Igepal CO-630	2% KCl + distilled water	N/A	N/A	N/A

* *Concentration of surfactants was all slightly above CMC value of surfactants.*
** *The dilution was different for different surfactants due to compatibility of certain surfactants.*

3.3.2 Testing Methods

Porosity and Permeability

The porosity of the core samples was measured using helium porosimeter and the permeability was measured using nitrogen gas permeameter. Picture of equipment is as shown in Fig 20e. Appendix A shows the theory behind the measurement of porosity and permeability.

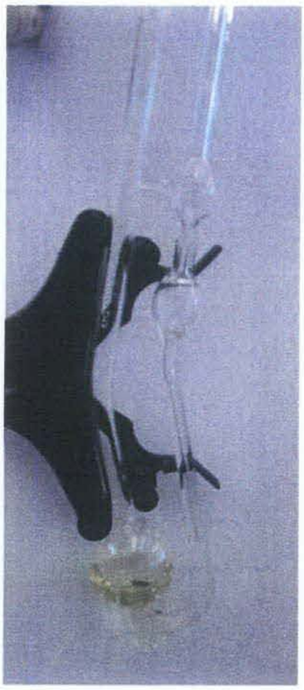
Spontaneous Imbibition Test

Spontaneous imbibition set up is as shown in Fig. 20b. All imbibition tests were run at ambient temperature. Diesel was injected into each core sample to reach almost 100% saturated with diesel. The core sample then was immersed in imbibition cell filled with brine and exposed to spontaneous capillary imbibition. The oil recovery was monitored against time. After brine imbibition, the core is dried in the oven and the flushed again with oil to resume the diesel saturation. The core was ready for chemical imbibition experiments. The oil recovery by spontaneous imbibition of brine was then compared with spontaneous imbibition of chemical (surfactant) solutions.

Core flooding

A coreflood apparatus (Fig 20c and Fig 20f) was built for saturate cores with fluid and to measure fluid permeability. It consisted of (1) a pump for injecting different fluids into the core (2) a pressure gauge to measure the pressure drop across the core during the floods (3) fluid loss cell inside which the core is placed and (4) a measuring cylinder to measure the flow rates at the outlet. Appendix B shows methods used to calculate permeability by using Darcy Law.

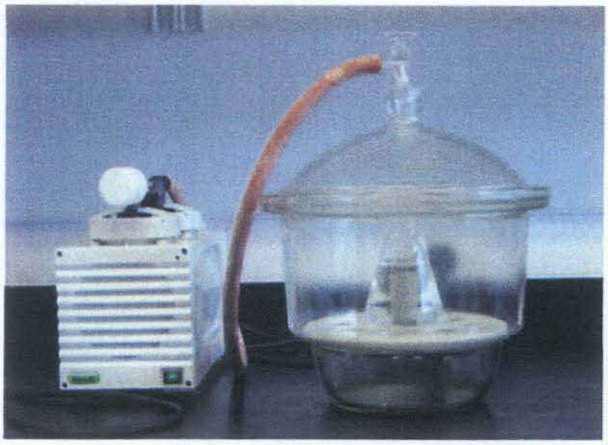
Experimental Equipment



(a)

(b)

(c)



(d)

(e) (f)

Figure 20. Experimental equipment (a) Capillary viscometer* (b) Imbibition cell (c) Fluid loss cell* (d) Desiccator is connected to a vacuum suction pump (e) Porosimeter and Permeameter* (f) Core flooding*

** Equipments in Schlumberger CSL equipment.*

3.3.3 Testing Procedures

Preliminary Screening

Preliminary test were carried to see the ability of surfactants with alter wettability. About 6 chemicals from different chemical company were tested. List of chemicals and specification as stated in Table 1.Core chips (sandstone and limestone) are used for contact angle test.

Preliminary screening test procedure:

a) Trim Berea core to approximately 1.5" diameter x 0.2" length.
b) Prepare chemical solutions. (As shown in Table 3)
c) Soak the core chips in the mixture overnight.
d) Dry the core chips.

Test wettability changes by placing a dropping the core in a beaker that contain diesel, a drop of water is slowly drop to the core chips. If the core is water wet then the contact angle is greater than 90°

Second Stage Testing (Imbibition Test)

From preliminary stage testing, 4 chemicals were chosen to further with second stage testing. Details about results obtained will be discussed in the following chapter.

Experiment procedure

1. Measure the length, diameter and initial weight of core receive.
2. Measure the gas permeability and porosity using Gas Porosimeter and Gas Permeameter.
3. Test the core with sessile drop method to determine the initial wettability of core. Sessile drop with water and oil.
4. Flush the core with 10 PV diesel using core flooding equipment. Measure the weight of core after saturated with diesel.
5. Run initial imbibition by placing core saturated with oil in imbibition that contains brine.
6. Dry the core in the oven
7. Flush the core with 10 PV diesel again to saturate with oil.
8. Prepare chemical solution by diluting surfactants with appropriate solvent. Measure specific gravity and viscosity of the solution.
9. Run imbibition by placing the core saturated with oil in imbibition cell that contains chemical solutions.

