Investigation of Suitable Surfactants in Enhanced Oil Recovery (EOR)

By

Phyllis Seli

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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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,

(A.P Dr. Syed Sakhawat Shah Syed Farman)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 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 the original work contained herein have not been undertaken or done by unspecified sources or persons.

Phyllis

PHYLLIS SELI

ABSTRACT

This Final Year Research Project involves the study of the various Enhanced Oil recovery techniques with special emphasis on the use of surfactants in enhanced oil recovery. Study involves literature review of various studies done on the enhanced recovery techniques; chemical flooding, miscible and immiscible displacements techniques and also thermal recovery.

Objective of the project is then to study in detail the mechanisms used in each of the recovery techniques and also to investigate the advantages and also the limitations. This paper also review the use of surfactants in different chemical flooding methods surfactant-polymer, micellar-polymer flooding and also alkaline surfactant polymer flooding (ASP).

The study, in particular emphasize on the mechanisms of chemical flooding through reduction of interfacial tension and also alteration of wettability. Optimum oil recovery occurs at ultra-low interfacial tension which is made possible through the addition of surfactants into the oil-brine system. Wettability is defined as the adhesion tension between the rock and the fluids contacting the rock. Water-wet conditions provide optimum conditions for enhanced oil recovery as compared to an oil-wet system.

In choosing the best enhanced oil recovery method, it is highly dependent on the reservoir conditions and crude oil characteristics. Chemical flooding and miscible/immiscible displacement processes are suitable for low to medium viscous crude oil while thermal recovery methods are highly successful in recovering heavy viscous crude oil.

ACKNOWLEDGEMENTS

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To A.P Dr Syed Sakhawat Shah, my Supervisor, I would like to thank you for your guidance and assistance during my Final Year Research Project. Thank you for giving me opportunity to learn as much as possible Enhanced Oil Recovery. I am very grateful for all the advice and guidance in completing my research project.

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CHAPTER 1

INTRODUCTION

1.0 BACKGROUND OF STUDY

Oil recovery can be divided into 3 stages; namely primary, secondary and also tertiary recovery, also known as enhanced oil recovery (EOR). There are 3 major stages of oil recovery. Primary recovery using natural pressure of the reservoir to drive oil into wellbore and artificial lifts techniques to produce the oil to the surface. Secondary recovery using water flooding or injection to displace the oil and drive the oil into the wellbore and tertiary recovery which are enhance oil recovery techniques to recover remaining oil trapped in rock formation.

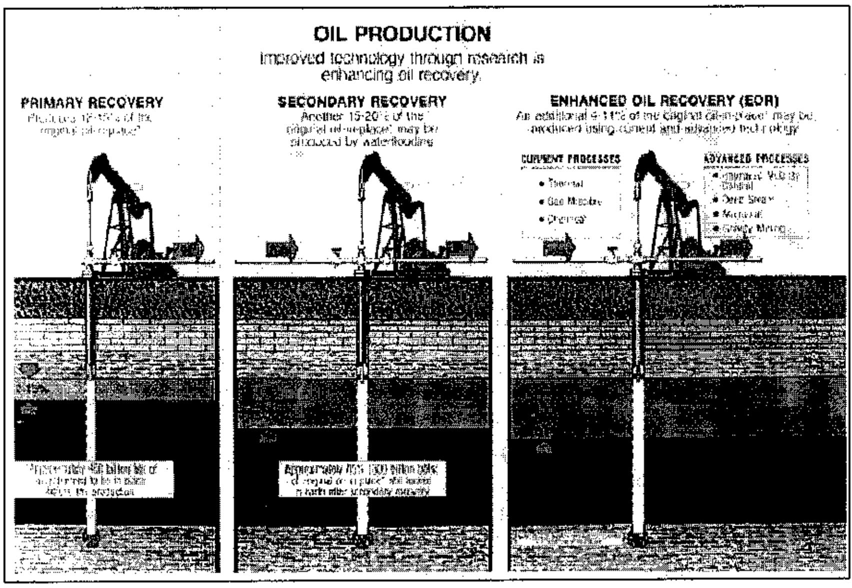


Fig. 1.1: Oil Recovery Stages

(Source: Thomas, C., "Future of Fossil Energy in Alaska Enhanced Oil Recovery", [1]) Tertiary recovery or Enhanced Oil recovery techniques are employed to recover the remaining oil trapped within rock formation after primary and secondary recovery steps can no longer recover anymore oil.

Figures quoted from DOE Fossil Energy website [1], the discovered but unrecoverable crude oil by current technology amounts to almost 377 billion barrels or 49% with respect to the 649 billion barrels of original oil in place. In the United States, only 800,000 barrels of oil per day is recovered by EOR as compared to the 6 million barrel of total domestic production.

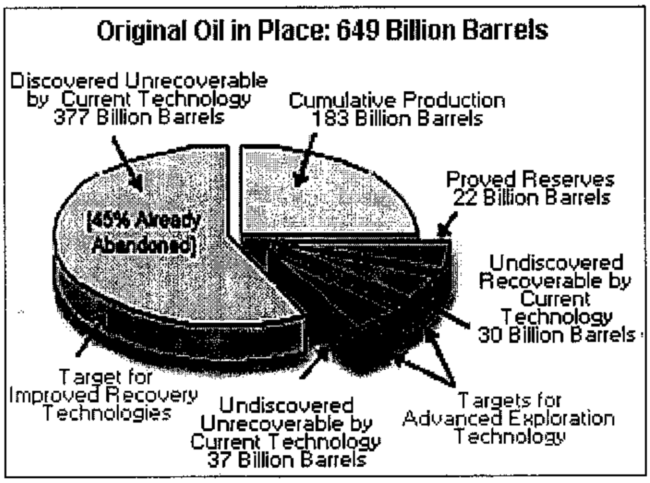


Fig 1.2: Original Oil Place
(Source: "DOE Fossil Energy Enhanced Oil Recovery /CO2 Injection", [2])

Currently, there are many different EOR techniques employed today, which are mostly divided into two categories; thermal and non-thermal processes. Some examples of EOR techniques employed today are:

- Non-thermal processes
    - Miscible displacement processes , Chemical flooding, Microbial enhanced oil recovery , Gas drives
- Thermal processes:
    - steam flooding , hot water injection, in-situ combustion

Between the 2 major classifications of enhanced oil recovery techniques; thermal methods accounts for the majority of EOR applications. Oil & Gas EOR 2004 survey [3], found that thermal methods produces the majority of the total US EOR production, followed by gas and lastly chemical. For thermal processes, steam produces the highest recovery compared to combustion in-situ and hot water. In Gas EOR, miscible CO2 accounts for the majority of the production as compared to nitrogen gas and the other miscible and immiscible hydrocarbon. For the chemical EOR, there seems to be a decline of its application. Its peak production was in 1988 using polymer flooding technique with production reaching 22500 barrels per day. However it then suffers a major decline from 1988 onwards with productions barely reaching 5000 bbls/day. For more detailed figures on the US EOR production, please refer to Table A.1 in Appendix II.

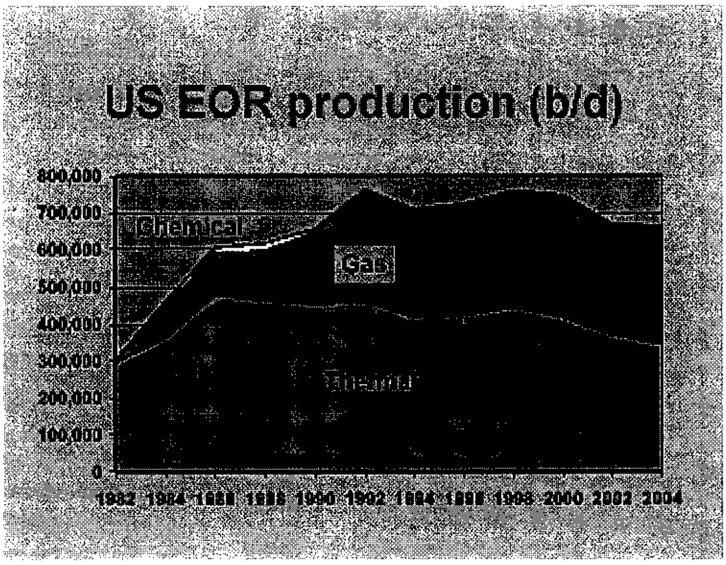


Fig. 1.3: U.S EOR Production

(Source: Tippee, B., "Oil & Gas Journal's 2004 EOR Survey", [3])

1.2 Problem Statement

This research project will identify the available EOR techniques and to gather as much literature on each method as possible so as to build an extensive collection of information regarding the topic Enhanced Oil recovery (EOR). Enhance Oil Recovery techniques are expensive investments and though there are many EOR techniques available, few of the methods actually known to work effectively. This study will then hope to give a better overview of Enhanced Oil Recovery and promote better understanding on the subject matter.

1.3 Objective and Scope of Study

Objective of this study is to gather the information on available types of Enhanced Oil recovery techniques, with special emphasis on the use of surfactants in chemical flooding in EOR.

1. This research project hopes to study the theoretical mechanisms of the various available EOR techniques, in particular, the use of surfactants in chemical flooding. This study will emphasize the roles of surfactants in terms of the types of surfactants and the mechanisms employed to enable for better crude recovery.

2. From the information gathered, a comparison between the methods can be made and to judge the suitability of the methods used in terms of cost, effectiveness oil recovered and also on the possible limitations or problems faced.

1.3 Objective and Scope of Study

Scope of EOR methods to be studied includes:

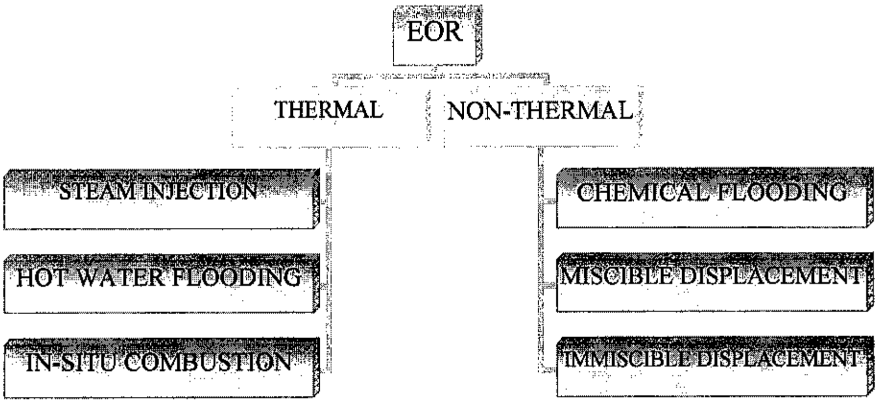


Figure 1.4: Scope of Enhanced Oil Recovery Methods to be studied

By the end of the given 14 week time frame, there would be an accumulated collection of literature on the various Enhanced Oil Recovery (EOR) methods used by the oil exploration and production industry today.

CHAPTER 2

LITERATURE REVIEW

Enhanced oil recovery also known as tertiary recovery involves adding external energy and introducing changes into the physicochemical properties of the reservoir system. These changes include changes in viscosity, interfacial forces, wettability of the reservoir.

Objective of enhanced oil recovery is to further recover the crude oil remaining in the reservoir. The residual oil can be categorised as either *microscopic* which refers to the oil capillary trapped droplets in the swept areas and *macroscopic* which refers to the virgin oil in unswept zones. Unswept zones are zones that were missed or have not been swept by the displacement fluids.

Enhanced Oil Recovery methods can be classified as either thermal or non-thermal. Non-thermal methods include chemical flooding, miscible displacements and gas drives. Chemical flooding involves the injection of chemicals into the injected water or gas to further recover crude oil. This is done by reducing the mobility of the injected fluid and by reducing the oil/water interfacial tension.

Other common methods in Enhanced oil recovery are also through miscible displacements. Miscible displacement processes involves introduction of fluid or solvent into the reservoir and mixes with the reservoir oil, to push the oil out of retention in the rock matrix.

Thermal methods on the other hand include steam injection, hot water flooding and also in-situ combustion, and utilize heat to help in recovery. New methods that are also being developed include the use of micro organisms to biochemically produce surfactants and polymers, a method known as Microbial Enhanced Oil Recovery (MEOR).

Table 1 shows a summary of the oil recovery mechanisms of the various enhanced oil recovery techniques. A comprehensive literature review regarding each of the three main enhanced oil recovery technique will be discussed in later sections of this report.