CHAPTER 4

PROJECT RESULTS AND DISCUSSIONS

Two different experimental methods are used to test the commercially available surfactant to meet the target criteria discussed in Chapter 3. The first method, contact angle test, is used for preliminary screening and the second method, imbibition test, is used for second stage screening. In the second stage, effects of adding alkali and with initial water saturation are also studied. The two stages are shown in Fig. 21. Details about preliminary and second stage testing will be further discussed later

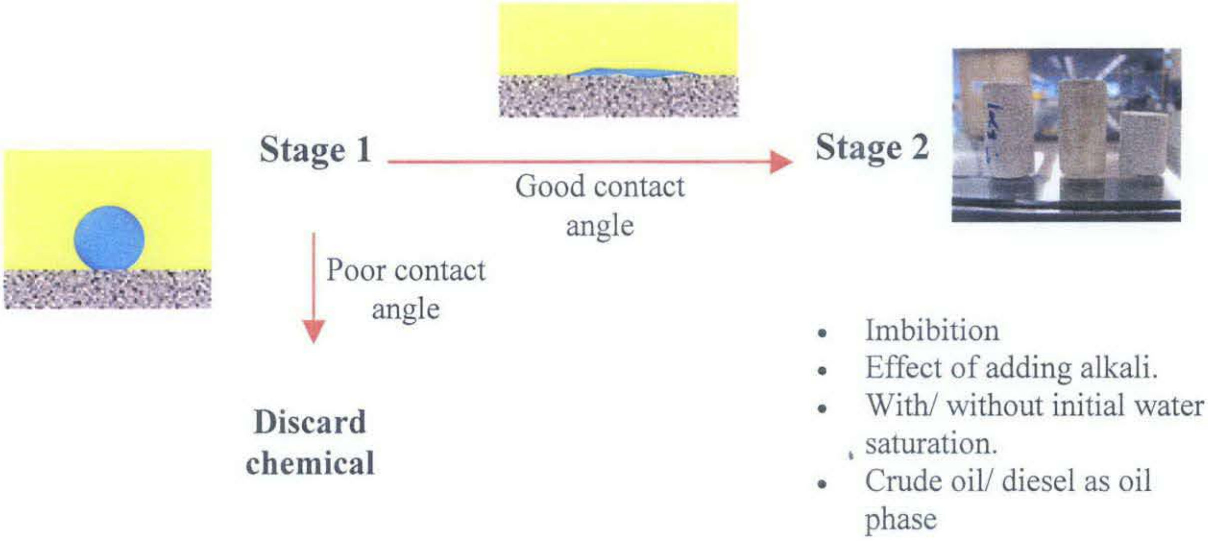


Figure 21. Testing plan

4.1 PRELIMINARY TESTING (CONTACT ANGLE)

Figure 22 shows the contact angle of a drop of water placed on an untreated Berea sandstone and local limestone. As shown in pictures, Berea high perm sandstone is initially mixed wet while medium perm shows water wet, local limestone also shows mixed wet.

Figure 23 and 24 show qualitatively the selected results of contact angle test after the cores chip been treated with different surfactants, it can be seen that after treatment, certain surfactants have altered the surface from oil wet to water wet while some remain the same or become more oil wet.. The results of preliminary screening are shown in Table 4. The oil repelling nature of the chemical is graded on a scale of 0-5, where 0 is no repellency and 5 is very good repellency shown by contact angle greater than 90°. A total of 4 chemicals were selected from the preliminary screening for second stage testing (highlighted in pink). Chemical system D (CTAB) was selected even though it did not give good results to ensure that contact angle test is accurate.

Table 4. Contact angle test results from preliminary screening The oil repelling nature of the chemical is graded on a scale of 0-5, 0 being no oil repellence (oil wet) and 5 is very good oil repellence (water wet).

Chemical System	Oil Repelling	
	Berea Sandstone	Local Limestone
A (F103)	4	4
B (DBSA)	0	4
C (SDS)	2	4
D (CTAB)	0	1
E (Geropon)	0	0
F (Igepal 520)	0	0
G (Igepal 630)	0	0

** Chemical systems highlighted in pink were selected for second stage testing.*

(a) (b) (c)

Figure 22. Core chip before treatment (a) Berea high perm sandstone (b) Berea medium perm sandstone (c) Local limestone.

(a) (b) (c)

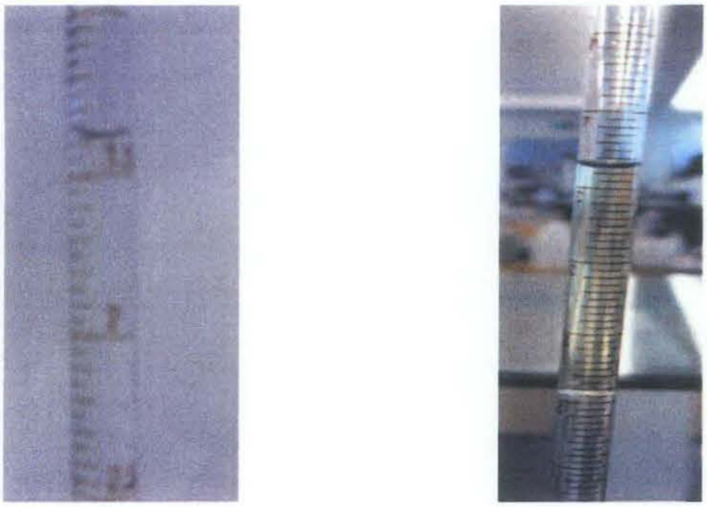
Figure 23. Berea high perm core chips after treatment with (a) 0.1 wt % F103 (b) 0.1wt% CTAB (c) 0.1 wt % SDS.

(a) (b) (c)

Figure 24. Local limestone core chips after treatment with (a) 0.1 wt% F103 (b) 0.1wt % CTAB (c) 0.1 wt % DBSA.

4.2 SECOND STAGE TESTING: SPONTANEOUS IMBIBITION TESTING

Spontaneous imbibition is a process in which a wetting phase displaces a non-wetting phase in a porous medium Spontaneous imbibition set up is as shown in fig. 20b. All imbibition tests were run at ambient temperature. Diesel was injected into each core sample to reach almost 100% saturated with diesel. The core sample then was immersed in imbibition cell filled with brine and exposed to spontaneous capillary imbibition. The oil recovery was monitored against time. After brine imbibition, the core is dried in the oven and the flushed again with oil to resume the diesel saturation. The core was ready for chemical imbibition experiments. The oil recovery by spontaneous imbibition of brine was then compared with spontaneous imbibition of chemical (surfactant) solutions.



(a) (b)

Figure 25. Burette on top of imbibition cell. (a) Imbibition started (no oil recovered) (b) Oil recovered after few hours.

Figure 25 shows the burette that is attached to the imbibition cell, when experiment just started, no oil is recovered, with time, oil is being displaced by brine and oil with lower density will moved to the top and the amount can be read from the gradation on burette.

4.2.1 Imbibition rate using Diesel and Crude Oil

Core 1-4 were saturated with Diesel as oil phase while Core 5 and 6 were saturated with crude oil. Due to the difference in viscosity, density and chemistry of both crude oil and diesel. Imbibition rate obtained were also different. Due to the nature of crude oil as heavier and more viscous (Fig. 27) than Diesel, imbibition with crude oil was slower, and the rate could not be obtained because the crude oil were sticking to the surface of the imbibition cell as shown in figure below.

Figure 26. Imbibition test with crude oil as oil phase.

Figure 27. Color and viscosity of crude oil.

Source: http://www.schoolscience.co.uk/

4.2.2 Imbibition rate for High perm and Medium perm

The rate of imbibition as given by Tang and Firoozabadi[15] (2000) is a function of the interfacial tension (σ), permeability (k) and porosity of the core (ϕ), viscosity of the fluid (μ), cross sectional area (A) exposed to the fluid and wettability of the core ($\cos\theta$). The volume V imbibed into the core is approximated by them using

$$V^2 = \sqrt{\frac{8k}{\phi}} \frac{\sigma A^2 \cos\theta_p}{2\mu} t \qquad [3]$$

From this equation it can be seen that the imbibition rate is slow in low perm cores and high in high perm cores if all the other parameters are maintained constant. However results obtained from experiment show a different result as shown in Figure 28. This shows that middle perm core is more water wet as compared to high perm cores ($\theta > 90^0$) as shown in contact angle testing (Fig. 22)

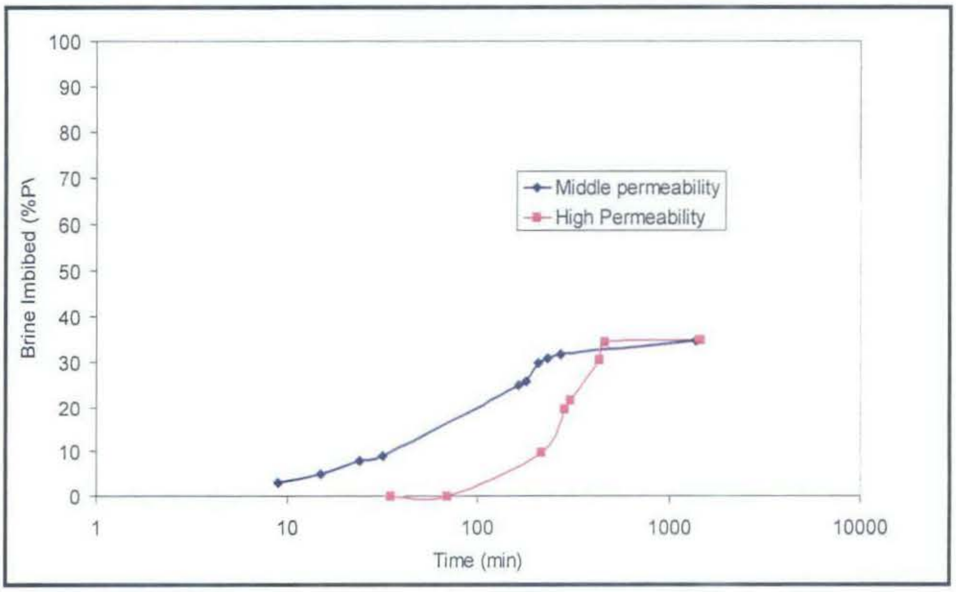


Figure 28. Imbibtion of brine into high perm and middle perm core saturated with oil.