Table 1: EOR mechanisms

Target	Mechanism	Process	Method
Action on oil droplets trapped in pores	• Displacements – mass transfer/multi contact/miscible • Lowering of IFT	Hydrocarbon gas CO2, N2; flue gas surfactant	Miscible/multi-contact/immiscible /drive Chemical
Action on oil trapped in unswept areas	• Increase in water viscosity • Conformance adjustment • Reduction of crude oil viscosity	Polymers Foams Polymer CO2 Steam In situ combustion	Chemical Chemical Thermal

(Taken from: Dawe, R.A., "Modern Petroleum Technology Vol. 1 Upstream", [4])

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Procedure Identification

A major part of the project would be literature research and collection of information regarding the Enhanced Oil recovery. Literature research will be done continuously throughout the project until a considerable collection of information has been gathered. Each method under the 2 classification of EOR methods; thermal and non-thermal will be explained individually in chapters. Each chapter will consist of

- Theory behind the enhanced oil recovery mechanism
- Advantages of the method used
- Possible limitations of method

At the end of the project, with the amount of information collected, a comparison between the various can be made, in terms of effectiveness of oil recovered, cost, and also the limitations faced. Please refer to Appendix I for Project Gantt chart and also Figure A.1 showing Project Methodology.

3.2 Identification of hardware/tools

Important resources during this project are:

1. Books, publications, journals e.g. Oil & gas industry journals
2. Internet resources and online journals
3. UTP Petroleum Engineering Dept. (Mechanical)
4. Industry resources

CHAPTER 4

CHEMICAL FLOODING

4.1 Types of Surfactants

There are 4 major types of surfactants; anionic, cationic, non-ionic and zwitterionic. Surfactants are defined by their hydrophilic head group.

Table 4.1: Types of Surfactants

Surfactant Type	Hydrophilic Head Charge
Anionic	Negative
Cationic	Positive
Amphoteric	Charge changes with pH
Zwitterionic	Both positive and negative charge
Non-ionic	No charge

Surfactants are surface active agents and consist of two parts; one water loving (hydrophilic) and the water repelling portion (hydrophobic). This structure results in the molecules trying to orient themselves so as to have the hydrophilic structure within the solvent and the hydrophobic structure away from the solvent, resulting in a concentration at the interface between the oil-water phases.

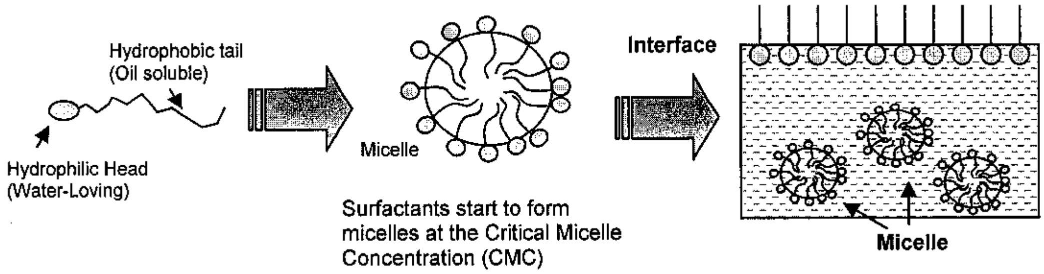


Figure 4.1 Surfactants Structures

Surfactants molecules at the oil-water interface reduce the surface tension present between the oil and water. Reduction of the interfacial activity of the surfactant depends on the concentration at the interface, which measures the surfactant effectiveness. Greatest concentration can be achieved with surfactants of least cross-sectional area or most efficient packing. Effectiveness determined by orientation and structural group of surfactants. Efficiency of surfactant is the ratio of concentration at the interface with that at the bulk solvent phase, $C_{interface}/C_{bulk}$. The ratio is determined by the free energy change. Efficiency of adsorption at the interface in an aqueous system is greater by increasing the hydrophobic nature of surfactant.

Surfactants also form spherical aggregates called micelles and are formed when surfactants reach a critical concentration. Critical micelle concentrations of surfactants are affected by surfactant structure, salinity of water, presence of organic additives and also temperature. As shown by Fig. 4.2, above the critical concentration, interfacial tension is reduced to low values.

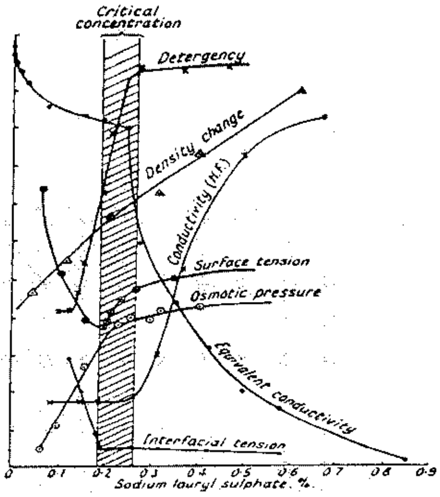


Figure 2. Illustration of the dramatic changes in physical properties that occur beyond the critical micelle concentration. (From Preston [48]. Copyright 1948 American Chemical Society, Washington.)

Fig. 4.2: Physical Properties occurring beyond the critical micelle concentration

(Taken from Schramm, L., Fundamentals and Applications in the Petroleum Industry, [5])

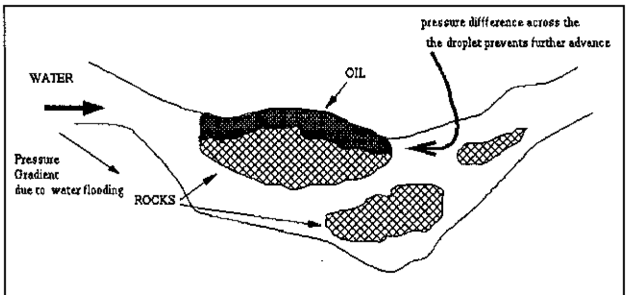
4.2 The role of surfactants in Chemical Flooding

For EOR, some chemical methods involving surfactants have been used in chemical flooding such as surfactant flooding, micellar flooding, emulsion flooding and also combinations e.g. surfactant-polymer flooding, alkaline surfactant polymer (ASP) flooding, among others. Surfactants behave like detergents and are significantly used for its ability to reduce interfacial tension between oil and water. Main causes of oil trapped inside the rocks are due to capillarity and wettability and the two main mechanisms by surfactants in enhanced oil recovery are through reduction of interfacial tension and in some cases, through alteration of wettability.

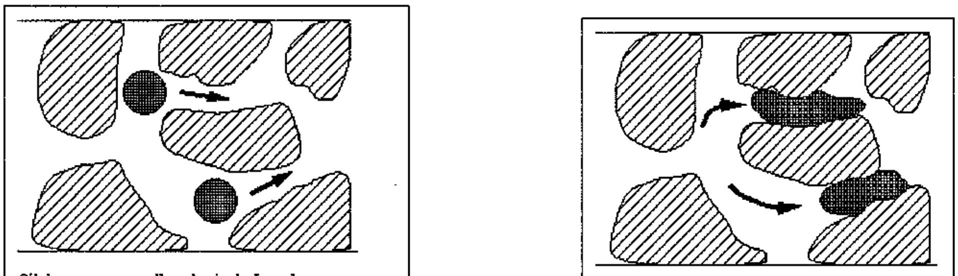
Surfactants can be used to overcome the capillary forces which trap the crude oil in the reservoir. With reduced interfacial tension between the water and the oil, the crude oil can be displaced, motion of oil no longer restricted by the capillaries. Surfactants can also alter the wettability of the reservoir rocks to water wet conditions instead of oil wet, through low interfacial tensions. Microemulsion are known as swollen micelles; homogenous mixtures of water and oil with large amounts of surfactants. With microemulsion flooding, fluid such as water and oil can become miscible by lowering the interfacial tension of water [6].

4.3 Trapping of Oil

While waterflooding may have rapid response in oil recovery through creating pressure gradient in the reservoir, however for chemical flooding, the change in the displacement process only takes place when the chemical has contacted the reservoir. In chemical flooding, a series of slugs is injected; surfactant, polymer and water, to reduce the oil saturation and create a 'bank' of oil.



Oil drop stuck in a capillary (before adding surfactant)



Oil drops are normally spherical. In order to pass through the constrictions they must be able to deform.
pores in the rock medium can be as small as 1 micron

The addition of surfactants enables the oil droplets to elongate and overcome the capillary forces.

Figure 4.3: Trapping of oil
(Source: Nihon-Emulsion, "Characteristic of surfactants", [7])

Figure 4.3 shows the trapped oil stuck in a capillary due to the pressure difference across the droplet which prevents the droplet from advancing. This is prior to addition of surfactant into the reservoir. Addition of surfactants will lower the interfacial tension and enable the oil droplets to overcome the capillary forces.

4.4 Capillarity

Capillary forces are as a result of the interfacial tension between the fluids in the capillary and the interfacial forces at the fluid-rock interface. The interfacial tension between the crude oil and water is approximately 20 dyne/cm^2. The retention of the residual oil in the porous media is due to the interfacial force at the fluid-rock interface (wettability) and also the capillary structure of the rock.

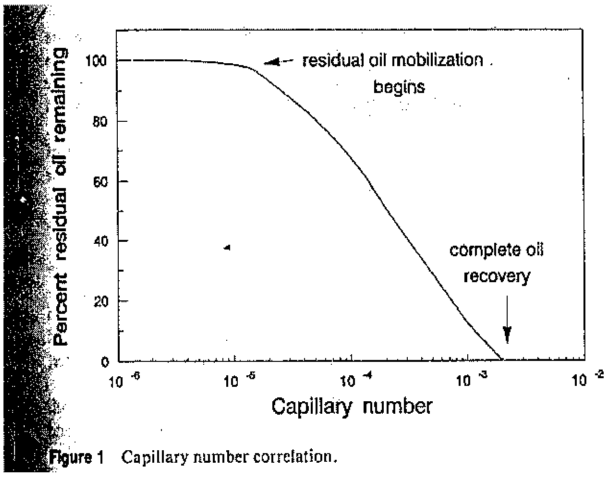


Figure 1 Capillary number correlation.

Figure 4.4: Capillary number versus Percent Residual Oil Correlation
(Taken from: Nasr-El-Din & Taylor, "The Role of Surfactants in Enhanced Oil Recovery" [8])

Capillary number is a unit less relationship that has been developed to describe the interdependence between the viscous forces (differential pressure) and surface forces (interfacial tension) and capillary flow. Capillary number is often used to estimate the displacement of waterflood residual crude oil trapped in a capillary system.

$$CapillaryNumber = \frac{ViscousForces}{CapillaryorSurfaceForces} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

The proportion of unswept area depends on the mobility ratio. Where, λ is the mobility, μ is the viscosity and k as the fluid permeability

$$M = \frac{\lambda_d}{\lambda_o} = \frac{k_d \mu_0}{k_o \mu_d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

Water soluble polymer increases the viscosity and decreases the fluid permeability. Capillary forces causes large amount of oil to be retained or left behind. In a water wet condition, each oil droplet can flow until it encounters a pore size smaller than its own diameter. Oil trapped in this way is called residual oil.

Capillary pressure by Laplace formula,

$$P_c = P_o - P_w = \frac{2\sigma}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

For flow to occur pressure gradient must be overcome and the interfacial tension must be reduced to 10^{-2} mN/m. The displacement of the residual oil is related to the viscosity and also the capillary forces. To achieve 'near-zero oil saturation' $(N_c)_{cnt} \approx 10^{-6}$ needs to be increased 3 or 4 magnitude therefore IFT reduced 10^3 or 10^4 to 10^{-3} mN/m using surfactants under the appropriate conditions.

$$\Delta\rho g h = -2\sigma \cos\theta / R$$

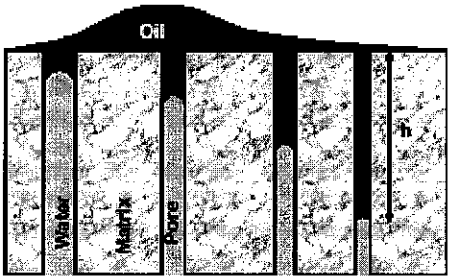


Fig. 1 The height of the retained oil in oil-wet matrix blocks is a function of the pore radius, interfacial tension, and contact angle.

Figure 4.5 Capillary Forces in pores

(Taken from: Hirasaki G., Zhang D.L, "Surface Chemistry of Oil Recovery from Fractured, Oil-Carbonate Formation", [9])

4.5 Factors affecting Interfacial Tension

A study [10] on the possible use of modified non-ionic surfactants in a sandstone reservoir with average salinity to investigate the parameters that influences the interfacial tension. Modified ionic surfactants used comprised of ethene oxide and anionic groups and were tested with crude oil samples from Velebit field. Included in the study were studies on the effects of temperature and also surfactant concentrations on the interfacial tension values.

4.5.1 Effect of temperature

Temperature was varied between 25 – 75°C and the effect of alcohol addition was also studied. Experimental results obtained showed that the range at which interfacial tension range is below that of 10^{-3} mNm^{-1} is that between 50-65°C. It was also found that addition of isopropyl to the surfactant shifts the temperature range slightly lower at which its exhibits interfacial tension of below $10^{-3}$$mN.m^{-1}$. This is important as the formation temperature during injection may decrease and therefore addition of alcohol could adjust the surfactants to exhibit low interfacial tension at a lower temperature range.