4.2.2 Imbibition data for core 1 (Surfactant: F103) with and without initial water saturation

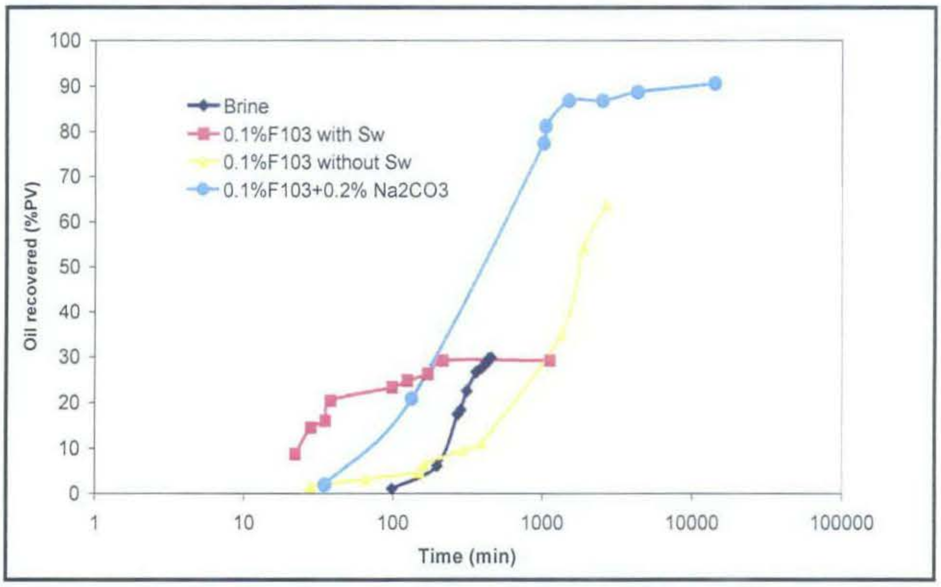


Figure 29. Imbibition of brine into Core 1, with brine, surfactant (with and without initial water saturation) and surfactant + alkali.

Babadagli[14] studies show that having initial water in the system resulted in faster recovery of light crude oil in limestones compared to sample without initial water for anionic surfactants. Figure 29 shows the imbibition data of Core 1. The initial imbibition without surfactants shows about 30 % OOIP were displaced by brine. After brine imbibition experiments, brine was injected into the core. Then, the core was flushed again with oil to resume an initial water saturation (S_{wi}) condition (the reason for introducing initial water saturation is most reservoirs contain water). The core was ready for chemical imbibition experiments. The same core was then cleaned with Toluene and re-flushed with oil to create 100% saturation with oil and placed in imbibition cell for chemical imbibition with 0.1 wt % F103. The pink color line shows the imbibition data for core with S_{wi}, while the yellow shows data for core without S_{wi}. Without initial water saturation, the amount of oil displaced is higher as compared to with S_{wi}; however with S_{wi}, the displacement process is faster. Addition of alkali (pH 10), the amount of oil displaced goes up to 90 % OOIP, the imbibition rate also faster. This proves that alkali can further decrease the interfacial tension and help in wettability alteration. Addition of alkali is believed to create another ultra low interfacial phase (neutral) as alkali mix with certain acidic compound in the crude oil.

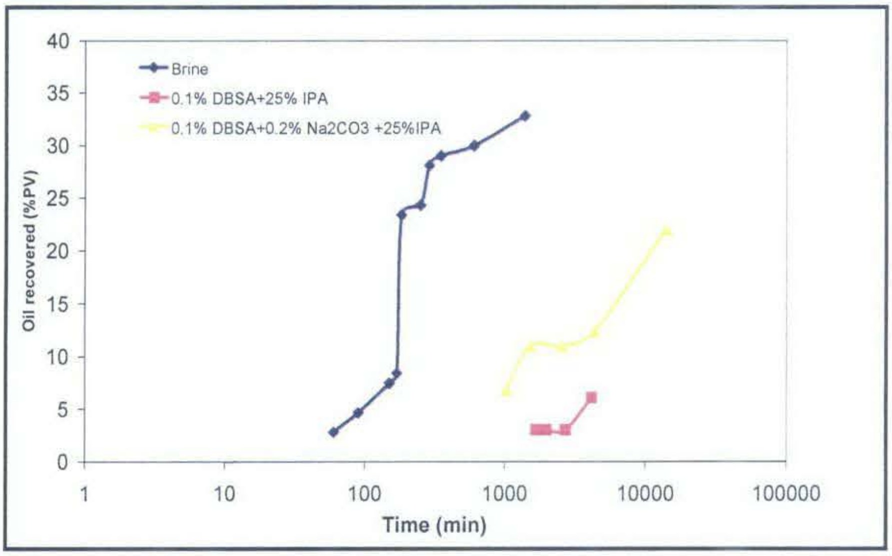


Figure 30. Imbibition data for Core 2 (Brine and 0.1 % DBSA.