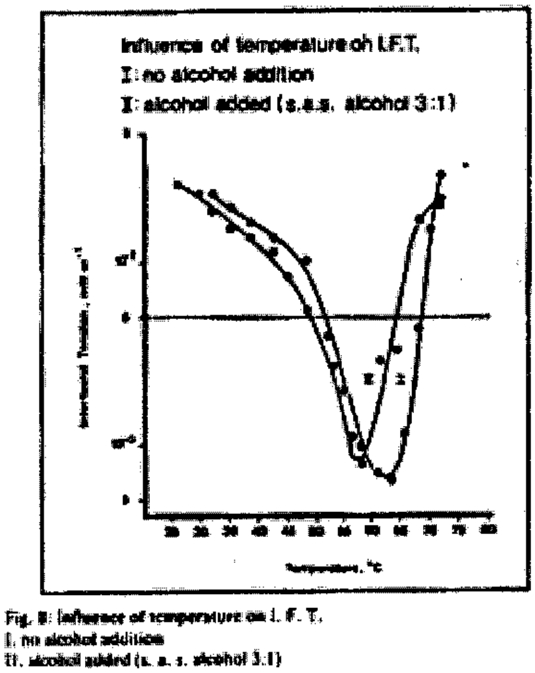


Fig. 4.6: Effect of Temperature on IFT

(Taken from Capelle & Littmann, “Enhanced Oil Recovery with Modified Non-ionic Surfactants”. [10])

4. 5.2 Effect of surfactant concentration

Concentrations of modified non-ionic surfactants used were between 100 g/m^3 and 100 kg/m^3. It was found that interfacial tension remains below 10^{-3}mN/m^{-1} at surfactant concentration of between 2 kg/m^3 to 30 kg/m^3 [10].

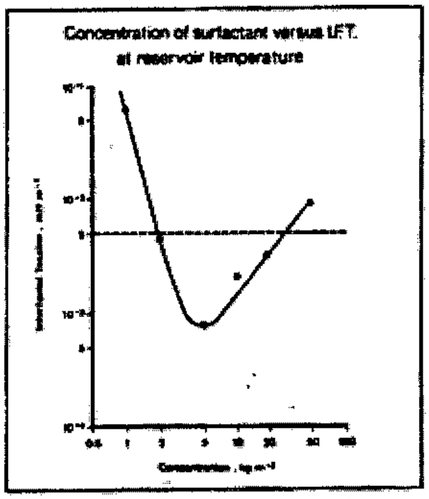


Fig. 9: Concentration of surfactant versus I. F. T. at reservoir temperature

Figure 4.7: Effect of Surfactant Concentration on IFT.

(Taken from Capelle & Littmann, "Enhanced Oil Recovery with Modified Non-ionic Surfactants" [10])

4.5.3 Effect of Salinity on Interfacial Tension

A study [11] showed the effect of electrolyte (NaCl) on the interfacial tension and also the partition coefficient of the surfactants. Interfacial tension reduces as the salinity increases (higher concentration of NaCl) and minimum interfacial tension occurs at partition coefficient of 1 [11]. Partition coefficient is the ratio of the surfactant component in oil with respect to the surfactant component in water. In other words, ultra-low interfacial tension occurs when the hydrophilic and hydrophobic component of the surfactants are equal to each other.

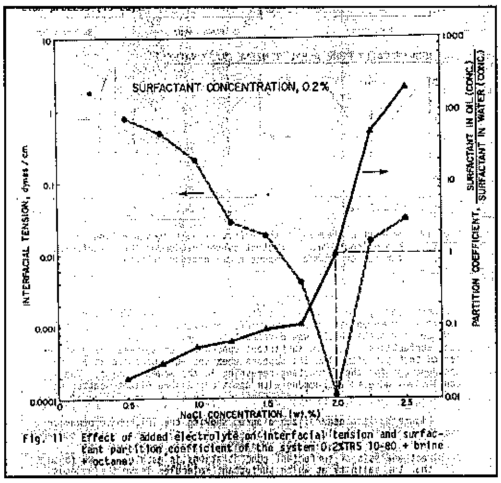


Figure 4.8: Effect of Salinity on Interfacial Tension

(Taken from D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [10])

4.5.4 Effect of pH on Interfacial tension

A study was done to investigate microemulsion and pH dependent systems by Rivas, Gutierrez, Zirrit, Anton and Salager [12]. It was reported that ultra-low interfacial tension can exist in crude oil/alkaline aqueous solutions. Interfacial tension of the can be affected by the pH and ionic strength of the aqueous solution.

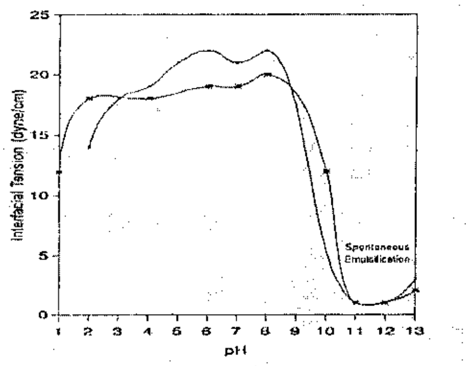


FIG. 6 Effect of pH on the interfacial tension for two Venezuelan heavy crude oils.

Figure 4.9: Effect of pH on Interfacial Tension for two Venezuelan Heavy Crude Oils

(Taken from Rivas, H., Gutierrez, X., Anton R.E & Salager J.L., "Microemulsion and Optimal Formulation Occurrence in pH-Dependent Systems as Found in Alkaline-Enhanced Oil Recovery", [12])

Figure 4.9 shows the experimental result studying the effects of pH for two Venezuelan heavy crude oils. It was found that the interfacial tension reduces significantly at pH value of above 8. Ultra-low interfacial is achieved at pH of 11-12 before a further increase in pH to 13 and higher increases the interfacial tension. This increase is attributed to the formulation of insoluble salts of sodium carboxylate. At pH of 11-12 significant reduction of interfacial tension is also attributed to the spontaneous emulsification occurring.

Use of alkaline flooding in crude oil containing carboxylic acid can help to neutralize the acidic crude and produce carboxylate ions. The caustic solution will react with the acids in the crude oil to produce a surface-active mixture (soap) through a saponification of the acid in oil.

4.6 Wettability

Wettability is a complex function of fluid and solid properties. Rock surface has affinity for either water or oil. Studies found that oil recovery is more effective in water-wet medium rather than oil-wet. Surfactants can be used to alter the wettability to water-wet system.

Wetting indicates a stronger attraction of the solid surface for one phase than for another. In petroleum reservoirs, the wettability of reservoir rock is strongly affected by the presence or absence of molecules in crude oil that absorb or deposit on the mineral surface of the rock. Clay coating rock surfaces will affect wettability. Therefore a combination of crude oil characteristics and mineralogy of the rock surface produce wetting conditions. Wettability is the adhesion tension between the rock and the fluids contacting the rock. Capillary pressure then combines these forces to define how oil is retained in the reservoir.

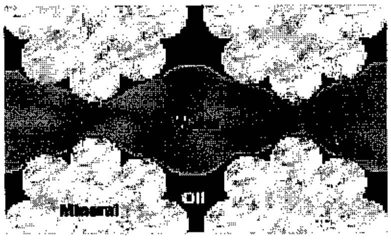


Fig. 2 Oil is trapped by surface trapping in oil-wet and small pores of oil-wet systems.

Figure 4.10: Oil trapped in oil-wet system

(Taken from: Hirasaki G., Zhang D.L, "Surface Chemistry of Oil Recovery from Fractured, Oil-Carbonate Formation", [9])

Surfactants are dual nature; hydrophobic and hydrophilic, producing strong affinity for interfaces between immiscible fluids such as water and oil and also fluid, solid interfaces. Concentration of surfactant at the interface will minimize the free energy of the total system. The surfactant adsorbs at the fluid/solid interface, reduces the interfacial tension and it changes the ability of water or oil to wet the solid surface.

Role of Surfactants in Wettability Alterations

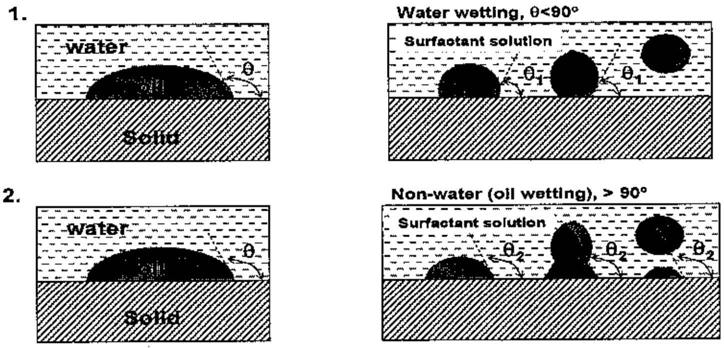


Fig. Illustration of spreading, beading and contact angle in solid/liquid/liquid system (Shaw, Copyright 1992, Butterworth-Heinemann, Oxford, U.K

Figure 4.11: Role of Surfactants in Wettability Alterations

Surfactant molecules that orient itself on a surface whereby its surfactant molecules have its hydrophobic tail groups away from the surface will promote towards oil-wetting conditions. A surfactant that orients itself such as the head group is away from the surface will induce water-wet conditions. During hydrophilization of rock surface γ_{sw} will decrease and γ_{so} will increase, while during hydrophobization of surface, γ_{sw} will increase and γ_{so} will decrease

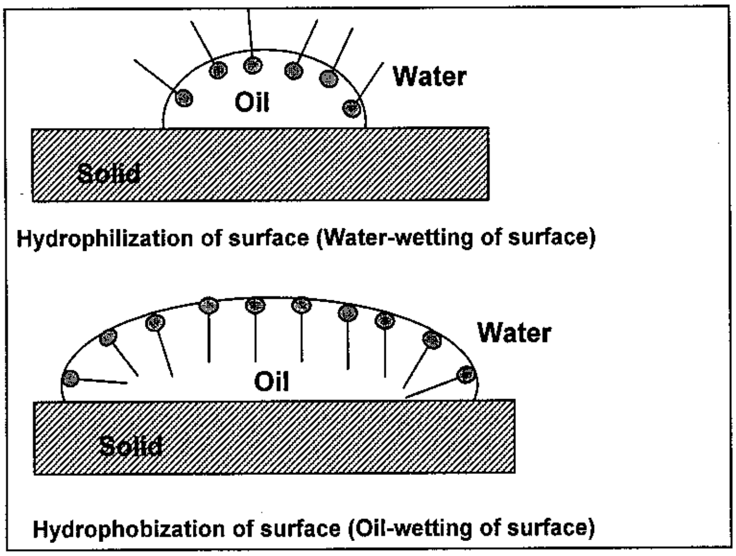


Figure 4.12: Hydrophilization and Hydrophobization of Surfaces

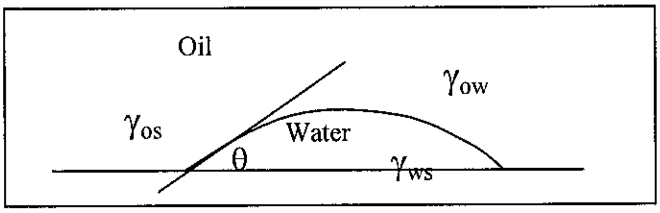


Figure 4.13: Adhesion Phenomena between Oil, water and Solid Surface

At positive adhesion tension is at 0°<θ<90°, water preferentially wets the solid while a negative adhesion tension means the oil preferentially wets the solid at 90°<θ<180°. Above phenomena can be related using an expression known as Young's equation. Young's equation denotes the equilibrium relationship between the 3 phases; oil, water and solid.

$$\gamma_{so} - \gamma_{sw} = \gamma_{wo} \cos \theta_{wo} \quad \text{.................................} \quad (4.4)$$

Whereby, γ_{so} is the interfacial tension between solid and the oil, γ_{sw} is the interfacial tension between solid and water, γ_{wo} is the interfacial tension between water and oil and θ_{wo} is the contact angle between water, oil and solid system.

The right side of equation is known as the adhesion tension, τ_{swo} for water and oil in contact with the solid.

$$\tau_{swo} = \gamma_{wo} \cos \theta_{wo} \qquad \text{.......................................} (4.5)$$

Any spontaneous spreading that occurs will reduce the free energy of the total system. This change of free energy is known as the spreading coefficient, S_{ws}, which can be defined as,

$$S_{ws} = \gamma_{so} - \gamma_{wo} - \gamma_{sw} \qquad \text{.......................................} (4.6)$$

Morrow reported that water-wet conditions are optimum for oil recovery. Imbibition forces will promote oil displacement from the lower permeability regions and maintaining a stable displacement front. With water-wet rock conditions, oil will be expelled from the pore spaces. In strongly water-wet systems, the injected water can fill pore throats by an instability mechanism known as snap-off, which leaves adjoining pore bodies filled mainly with oil.