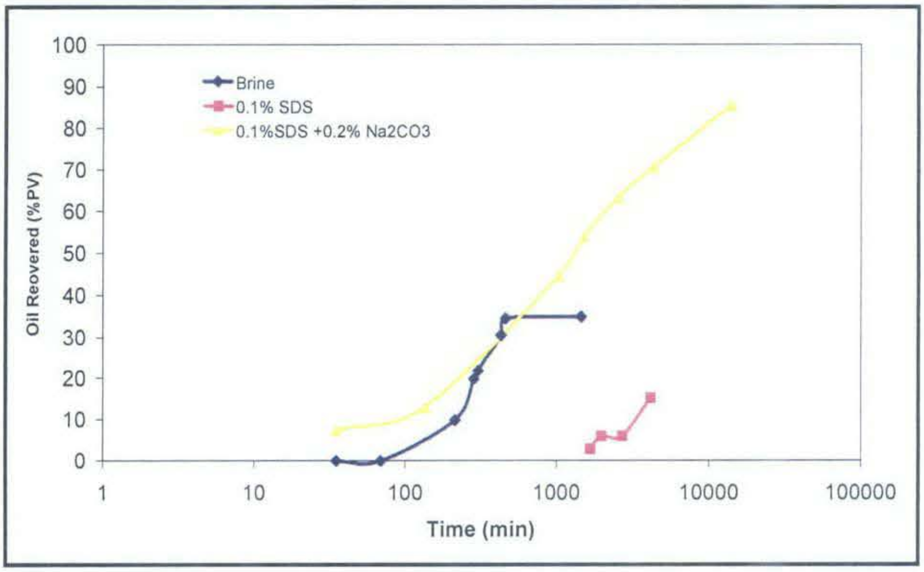


Figure 31. Imbibition data for Core 3 (Brine and 0.1% SDS).

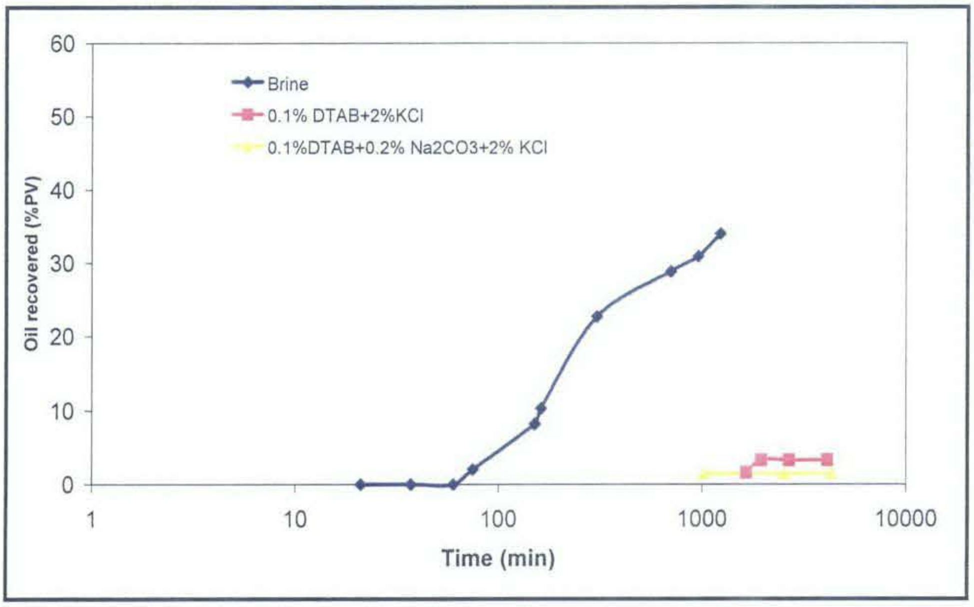


Figure 32. Imbibition data for Core 4 (Brine and 0,1% DTAB).

Figure 30, Figure 31 and Figure 32 show imbibition data of Core 2, Core 3 and Core 4, the chemical imbibition is run with chemical system B, C and D. All three did not show positive results as compared to F103. For Core 3 with chemical system C, the amount of oil recovered with addition of alkali goes up to 85% OOIP, this shows that SDS perform best in high pH. Core 2 and Core 4 did not show positive results even with the addition of alkali, this maybe due to incompatibility of alkali with surfactants, some literatures reports that alkali will slow down the adsorption of surfactants to surface.

This proves that anionic surfactants work best in wettability alteration for sandstone since F103 and SDS is anionic while DTAB is cationic surfactant.

4.3 SUMMARY OF DATA

A total of 4 complete experiments have been conducted, complete experiment include imbibition with brine, imbibition with diluted surfactant and imbibition test with diluted surfactant and alkali. A complete experiment needs more than 2 weeks to complete. Table 4 shows the summary of data. Core 1 treated with Surfactant F103 shows the best results as compared to other surfactant systems.

Table 5. Summary of data.

CORE	SURFACTANT	PORE VOLUME	AMOUNT OIL SAT (FINAL WEIGHT-INITIAL WEIGHT)/PORE VOLUME,%	OIL RECOVERED WITH BRINE, % OOIP	OIL RECOVERED WITH SURFACTANT SOLUTIONS, % OOIP	OIL RECOVERED WITH SURFACTANT+ ALKALI SOLUTIONS, %OOIP
1	F103	4.886	64.2	30	65	90.5
2	DBSA	5.336	60.6	33	6	22.03
3	SDS	5.078	64.2	35	25	85.5
4	N-CTAB	4.851	61.3	36	3	1.48

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

As a conclusion, the research work done has met the objectives set earlier that is to increase the recover of OOIP from initially 30% OOIP to more than 80 % OOIP by using diluted surfactants that can alter the wettability of the formation. Below are the experimental conclusion and recommendation for future research:

5.1 CONCLUSION

A total of 8 contact angle tests and 6 imbibition tests have been conducted to screen 6 surfactant systems for the ability to decrease interfacial tension and wettability alteration from oil wet to water wet. 4 chemicals were chose to proceed with second stage testing. Imbibition tests were conducted using imbibition cell designed and cores used were Berea sandstone and local limestone. Limestones were not used to proceed for second stage testing due to low porosity and permeability to contain oil. Out of the 6-imbibition tests, 4 cores were saturated with Diesel while the other 2 medium permeability cores were saturated with crude oil. The following are the conclusions from the experimental results:

- The contact angle test can be used to determine the performance of the surfactant system.
- Imbibition test can be used to measure the effect of wettability alteration.
- Water wet cores recovers more oil as compared to intermediate/oil wet cores.

- Addition of surfactants can alter the wettability of the surface and lovers the interfacial tension.
- By using crude oil as oil phase, the recover rate is a lot slower as compared to using Diesel.
- Out the 4 chemicals tested, F103 shows the best results and able to recover more than 60 % OOIP.
- With addition of alkali, cores treated with F103 and SDS shows good wettability alteration and able to recover more than 80 % OOIP.
- Core with initial water saturation recovers less oil as compare to core without initial water saturation.
- Anionic surfactants help in recover more oil for sandstones as compared to cationic surfactants.

5.2 RECOMMENDATIONS

The following are some recommendation for future work:

- **High temperature testing**

-Since all the experiments were run in room temperature, future work can include real reservoir temperature testing, certain surfactants structure might change at high temperature and losses it's effectively in wettability alteration. Repeating the experiments with real reservoir temperature (90 deg F to 150 deg F) can further verify the best chemical system.

- **Different concentrations of surfactants with different solvent to select the chemical system with best wettability alteration.**

-Most literature suggest the low concentration of surfactant or slightly above CMC, more experiments can be conducted to further verify the statement. CMC values of surfactants increase with temperature.

- **Perform the experiments with limestones, dolomites and some other sedimentary rocks.**

-Different minerals have different properties and charges, by repeating the experiments on different sedimentary rocks can identify the best types of surfactants for different types of formation.

- **Comparison of results with computer simulation generated results.**

-Commercially available software, such as Schlumberger Eclipse are able to simulate a real reservoir condition in a bigger scale as compared to laboratory small scale testing, Comparison of results from both lab scale and real reservoir computer simulated scale can further confirmed the system before it is being testing in the field.

- **Using other commercially available surfactants and other alkalis.**

- **Mixtures of surfactants.**

- Certain literatures states that mixtures of compatible surfactants create the lowest interfacial tension, experiments can be carried out to verify using the surfactants used in this project. Solvents also play a very important role.

References

[1] Business, The Star Publication, 10 August 2005.

[2] Hamdan, M.K., Darman, N., Hussain, D. Ibrahim, Z., **Enhanced Oil Recovery in Malaysia: Making it a Reality**, SPE 93329, presented at 2005 Asia Pacific Oil and Gas Conference and Exhibition in Jakarta, Indonesia, 5-7 April.

[3] Yasin, A.A.M., **Enhanced Oil Recovery in Malaysia**, SPE 17693 presented at 7th Offshore South East Asia Conference in Singapore, 2-5 Feb 1988.

[4] Lake, W. Larry, Schmidt, L. Raymond, Venuto, B. Paul, **A Niche for Enhanced Oil Recovery in the 1990s,** Schlumberger Oilfield Review, 1992. http://www.oilfield.slb.com/media/services/resources/oilfieldreview/ors92/0192/p55_61.pdf, 4 August 2005.

[5] Hawkins, B., Singhal, A., **Enhanced Oil Recovery Water Usage, presentation to Advisory Committee on Water Use Practice and Policy**, 2 Mar 2004, http://www.waterforlife.gov.ab.ca/docs/enhanced_oil_recovery_march_2004.pdf, 4 August 2005.

[6] Latil, M**., Enhanced Oil Recovery**, Gulf Publishing Company, Houston, 1980.

[7] Pei Ling Koh, Final Industrial Internship Report at Schlumberger MEA CSL, 5 Aug 2005, Universiti Teknologi PETRONAS.

[8] Schramm L. Laurier, **Surfactants:Fundamentals,and Application in the Petroleum Industry**, Cambridge University Press, United Kingdom, 2000.

[9] D.O Shah, **Fundamental Aspects of Surfactants-Polymer Flooding Process,** Chemical Flooding, Enhanced Oil Recovery Department of Chemical Engr. And Anaesthesiology, Uni. Of Florida

[10] Lake, W. Larry, **Chemical Flooding,** Petroleum Engineering Handbook.