4.7 Mobility Control

Oil recovery efficiency of any oil recovery process also depends on:

1. unit displacement efficiency – pore to pore displacement efficiency effect
2. volumetric displacement efficiency – macroscopic displacement efficiency effect

Unit displacement efficiency is the percentage of oil swept out of an element of reservoir rock which has been completely swept by the displacing fluid. It is a measure of how effective the displacing fluid such as water to displace oil from the rock volume contacted.

Unit displacement efficiency is affected by agents such as alkali, micellar-polymer, surfactants that affect the capillary forces trapping the oil in the rock.

Volumetric displacement efficiency refers to the fraction of the total reservoir volume that was contacted by the displacing fluid. Volumetric displacement efficiency is the affected by mobility control polymer flooding and by cross-link polymer followed by water flooding. Volumetric sweep efficiency can be divided into areal sweep efficiency and also vertical sweep efficiency. Areal sweep efficiency is the percentage of the total reservoir area swept by the displacing fluid. Vertical sweep efficiency is the measure of the conformance of the reservoir which may contain many layers of varying permeability. Conformance is the percentage of total rock volume within the swept area that has been contacted by the displacing fluid.

Mobility ratio is defined as the mobility of the displacing phase divided the displaced phase; in the reservoir, water is assumed as the displacing phase and oil as the displaced phase. A mobility ratio of 1 means that the displacing fluid is moving at the same velocity as the displaced fluid, and mobility ratio of greater than 1 means that the displacement of oil from the porous media is not favourable. From study done by Marathon Oil, it was found that as mobility ratio increases, areal sweep efficiency decreases.

Mobility control,

$$M = \frac{\lambda_{displacing}}{\lambda_{displaced}} = \frac{k_{wro}}{\mu_w} \cdot \frac{\mu_o}{k_{onw}} \quad \text{.........................} \; (4.7)$$

Increasing the water phase viscosity will reduce the mobility ratio. Low concentrations of various polymers can impact the viscosity of the solution. Adsorption of polymer can also impact permeability. Adsorbed polymer restricts the flow along the sand grains resulting in a decreasing the k_{wro} which can also help reduce the mobility ratio.

4.8 Screening criteria of surfactants for EOR processes

Surfactants are divided into 4 functional groups; anionics, cationics, amphoterics and also non-ionics. Not all surfactants are suitable to be used in EOR processes. Among the limitations include cost of the surfactants as well as the characteristics of the surfactant itself. Akstinat [13] has provided a good background of the screening processes in selecting suitable surfactants for the EOR process. Prior to testing of the surfactants, several parameters need to be considered:

1. Types of crude; crude oil can be divided into basic types such as paraffinic oil, naphthenic oil, aromatic or mixed type.
2. Colloidal chemistry of crude; content of asphaltenes and resins
3. Adsorption phenomena; composition of reservoir rocks
4. Characteristics of Reservoir Environment; pH, temperature, wetting conditions, salinity
5. Diffusion Phenomena; rapid diffusion to the oil-water interface

4.8.1 Surfactants Selection

EOR suitable surfactants should have low adsorption on reservoir rock, favourable partition coefficient, long-term stability in temperature range of 30-80°C, and also low interfacial tension in the brine/crude oil system ($\gamma < 1$ mN.m^{-1}). More commonly used surfactant for EOR is anionic surfactants. Anionic surfactants have a wider range of molecular structure and functional groups therefore provide a wider range of properties. It is least adsorbed onto negatively charged surfaces therefore minimizing adsorption losses.

Example of anionic surfactant used is alkylaryl sulfonates. According to [13] there are different types of surfactants, anionics and also amphoteric surfactants that are suitable for EOR processes. Anionic surfactants such as α-Sulfo fatty acid esters, sulfates of iosalkyl-phenyl polyether sulfonates and amphoteric surfactants such as sulfobetains, betain are some the example of surfactants suitable for use in EOR.

Cationic and also amphoteric surfactants are attracted to negatively charged reservoir rocks such as clay surfaces hence possibility of high adsorption, therefore cationic surfactants are not suitable for EOR. Non-ionic are brine tolerant however, they are in liquid or paste forms, which make them more expensive than anionic surfactants.

Most surfactant sources are from the industrial waste products such as paper industry or white oil industry (lignin sulfonates or petroleum sulfonates). According to [14] most suitable surfactant weight for CEOR is in the 350-475 daltons range. Lower equivalent weight surfactants do not interact well with oil and those with higher molecular weight tend to be insoluble in water. Also need to be noted that surfactant adsorption by rock increases with molecular weight but the CMC decreases with increasing molecular weight.

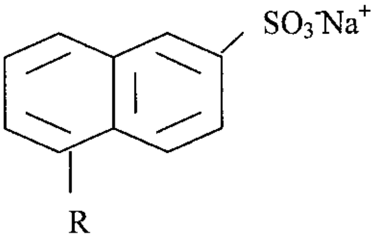


Figure 4.14: Petroleum sulfonates component
Taken from: Schmitt, T.M., "Analysis of Surfactants", 2nd Edition. Marcel-Dekker Inc, New York: 2001; pg 5-6.

Petroleum sulfonates performances drop as salinity and divalent cation concentration increases, which results in low brine solubility and poor interfacial efficiency. Other surfactants such as sulphated/sulfonated ethoxylated alcohols are usually used as co-surfactants. C3-C5 alcohols are usually used as co-solvents to improve the solubility and also prevent formation of highly viscous phases.

4.8.2 Diffusion Phenomena

Diffusion Phenomena is dependent on the structure of the surfactants. The diffusion coefficient is directly proportional to temperature and for dissolved surfactants; it is inversely proportional to the viscosity of solvent. Interfacial tension depends on the oil composition; according to [13], naphthenic oil has the highest value of interfacial tension in high-salinity brines.

4.8.3 Surfactants Losses through Adsorption on reservoir rocks

Adsorption is a result of the attraction between the monomer surfactant molecules and mineral surfaces especially clay. The attraction is due the Van Der Waals and also Coulombic forces as well as hydrogen bonding. .

Adsorption phenomena of surfactants are found to be a function of surfactant structure and reservoir rocks. The higher the solubility of the surfactants, the smaller is its adsorption. Adsorptions of surfactants are higher in high salinity water due to the lower solubility conditions. Adsorption decreases at increasing temperature, and viscosity of the solvent however, it will increase as concentration of the surfactants increases. Baviere and Canselier [15] in their study on microemulsion in the Chemical EOR Process summarized the parameters affecting adsorption in the table below.

Table 4.7: Parameters affecting Surfactant Adsorption

Parameters Increased	**Effect on Adsorption**
Temperature	Decreases
Specific surface area of rock	Increases
Brine Salinity	Increases
pH	Decreases if Anionic
Surfactant Chain Length	Increases

Taken from Marc Baviere & Jean Paul Canselier, “Microemulsion in the Chemical EOR Process”, [15] Hydrophilic rocks are easily water-wettable rocks such as quartz and clay while hydrophobic rocks are poorly water-wettable rocks such as carbonates. According to [13], cationic surfactants are more readily adsorbed especially in clay rocks while non-ionics are slightly adsorbed in silicate rocks, as such; cationic surfactants are not very suitable to be used for EOR.

4.9 Types of Chemical Flooding

Addition of chemicals for example alkaline, surfactants or polymers can help to change the physicochemical properties of the displacing water and also the oil. Surfactant flooding is also known as micellar-polymer flooding, surfactant-polymer flooding or microemulsion flooding. The term micellar is used as the surfactants used are above their critical micelle concentration. Most common surfactants used are Petroleum sulfonates, also used are ethoxylated alcohol sulphates. In micellar-polymer flooding, surfactants, in the form of microemulsion are either injected into the formation or the surfactants will form microemulsion once in contact with the oil in the formation.

4.9.1 Role of Polymers in Chemical Flooding

Polymers are usually an accompaniment to waterflooding. High molecular weight polymer will help to increase the viscosity of water hence help to improve waterflood sweep efficiency. It can also help reduce aqueous phase permeability without changing the relative permeability to oil. Among the constraints facing use of polymer flooding: high cost, low injection rates due to high viscosity, degradation at high temperatures, intolerance to high salinity and also polymer deterioration from shear stress (pumps, flow through perforations etc).

4.9.2 Traditional surfactant/polymer flooding

Assuming that waterflood activities have been done prior to the chemical flooding, 4 zones will be formed:

Zone 1: water flooded residual oil saturation, water only flowing

Zone 2: formation of oil bank, both oil and water flowing

Zone 3: surfactant slug injected in to form low IFT region; 3 phase formation, oil, brine and microemulsion

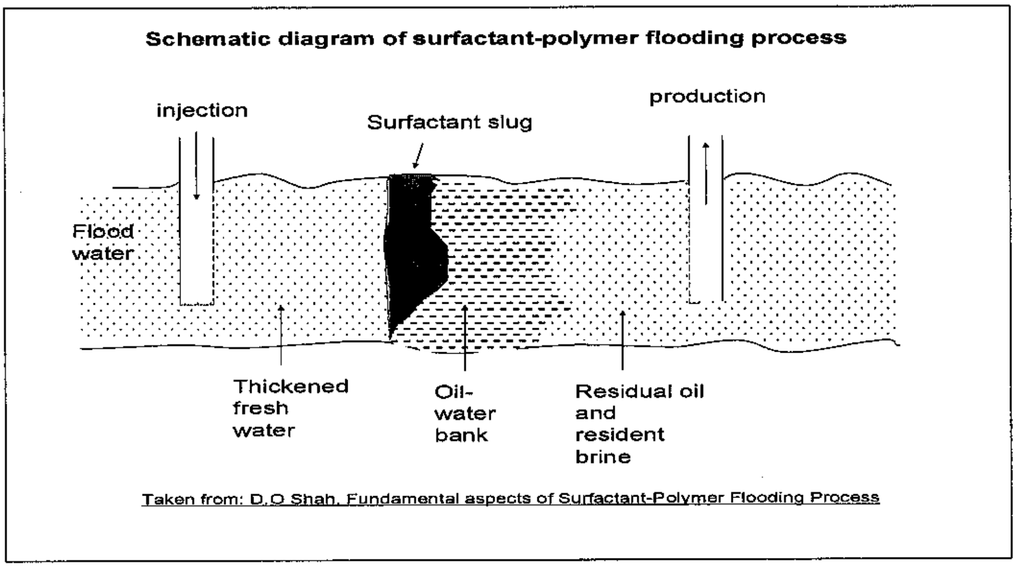
Zone 4: polymer solution injected to introduce mobility control, only water phase flowing

Flow direction →

Region 4 Polymer	Region 3 Surfactant	Region 2 Oil bank	Region 1 Water with residual oil saturation

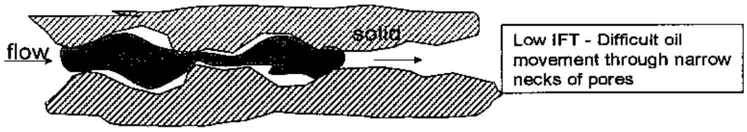
Figures 4.15: Oil Recovery Mechanism for Surfactant-Polymer Flooding

(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])



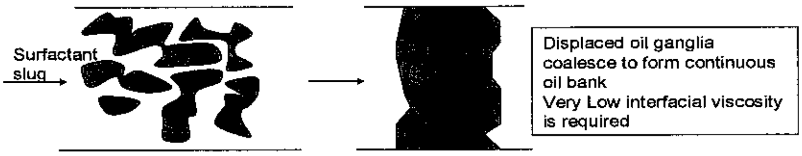
Figures 4.16: Surfactant-Polymer Flooding Process

(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])



Low IFT - Difficult oil movement through narrow necks of pores

Fig a: Role of low interfacial tension in surfactant-polymer flooding process

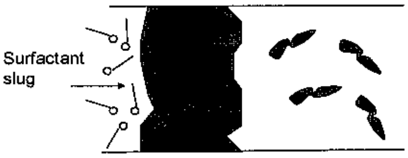


Displaced oil ganglia coalesce to form continuous oil bank
Very Low interfacial viscosity is required

Fig b: Role of low interfacial viscosity in surfactant-polymer flooding process

Taken from: D.O Shah, Fundamental aspects of Surfactant-Polymer Flooding Process

Figures 4.17: Role of Interfacial Tension and Interfacial Viscosity in Surfactant-Polymer Flooding
(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])



Maintenance of ultra low IFT at oil/bank/surfactant/slug interface to minimize entrapment of oil in porous medium

Fig c: Coalescence of Oil Ganglia with oil resulting in further displacement of oil

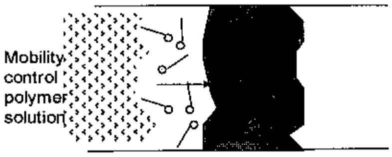


Fig d: Movement of oil bank, surfactant slug and mobility control polymer slug in porous medium

Taken from: D.O Shah, Fundamental aspects of Surfactant-Polymer Flooding Process

Figures 4.18: Displacement of Oil Ganglia in surfactant-polymer flooding
(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])

Thermodynamically stable microemulsion phase between the oil and water at optimum conditions was were developed to yield equal solubilization of oil and water to produce an ultra low IFT between the microemulsion and the oil and brine phase. High amount of polymer is needed to maintain the mobility control due to the viscous middle phase microemulsion. Good mobility control is necessary to protect the small slug of chemicals injected against the fingering, channelling, mixing and other reservoir mechanisms.

4.9.3 Microemulsion in EOR

Micro-emulsions are homogeneous mixtures of hydrocarbons and water with large amounts of surfactants. It is thermodynamically stable isotropic single phases. Surfactant molecules are usually found at the interface between the polar and non-polar fluids. In most surfactant formulations involving micro-emulsions, an alcohol or other amphiphilic co-surfactant is used together with the primary ionic surfactant. Alcohol is used to eliminate the formation of liquid crystalline or gel structures that can obstruct the microemulsion from forming.

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The microscopic displacement efficiency of oil is interpreted by the capillary number. If the capillary number can be increased by 3 to 4 orders of magnitude by reducing the interfacial tension (IFT) of the oil ganglia below 10^{-3} dynes/cm, this will enable for better oil displacement efficiency and thus enable for stubborn oil ganglia to propagate through the reservoir. Critical parameters that ensure the success of the flooding process are the ability to create an ultra low interfacial tension and also the role interfacial viscosity in coalescence of oil ganglia and formation of oil bank.

There are two regions of ultra-low IFT; in the low surfactant concentration regions (0.1-0.2%) and also in the high surfactant concentration region (2.0-10.0%). The low concentration surfactants region occurs when the aqueous phase of the surfactant solution is almost the at the apparent critical micelle concentration. The migration of surfactant form the aqueous phase to the oil is responsible for the ultra low interfacial tension.

The high surfactant concentration region, on the other hand, creates a middle phase microemulsion. In the middle phase microemulsion system, the excess oil and excess brine exist, at in a narrow salinity range. The salinity, at which this occurs, is known as the optimal salinity region whereby the interfacial tension of both phases is equal.

From studies it was found that at optimum salinity, the coalescence rate or phase separation time and also the apparent viscosity are minimal for the flow of microemulsion through the porous media. Presence of alcohol was also found to promote the mass transfer of surfactant from the aqueous phase to the interface and also the coalescence of oil drops through the decrease interfacial viscosity.

4.9.3.1 Effect of Salinity on Phase Behaviour

Microemulsions exist in 3 different types of phases; lower phase emulsion, middle phase microemulsion and upper phase microemulsion. One of most characteristic properties of multiphase microemulsion is the ultra low interfacial tension between oil and water. Salinity plays a major role in determining the type of microemulsion that will form. When alkyl chain length in surfactants (SCN) decreases, the salinity range in which the middle-phase microemulsion forms increases [11]. Middle phase microemulsion forms when water and oil exist in equilibrium and water and oil volume solubilized in the middle phase. The hydrophile and lipophile components are equilibrated. Optimum salinity for middle-phase microemulsion forms with increasing temperature and the alkyl chain length in n-alkanes but decreases in increasing alkyl chain length in surfactants [11].

A study done [11] studied the effect of TRS 10-410 + IBA in 1.5% NaCl with dodecane concentration on ultra-low interfacial tension. Study found that there are two regions of ultra-low interfacial tension, at low surfactant concentration and also at high surfactant concentration. At low surfactant concentration, system appears as a two-phase system (oil-brine) in equilibrium with each other while at high surfactant concentration, a middle phase microemulsion exist in equilibrium with excess oil and brine.

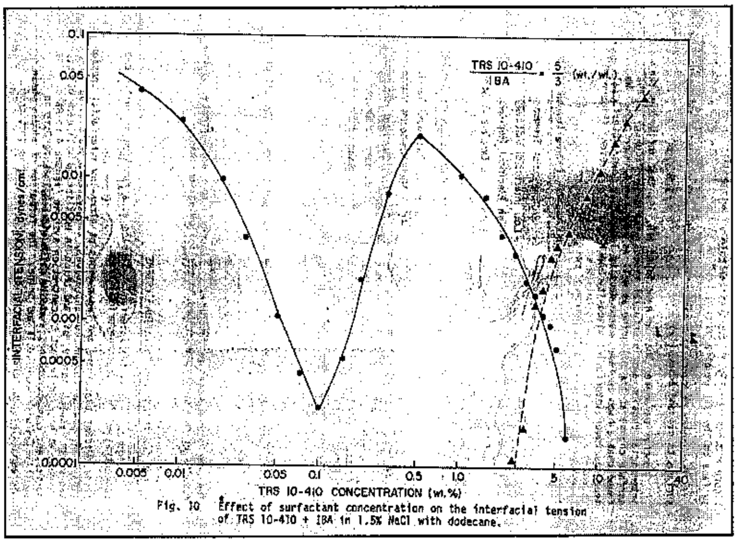


Fig. 10 Effect of surfactant concentration on the interfacial tension of TRS 10-410 + IBA in 1.5% NaCl with dodecane.

Figure 4.19: Effect of Surfactant Concentration on IFT.
(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])

Low Surfactant Concentration System and Optimal Salinity

From studies done [11], also found that in the low surfactant concentration systems, two phases exists, the oil and brine in equilibrium with each other. Ultra low IFT occurs when the surfactant molecules propagate from the aqueous phase to the oil phase at a partition coefficient of 1.0. Partition coefficient is the ratio between the concentration of surfactant in oil and concentration of surfactant in water. It was also found that the ultra low IFT occurs at the apparent critical micelle concentration for the remaining surfactant in the aqueous phase. Low Tension Polymer Water Flood (LWTPWF) or low surfactant concentration enhanced water flood involves injecting low concentration of surfactants.

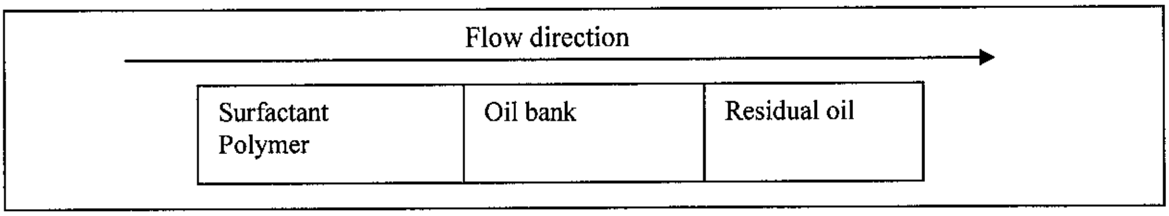


Figure 4.20: Low tension polymer water flood

High Surfactant Concentration System and Optimal Salinity

Formation of middle phase emulsion in high surfactant concentration involves several transitional steps lower to middle to upper (l→m→u). See Fig. 4.21. Increase in salinity, decreases the critical micelle concentration (cmc) and increases the aggregation number of micelles and also the solubilization of the oil within micelles. The repulsive forces within the micelles will decrease and attractive forces will increase, bringing the micelles closer together and separation of a micelle rich phase will form the middle phase microemulsion. As the salinity is increased, the solubilization of oil in the middle phase will increase, while the solubilization of the brine will decrease [11].

Optimal salinity occurs at the salinity at which equal volume of oil and brine is solubilized in the middle phase microemulsion. The study also found that the transition from l→m→u can also occur by varying other parameters such as increasing alcohol concentration, total surfactant concentration, brine/oil ratio, surfactant solution/oil ratio and also molecular weight of surfactant or also by decreasing oil chain length and temperature.

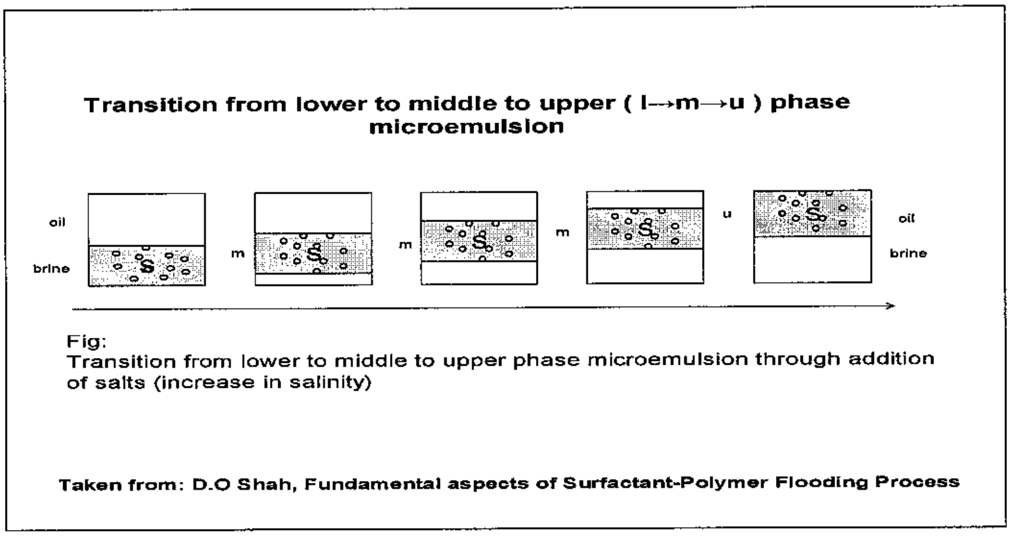

Transition from lower to middle to upper (l→m→u) phase microemulsion

Fig:
Transition from lower to middle to upper phase microemulsion through addition of salts (increase in salinity)

Taken from: D.O Shah, Fundamental aspects of Surfactant-Polymer Flooding Process

Figure 4.21: Transition from lower to middle to upper microemulsion phase
(Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])

Optimal Salinity concept for Enhanced Oil recovery

At optimal salinity, fastest coalescence rate or phase separation time occurs. This promotes the formation of an oil bank from the mobilized oil ganglia. This suggests a correlation the low interfacial viscosity at optimal salinity. A summary of the various occurrences at optimal salinity on can be seen in Figure 4.22.

Most surfactant formulations for enhanced oil recovery include the addition short chain alcohols. Presence of alcohol has a prominent effect on the flattening time of the oil molecule. An interesting correlation was found between reduced flattening time of the spherical oil drop and to maximize the oil recovery. Flattening time reflects the rate what which the molecules accumulate at the oil-brine interface. Alcohol provides efficient mass transfer to the interface while reducing the interfacial tension.

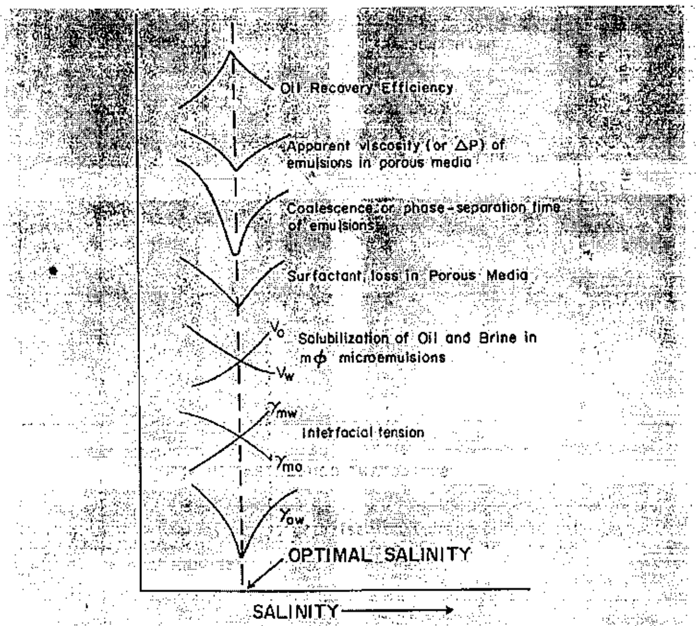


Fig. 32 A summary of various phenomena occurring at the optimal salinity in relation to enhanced oil recovery by surfactant-polymer flooding.

Figure 4.22: Phenomena occurring at optimal salinity
Taken from, D.O Shah, "Fundamental Aspects of Surfactant-Polymer Flooding Process", [11])

4.9.4 Caustic/Alkali Flooding processes

Caustic or alkali flooding processes involves chemical reaction between caustic and organic acids in crude oil to produce in-situ surfactants. Usually alkali such as sodium or potassium hydroxide is used. Production of in-situ surfactants help to lower interfacial tension of water and oil, alter rock water-wet rather than oil-wet and causes emulsification which lowers viscosities.

Alkaline flooding uses alkaline solutions as a method to recover the residual oil after waterflood activities are completed. When the ion hydroxide ion in the alkaline solution reacts with the acidic components of the crude oil, carboxylate soap will be formed. Carboxylate soaps are petroleum soaps that can adsorb at the water-oil interface and thus lower the IFT.