[11] A. Seethephaki, B. Adibhatla, K.K. Mohanty, **Wettability Alteration During Surfactant Flooding of Carbonate Reservoir,** SPE 89423 presented at SPE/DOE Fourteenth Symposium on Improved Oil Recovery in Tulsa, Oklahoma, 17-21 Apr 2004.

[12] F.Craig Jr, Forest. , **The reservoir engineering aspect of Waterflooding**, Fourth Printing, Society of Petroleum Engineers of AIME, 1993

[13] K.K. Mohanty, **Dilute Surfactant Methods for Carbonate Formations,** Department of Chemical Engineering, University of Houston, 2004

[14] T. Babadagli, Analysis **of Oil Recovery by Spontaneous Imbibition of Surfactant Solution**, SPE 84866 presented at SPE International Improved Oil Recovery Conference in Asia Pacific in Kuala Lumpur, Malaysia, 20-21 Oct 2004

[15] G.Q. Tang, A. Firoozobadi," **Relative Permeability Modification in Gas/Liquid Systems Through Wettability Alteration to Intermediate Gas Wetting**", SPE 81195 presented at SPE Annual Technical Conference and Exhibition 2000 in Dallas USA Oct 1-4.

[16] Dag C. Standnes, T. Austad, **Wettability Alteration in Carbonates Low-cost Ammonium Surfactants based on Bio-Derivatives from Coconut Palm as Active Chemicals to Change the Wettability from Oil-Wet to Water-Wet Conditions,** Colloids and Surfaces A: Physiochemical Eng. Aspects, 2002

Appendices

APPENDIX A

Measurement of Porosity and Permeability using Gas Permeameter and Gas Porosimeter

Figure 1. TerraTek PoroPerm to measure porosity and permeability.

Porosity and permeability are important properties for a reservoir rock. Porosity is a measure of storage capacity of a reservoir. It is defined as the ratio of the pore volume to bulk volume.

$$\phi = \frac{pore \quad volume}{bulk \quad volume} = \frac{bulk \quad volume - grain \quad volume}{bulk \quad volume} \qquad [1]$$

Permeability is a measure of rocks ability to transmit fluids. Darcy's law generalized relationship between permeability, differential pressure, flow rate, viscosity of fluid and length.

$$K = \frac{Q\mu L}{A\Delta P} \qquad [2]$$

Where: Q is volumetric flow (cm^3/s)

K is permeability (Darcy)

μ is viscosity (centipoise)

ΔP is differential pressure (atm)

L is length (cm)

A is area of fluid flow (cm^2)

The model 8400 **PoroPerm™** by TerraTek is a self-contained low-pressure nitrogen gas permeameter and helium gas porosimeter.

Porosity Measurements using Helium Gas Porosimeter.

In order to calculate porosity, three main quantities that need to measure is bulk volume, pore volume or grain volume. Bulk volume measurement may be computed from the measurements of the dimensions of a uniformly shaped sample by using caliper measurement. Helium porosimeter is used to find grain volume, it uses the principle of gas expansion as described by Boyle's law (Eq. 3) and helium gas follow ideal gas law.

$$P_1V_1 = P_2V_2 \quad [3]$$

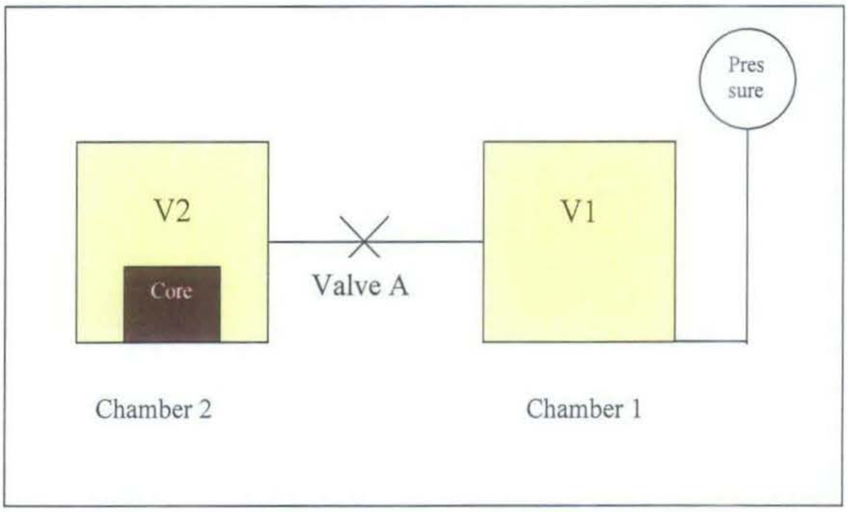


Figure 2. Simplification of porosimeter circuit.

Initially, Valve A is closed and helium gas with known pressure is supplied to Chamber 1 with known V1, then Valve A is open so that gas can isothermally expand to Chamber 2 and core, pressure is taken as P2. Since gas already expanded through the core, grain volume can be calculated as show below.

$$P_2(V_1 + V_2 - V_g) = P_1V_1$$

$$V_g = \frac{P_2(V_1 + V_2) - P_1V_1}{P_2} \quad [4]$$

Pore volume is calculated simply by subtracting grain volume from the bulk volume. Porosity thus can be calculated using Eq. 3.