Among the limitations of classical alkaline flooding is lack of mobility control, petroleum soaps are too sensitive to ionic strength, low acid content in oil, and also alkali consumption due to alkali-rock interactions. Alkali consumption reduces the concentration of the hydroxide ion and decreases the efficiency alkaline flooding. To solve these limitations, various flooding schemes have been proposed different by researchers [15], which include the injection of polymer to improve mobility control and also surfactants to increase the salinity range for optimal phase behaviour.

4.9.5 Alkaline-Surfactant-Polymer Flooding, ASP

Alkaline-Surfactant-Polymer Flooding, ASP is another variant of surfactant-polymer flooding through addition of alkali. This method is still a relatively new with promises of solving the limitations of surfactant-polymer faced. ASP also promises for a more economically attractive method of oil recovery as compared with surfactant-polymer flooding through lower consumption of polymer and cheaper alkali.

Studies done [8] found that for ASP slugs, oil recovery is a function of alkali concentration and slug size. It was found that slugs containing low sodium carbonate concentrations (<0.5 wt %) have relatively low oil recovery. At low concentration of alkali, the studies showed that high slug viscosity is not a factor that determines high oil recovery since IFT readings are still high. Clearly, this indicates that lowering of IFT is the critical factor for oil recovery. Slugs with higher alkali concentration containing >1.0 wt% concentration gave a higher oil recovery. Higher alkali concentration provides a better mechanism for oil recovery through lowering of IFT, salinity changes and wettability reversal.

Higher capillary number corresponds to lower IFT values thus at increasing capillary number, oil recovery also increases. Higher capillary number indicate lower capillary forces that act upon the trapped oil, through lower interfacial tension between the water and oil, consequently enabling for more oil to be recovered at higher alkali (sodium carbonate) concentrations. Results from studies done [8] showing the level of oil recovery and the variations in the capillary number is shown in Table 4.9.

Table 4.9: Variation of Oil Recovery with Capillary Number for Radial Cores

	Sodium carbonate concentration (wt %)						
Parameter	0	0.17	0.37	1	2	3.9	5.2
μ (mPa.s)	28.4	24.1	21.4	17.5	14.5	12.8	12.8
IFT (mN/m)	2.5	0.649	0.153	0.038	0.031	0.013	0.021
Nc x 105	2.89	9.47	35.47	117.6	119.4	250.5	154.9
Tertiary recovery (%)	17.2	23.3	46.5	55.6	65.5	71.6	72.7

Taken from: H.A Nasr-El-Din, & Taylor, K.C, "The Role of Surfactants in Enhanced Oil Recovery", [8]

Below are Figures produced using the data obtained from Nasr-El-Din and Taylor.

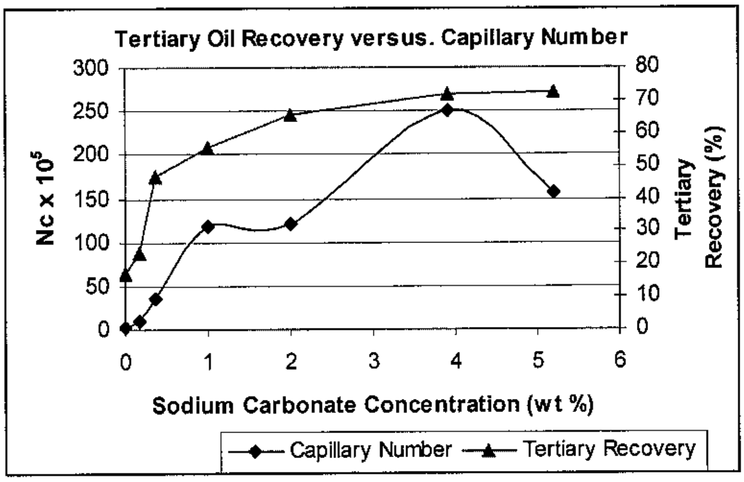


Fig. 4.23: Capillary Number and Oil Recovery

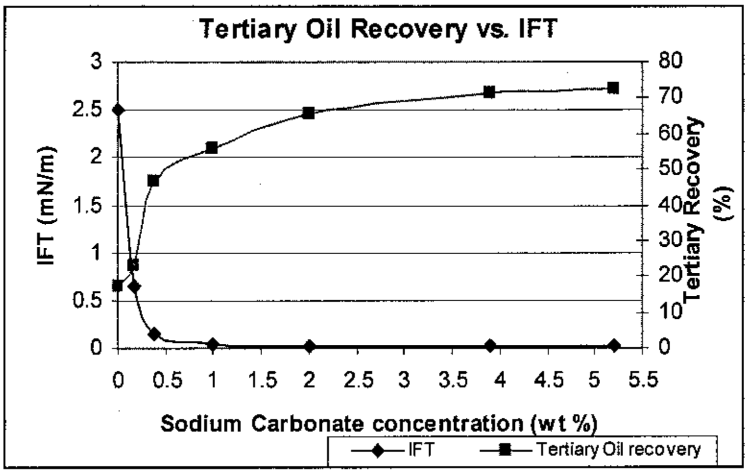


Fig. 4.24: Interfacial Tension (IFT) and Oil Recovery

In [8] studies on ASP flooding showed effects of capillary number on oil recovery is similar to results obtained by other researchers for micellar flooding. Increase in capillary number which relates to lowering of interfacial tension is important to ensure successful oil recoveries.

At lower concentration of sodium carbonate, capillary number and also the oil recovery are relatively low. Low capillary number indicates that the capillary forces are still dominant and oil droplets are trapped in the core. At high sodium carbonate concentration, there is a significant increase in the oil recovery.

Wettability is another factor that may determine the oil recovery, especially at high sodium carbonate concentrations it is at high ionic strength. High salinity (high ionic strength) drives the anionic surfactant out of the aqueous phase, causing a significant amount of surfactant to be adsorbed onto the rock surface during flooding. This will produce a reversal of wettability in the core; the core will change from being water-wet to oil-wet.

4.10 Overview on Chemical Flooding Method

Chemical flooding exhibit one the most successful means of methods of enhance oil recovery from depleted reservoirs at low pressure. Addition of chemicals e.g. alkaline, surfactants and polymers can help to change the physicochemical properties of the displacing water and also the oil. Surfactants are used mostly to recover the microscopic drops of oil (residual oil in the swept areas). It reduces the oil-water interfacial tension to overcome the capillary forces. Very low interfacial tension value is needed in order to increase the capillary number by three to four orders of magnitude.

Principal components used in chemical flooding are surfactants and polymer. Surfactants has the ability to lower the interfacial tension between the injected water while polymer exhibit the characteristic of being able to provide good viscosity conditions and mobility control for the surfactants flood.

CHAPTER 5:

Miscible and Immiscible Gas Displacements

There are two types of displacement methods using gases; miscible gas displacement and also immiscible gas injection. This section will discuss briefly on the basic mechanisms involved in these two methods.

5.1 Miscible Gas Displacement Methods

This process involves injecting gas into the reservoir that can dissolve in the oil. Most commonly used is carbon dioxide gas. It was first used in the Kelly-Snyder field in Texas in 1972. Major limitation of using the carbon dioxide is the very low viscosity of carbon dioxide thus causing it to fingers to break through the producing wells, leaving unswept areas in the reservoir.

To account for this limitation, an improved technique involves injecting alternating water and gas in a process called WAG or water alternating gas process. Other gases that is also miscible with oil is liquefied natural gas (LPG) used in LPG drive. The LPG usually consists of propane or propane-butane mixture. Another method is using inert gas for injection. Air is not used as it will corrode the metal equipment in the well and can form an explosive combination when mixed with the natural gas in the reservoir.

5.2 Miscible Flood Displacement Processes

Miscible displacement is to reduce the interfacial tension forces between the displacing and displaced fluids. Miscibility refers to the ability of the displacing fluid and the displaced fluid to mix completely in all proportions. This enables the residual oil saturation in the swept zone (the target oil) to be reduced to near zero. Two substances are miscible in each other if they are mixed and form a single homogenous phase. 3 major processes in miscible displacement:

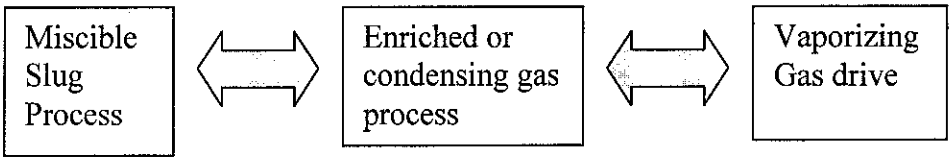


Fig.5.1 Miscible Displacement Processes

Displacing fluid used for this application include hydrocarbon gases, carbon dioxide, nitrogen, flue (exhaust) gases, LPG and even some alcohols. Though miscibility is not achieved immediately, miscibility in gas injection is achieved as result of either a vaporizing or a condensing drive, through multi-contact (MCM) process [19].

In the condensing drive, a rich gas loses its intermediate components to the oil during successive contacts, until the oil phase in the trailing region of the gas bank becomes sufficiently modified to allow miscibility with the injected gas. The enriched gas process, the gas contains relatively high percentages of hydrocarbon from the ethane to hexane range, in which miscibility is immediate [20].

In the dry-gas process, the miscibility is gradually achieved by the component transfer during vaporization from the oil to the gas. Miscible displacement processes are best applied in steeply dipping, high permeability reservoirs with light oil, where displacement is stabilized by gravity forces. Gas miscibility works best in high pressure conditions in order to achieve MCM.

5.3 Gas Drives

Among the gases used for gas drive techniques can be inert gas, flue gas (see Fig. 5.3) and also immiscible CO_2. Immiscible gas flooding methods are usually used for recovery of medium to high oils. Gas injection (immiscible displacement) in an oil reservoir takes place either in a gas cap or directly into the oil zone.

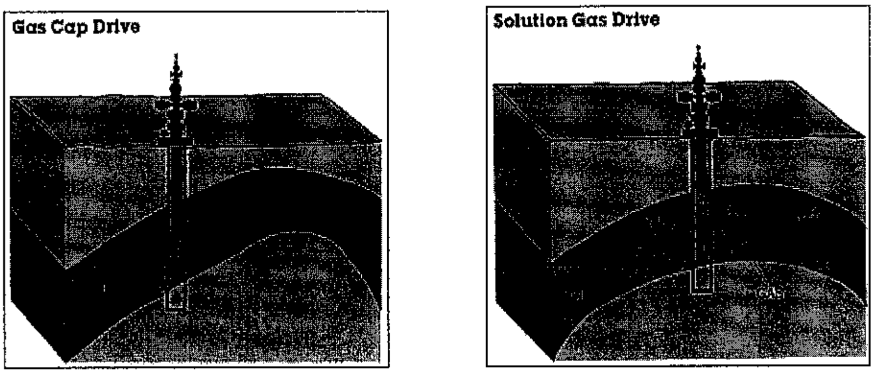


Figure 5.2: Gas Drives Methods (Source: www.leeric.lsu.edu)

Gas caps (see Fig 5.2) can be found naturally existing in reservoirs or formed by segregation in primary production. Gas injection of immiscible gas into a gas-cap helps to maintain the reservoir pressure. The gas is forced into the oil zone and hence drives the oil towards the production wells [21].

In gas injection into an oil zone, the injected gas will flow radially from the injection wells. If the gas dissolves in the oil, this can cause the oil to swell and hence reduces the residual oil saturation and improves the mobility of the oil. The subsequent contact or blow down will liberate the gas and form solution gas drive, thus displaces the oil towards the production wells. Gas injection is usually used in thin reservoirs. However gas injection suffers from undesirable mobility ratio in very viscous oil. There is also potential asphaltene precipitation in the reservoir and in production equipment and corrosion.

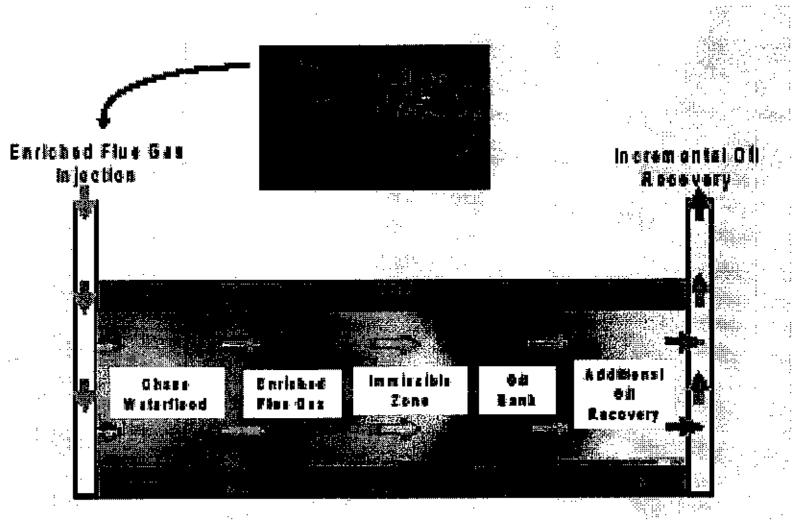


Fig 5.3: Enriched Flue Gas Heavy Oil Recovery

Taken from: 'Enriched flue gas heavy oil recovery', Petroleum Technology Research Centre (PTRC)

5.4 Displacement Methods Using Carbon Dioxide (CO_2)

High solubility of carbon dioxide in oil can produce positive results that can enhance oil recovery. High solubility in oil will lead to significant reduction in oil viscosity and slight increase in water viscosity which produces improvements in oil mobility in the reservoir. High solubility in oil will also aid lowering the interfacial tension of the oil-water. At high enough pressure, carbon dioxide will be miscible with oil to produce a single phase fluid.

5.4.1 Non-miscible displacement by CO_2

Injection of CO_2 not only causes swelling of the oil by 10-20%, depending on the saturation pressure, it also affects the relative permeabilities of the reservoir through its effects on the fluid viscosities and also interfacial tensions. Residual oil saturation obtained using carbon dioxide is lower than using natural gas and in addition, its ability to induce swelling of oil will enable for better improvement in oil recovery [21].

5.4.2 Miscible Displacement by CO_2

As carbon dioxide is injected into the reservoir, the gas will become more miscible with the oil, causing the oil to become more fluid. The carbon dioxide gas will then push the fluid oil through the reservoir toward the producing wells. Miscibility of carbon dioxide in oil may be partial or complete. Solubility of carbon dioxide in oil is dependant on the oil properties and the pressure and temperature of the system. Injected carbon dioxide will mix with the oil by dissolution. During the displacement process of CO_2, there will be a large contact area between the gas and oil within the porous medium, whereby rapid mass transfer between the oil and CO_2 will take place. Mass transfer between the oil and carbon dioxide will take place through fractionation of the oil. (Figure 5.4 & 5.5)

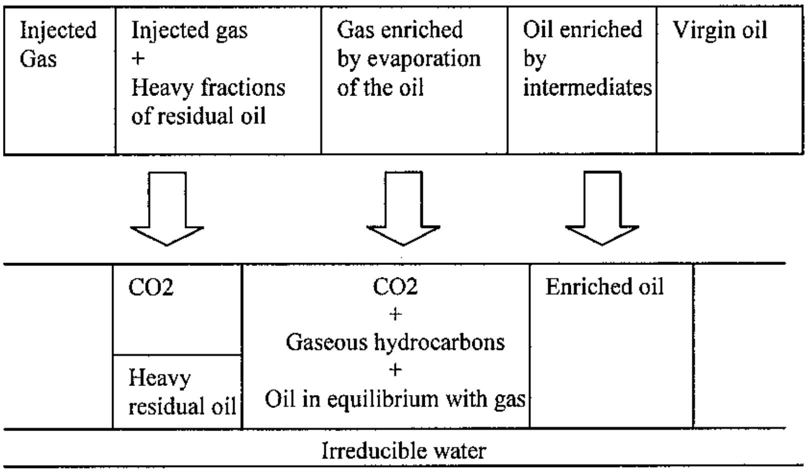
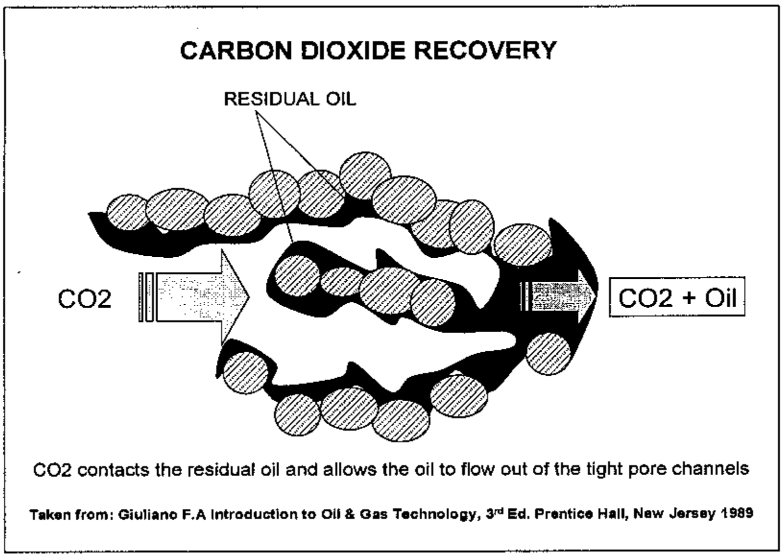


Fig 5.4: Miscible CO_2 Displacement Mechanism

(Taken from: Latil, M., Enhanced Oil Recovery, [21])



CO2 contacts the residual oil and allows the oil to flow out of the tight pore channels

Taken from: Giuliano F.A Introduction to Oil & Gas Technology, 3rd Ed. Prentice Hall, New Jersey 1989

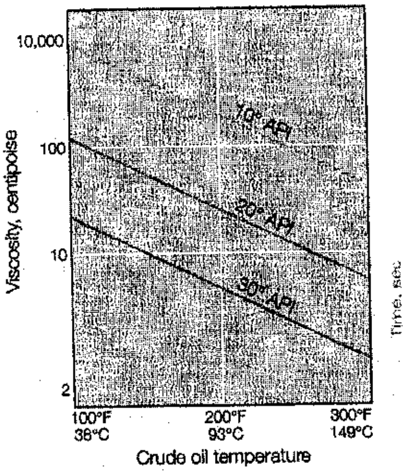
Fig 5.5: CO_2 oil recovery mechanism at pore level

(Taken from: Giuliano F.A (Ed), Introduction to Oil & Gas Technology, [22])

CHAPTER 6:

Thermal Recovery Methods

Thermal recovery is encompasses another group of enhanced oil recovery techniques that utilizes heat as a means to improve sweep efficiency, mobility ratio through lowering of viscosity. Viscosity will decrease with increasing temperature. Since viscosity and temperature are exponentially related, hence, the higher the viscosity of the fluid the greater the reductions in viscosity for a temperature increase. Thermal recoveries are especially successful in recovery of the heavier, viscous oil (gravity less than 20° API). There are two categories of thermal methods; heat is produced at the surface (hot fluid injection) and heat created in the formation (in-situ combustion).



☐ ***The empirical relationship of crude oil viscosity and temperature depends on oil composition.*** *(Adapted from Lake LW, reference 10.)*

Figure 6.1: Crude Oil Viscosity versus Temperature

(Taken from: Lake, L.W., Schidmt, R.L and Venuto, P.B, 1992, "A niche for Enhanced Oil Recovery in the 1990s", [23])

6.1. Hot fluid Injection

Water has a much higher heat transport capacity than any other fluid, both either in liquid or vapour phase. In comparing between the displacement by cold water, hot water and also steam, laboratory experiments [24] showed that the recovery by steam can achieve more than 80% breakthrough. In steam injection, oil is produced even after water breakthrough and until the breakthrough of the steam front.

Displacement using steam is more favourable than using hot water because produces a higher sweep efficiency, greater stability and also able to carry a larger quantity of thermal energy per unit mass of the injected fluid. [24] There are several hot fluid injection techniques: cyclic injection of steam (huff and puff method), injection of steam slug followed by cold water and also injection of hot water.

6.1.1 Steam Injection

Thermal recovery techniques use heat to recover heavy oil. In cyclic steam injection uses a single well to inject steam into the heavy oil reservoir for a period of time. During the following soak period, the well is shut-in for several days to allow the steam to heat the heavy oil and make it more fluid. At the same well, a sucker-rod pump is used to produce the heated heavy oil for a similar amount of time as the injection period. This method is called the 'huff and puff'. Another thermal recovery method is the use of steam flood or steam drive. This method also uses injection wells to pump steam into a heavy oil reservoir. Similar to the cyclic steam injection, the steam is used to heat the heavy oil and greatly reduce its viscosity. As the steam releases the heat, the steam condenses into hot water that will then drive the oil towards the producing well.

Steam flood or steam uses injection wells to inject steam into the heavy oil reservoir. Steam will be used to heat up the heavy oil and will lower the viscosity of the oil. As the steam releases its heat, it will condense into hot water that will drive the oil towards the producing wells. (See Figure 6.2)

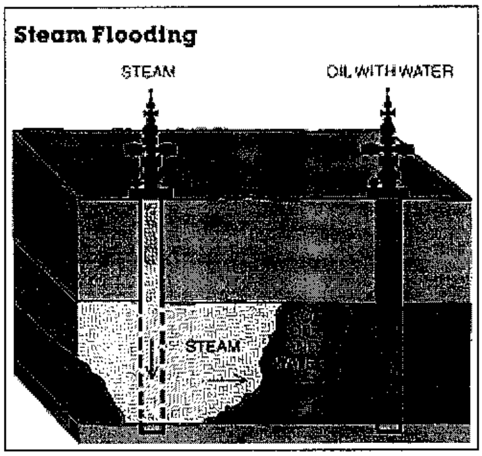


Fig.6.2: Steam Flooding, (Source: www.leeric.lsu.edu)

6.1.2 Cyclic injection of steam (huff and puff method)

The cyclic technique uses only one well as both injector and producer. There are 3 phases in this technique. First phase is the injection phase, which involves periodic injection of steam into the production wells. This is followed by the soak period and finally the production phase.

During the injection phase, heat is transported by steam injected into the formation. In the soak period, the well is shut-in, the heat will diffuse and the injected steam will condense, resulting in an increase in oil temperature and reduction in warm water production. Addition of heat will greatly reduce the viscosity of the heavy oil, and thus enhancing the oil flow rates in the production phase.

In the production phase, the oil production stabilizes at a much higher level as compared to the beginning the process. The steam injection phase may last from a few weeks to months followed by a soak period before the production phase takes place which can be a few months to over a year. [4] The cycle can be repeated until the reservoir energy becomes too low to support economic production rates. Once the process becomes uneconomic, the cyclic steam process is usually converted to a steam flood.

6.1.3 Injection of a steam slug followed by cold water

Often, after steam is injected into the formation, some heat is lost by conduction to the rock matrix. To recover this thermal energy stored in the reservoir rocks, cold water is often injected. Since the steam has the capacity of carrying a large amount of heat per unit mass, its temperature imposed by the reservoir pressure is much higher than the required temperature to obtain the desired mobility ratio. Hence, the injection of cold water will absorb the dissipated heat in the reservoir and 'heated' into hot water, enough to ensure the high recovery efficiency.

6.1.4 Hot water injection

Hot water cools as it makes contact with the rocks and fluids in place and under steady state conditions, two principal zones will be distinguished from the temperature and saturation profile. In zone II, the hot water will displace the oil at the same temperature. However, in zone I, the temperature will steadily increase as the residual oil saturation decreases. The swelling of the fluids and matrix, means that at any saturation, the mass of oil trapped will decreased as the temperature is increased. [24] However the displacement by hot water suffers from instability problems as cold water injection. Hot water displacement with no mass transfer between the two phases will produce a high viscosity ratio, thus resulting in a low areal sweep efficiency and unstable displacement. Decrease in the viscosity ratio is important in improving the recovery factor in displacement of oil by water.

6.2 Fireflood or in-situ combustion

Fireflood or in-situ combustion is another type of thermal recovery method whereby heat is created in the formation; the injected fluid is involved in an exothermic reaction taking place in the reservoir. The oil may start to burn spontaneously upon contact with the injected air or a heater or chemicals need to be injected into the injection well to initiate combustion.

The combustion can then be controlled by tuning the amount of air injected into the well. As the oil begins to burn, the heat of combustion will vaporize the lighter fractions of the crude oil which then will drive them ahead of the combustion front. The heat of combustion will also vaporize water in the combustion zone thus producing steam in-situ.

The air combustion products such as nitrogen and carbon dioxide will form a steam drive with some immiscible/miscible gas displacement [19]. Through reduction of viscosity due to heat and also the gas drive, this will help to drive the oil to the production wells. There are different types of fireflood forward combustion, dry combustion and wet combustion or combination of forward combustion and waterflooding (COF-CAW).

In forward combustion (Fig 6.3), zone of burning oil (combustion front) is spread from the injection wells to the producing wells. Oil is pushed to the producing wells by the injected air and combustion gases. In reverse combustion (Fig 6.4), the spreading of the combustion front is in reverse; from the producing wells to the injection wells. The oil must flow through a zone that has already been heated up by the combustion front. In reverse combustion, the oil receives more heat than in the forward combustion method. It is particularly useful in recovery of heavier oils which are more resistant to flow.

Another type of forward combustion is the wet combustion which incorporates injection of water. Wet combustion takes advantage of the enthalpy difference between liquid water injected and steam formed upon contact with the hot matrix to recover the thermal energy that is accumulated upstream from the combustion front and propagated downstream.