Helium has advantages over other gases because (1). Its small molecules rapidly penetrated small pores, (2) it is inert and does not adsorb on rock surfaces as air may do, (3) helium can be considered as an ideal gas for pressures and temperatures usually employed in the test and (4) helium has high diffusivity and therefore affords a useful means for determining porosity of low permeability rocks.

Permeability measurement using Nitrogen gas permeameter

Schematic diagram of permeameter can be seen in figure 2, the inlet pressure of the nitrogen source is controlled by the nitrogen regulator. The pressure is set at around 400 psi. Permeameter consists of a Hassler sleeve where confining pressure is being applied to the core so that nitrogen gas is fully flowing through the core. A front regulator is used to set upstream test pressures. Orifice tube down stream is used to measure the flow rate from the permeameter sample. The operation of orifice is based on an increase in velocity causes a decrease in pressure. The flowmeter has some retriction within the pipe to measure the pressure difference b

When using gasses, Darcy's law in Eq. 1 is modified, mean pressure P_m and mean flow rate Q_m are used.

$$K = \frac{\mu.L.Q_m}{A(P_1 - P_2)} \quad [5]$$

Where P_1 is absolute pressure upstream pressure, P_2 is absolute downstream pressure. Qm is not a measurable quantity; a system of equalities can be established using Boyle's Law

$$P_1Q_1 = P_2Q_2 = P_mQ_m = P_bQ_b \quad [6]$$

The subscripts 1, 2, m and b respectively denote upstream, downstream, mean and basis conditions (measure using orifice). Basis is equivalent to atmospheric conditions. Q_m can be rearranged from Eq. 6 as follows

$$Q_m = \frac{P_bQ_b}{P_m} \quad where \quad P_m = \frac{P_1 + P_2}{2}$$

Substituting into[4], the permeability is given by

$$K = \frac{2\mu L}{A} \cdot \frac{P_bQ_b}{P_1^2 - P_2^2} \quad [7]$$

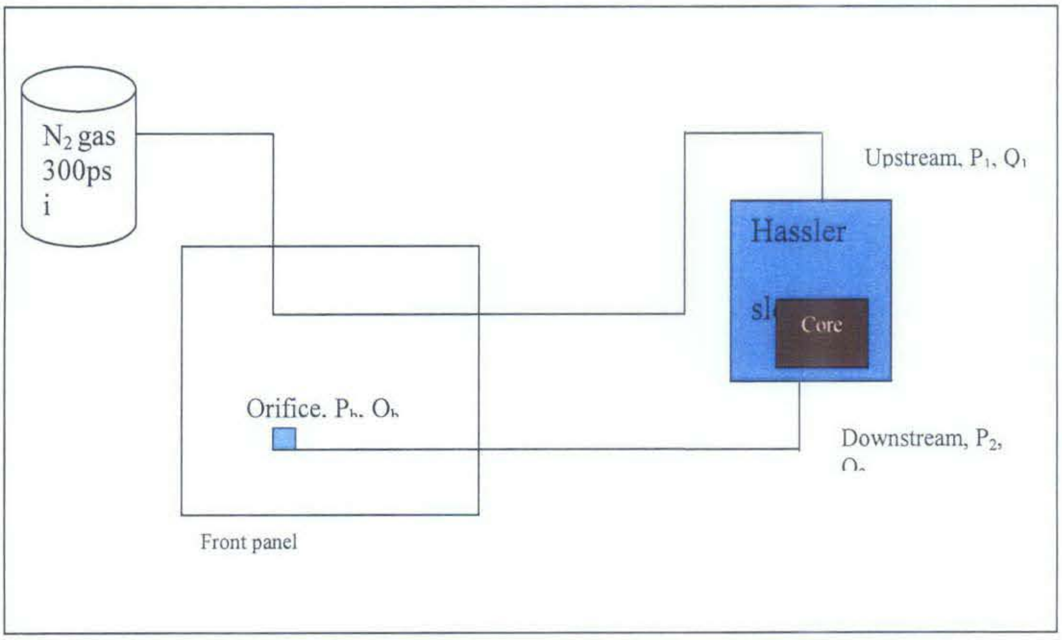


Figure 3. Simplify Schematic Diagram of Permeameter.

APPENDIX B

Basics on Darcy's Law

Darcy's Law is generalized relationship for flow in porous medium. It shows that volumetric flow is a function of the flow area, elevation, fluid pressure, permeability, viscosity of the fluid and the length. In petroleum industry, permeability is measured in Darcy where 1Darcy ~10^{-8}cm^2. Viscosity of water is 1cp and viscosity of natural gas is 0.01cp.

$$Q = \frac{kA\Delta P}{\mu L}$$

where: Q is volumetric flow

K is permeability

μ is viscosity

ΔP is differential pressure

L is length

A is area of fluid flow

Darcy law applies to porous medium. Hagen-Poiseuille flow applied to laminar flow in a horizontal pipe.

$$Q = \frac{\pi r^4 \Delta P}{8\mu L}$$

Where r is the radius of the pipe and other symbols remain the same as above. It can be clearly seen Darcy's Law can be compare with Hagen-Poisueille relation. The comparison gives K~$r^2/8$. Thus, permeability is crude approximate to square of radius.