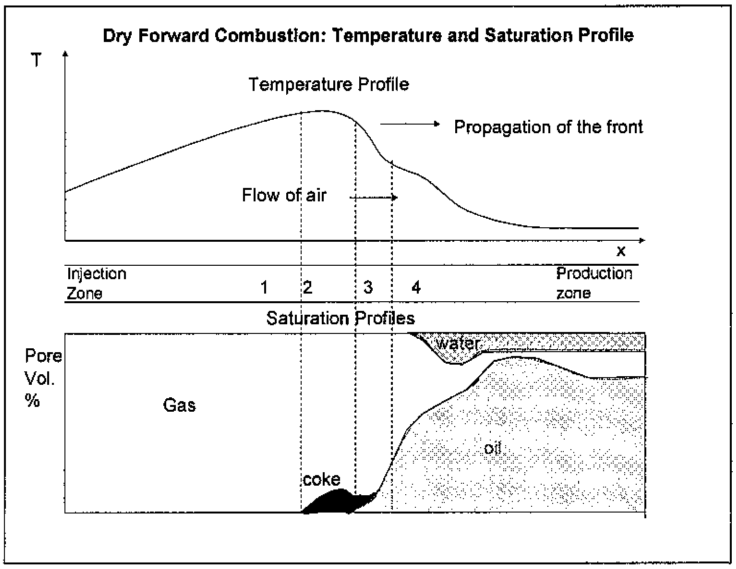


Fig. 6.3: Dry Forward Combustion Temperature and Saturation Profile
(Taken From Burger J., Sourieau P., Combarnous M., "Thermal Methods of Oil Recovery" [24]

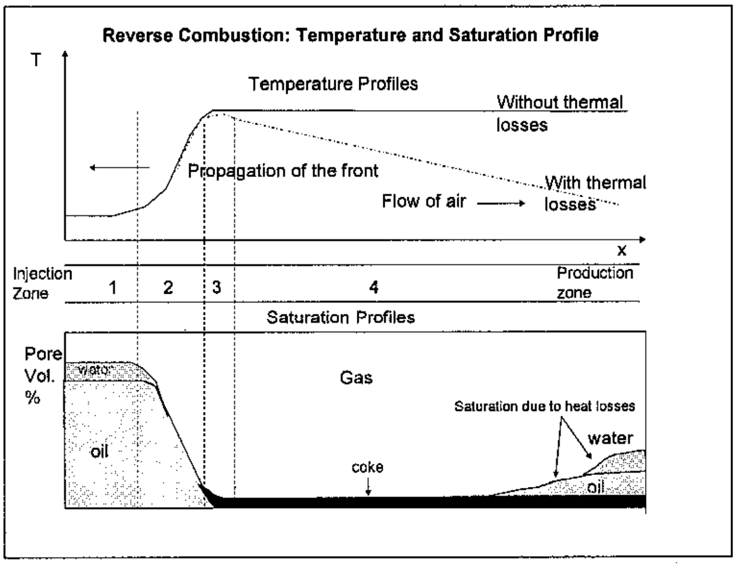


Fig 6.4: Reverse Combustion Temperature and Saturation Profile

Taken From Burger J., Sourieau P., Combarnous M., "Thermal Methods of Oil Recovery" [24]

6.3 Overview on Hot fluid injection and in-situ combustion methods

From Figure 6.5, statistically, it shown that steam drives accounts for the majority of crude oil production as compared to in-situ methods. In-situ combustion has potential for high recovery, [3]; with efficient drive mechanism and reduced heat losses as compared to steam based processes. Reasons for this may be the fact that in-situ methods are more risky as compared to steam processes. In-situ combustion is a highly complex process. The degree and style of combustion depends on the temperature and amount of oxygen available. Among the common failure reasons for in-situ combustion methods include, insufficient air supply, too large a well patterns and also there are safety concerns regarding high-pressure air compressors.

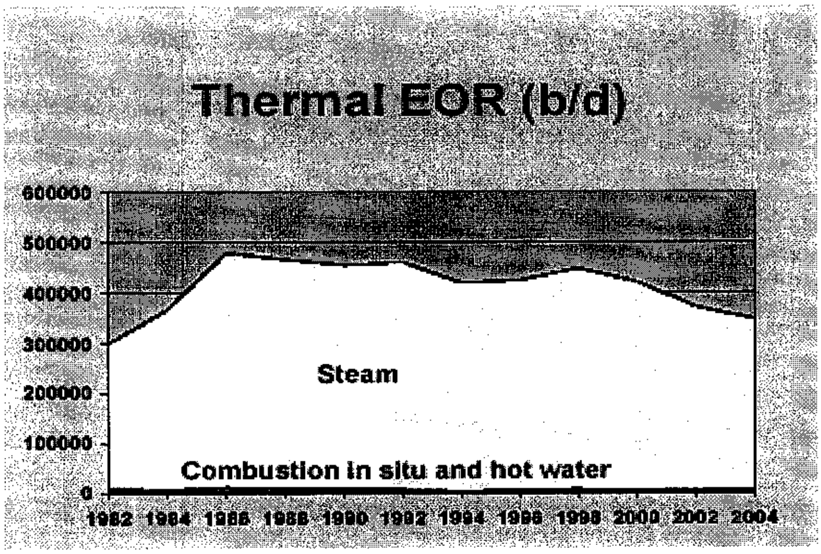


Fig. 6.5: U.S Thermal EOR production

Source: Tippee, B. “Oil & Gas Journal’s 2004 EOR Survey”, [3]

CHAPTER 7

Overview of the Enhanced Oil Recovery Methods

Generally, current primary and secondary recovery methods are able to extract 1/3 of the oil with remaining 2/3 of the oil still in the reservoir. Conventional oil recovery techniques; primary recovery using natural flow and artificial lift techniques can only recover 10 to 25% of the original oil in place (OOIP) while secondary recovery techniques using waterflood and pressure maintenance techniques can recover another 15% of OOIP.

The impending scarcity of global oil resource in the near future is one of the main drivers to recover as much oil as possible. However, there are limitations to recovering the oil; difficulty in recovering the oil due to complex reservoir structures and the high cost that entails it. Some reservoirs are abandoned as the incremental cost for the recovery versus the crude oil price is not economically favourable.

Advances in technology have enabled for developments of new enhanced oil recovery methods. There are currently 3 major EOR processes; chemical flooding, miscible displacement techniques and also thermal methods. These EOR methods employ more complicated oil recovery mechanisms than simple waterflooding or gas injection methods such as reduction of interfacial tension of water and oil and increase of mobility of displacement medium through decreasing viscosity of oil or increasing viscosity of water.

The most successful EOR technique, accounting for almost 70% of crude oil production through EOR is by thermal recovery [23]. Other EOR techniques such as miscible displacement methods and also chemical flooding techniques are still slowly increasing in their applications in EOR activities all around the world.

Miscible flooding method continues to gain widespread use as an EOR method, contributing to 18% of EOR application worldwide [23]. As compared to thermal and also miscible displacement methods, chemical flooding remains underutilized as an EOR technique. Chemical flooding encompasses the use of various chemicals such surfactants, alkaline and also polymers for the purpose of enhancing the oil recovery of the remaining oil in place in reservoirs. Though chemical flooding has great potentials, however the greatest barrier towards its widespread use is its high cost and also technical problems. To summarize the various applications of the enhanced oil recovery method, please refer to Appendix II, for Table 3.

CHAPTER 8

CONCLUSION & RECOMMENDATIONS

This research study hopes to contribute towards providing greater knowledge and understanding on Enhanced Oil recovery and its techniques, and in particular, on the use of surfactants in enhanced oil recovery.

In choosing the best Enhanced Oil Recovery method, it very much depends on the characteristics of the reservoir itself. Thermal recovery dominates EOR oil production with most successes and applications in particular in recovering heavy crude oil, accounting for almost 70% of crude oil production by EOR. Applications of other methods such as chemical flooding, miscible displacements continue to gain widespread tertiary oil recovery methods, though limited by its expensive cost and lack of technical developments. Lack of studies and technical developments makes it difficult to predict the oil recovery behaviour and thus creates a significant uncertainty in the successes of these methods.

Today chemical flooding still remains relatively underutilized as an EOR technique, its greatest barrier towards its widespread use is its high cost and also technical problems due to chemical loss by adsorption on the reservoir rocks. However, with new technological advancement and cheaper chemical flooding formulations such as Alkaline Surfactant Polymer (ASP), chemical flooding could play an even greater role in future tertiary oil recovery activity.

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APPENDICES

Appendix I

Gantt chart

RESEARCH PROJECT PLAN: SURFACTANTS IN ENHANCED OIL RECOVERY (EOR)

Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
date ending	23/7	30/7	6/8	13/8	20/8	27/8	3/9	10/9	17/9	24/9	1/10	8/10	15/10	22/10	29/10
Preliminary research work	▨	▨	▨												
Preliminary report submission			▨												
Project work															
Non-Thermal EOR															
1. Chemical Flooding				▨	▨										
polymer flooding surfactant flooding alkaline flooding micellar flooding emulsion flooding															
2. Miscible Displacement						▨	▨								
miscible slug process enriched gas drive carbon dioxide flooding nitrogen flooding															
3.Gas Drives								▨							
inert gas flue gas immiscible carbon dioxide															
Thermal EOR									▨	▨					
1. steam injection 2. hot water flooding 3. In-situ combustion 4. Electrical Heating															
Compilation of information											▨				
Submission Draft Dissertation												▨			
Oral Presentation													▨		
Submission Final Dissertation														▨	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

PROJECT METHODOLOGY AND PROCEDURES

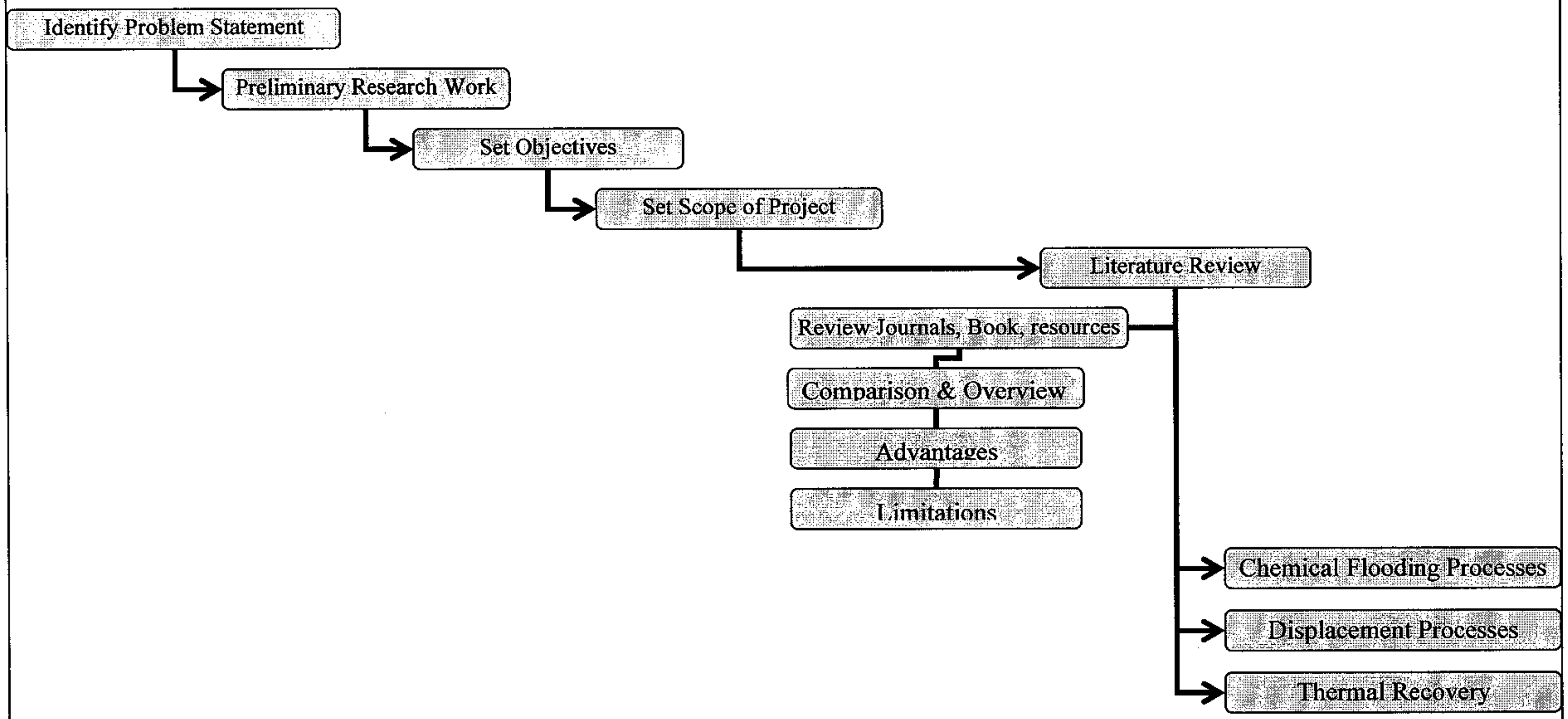


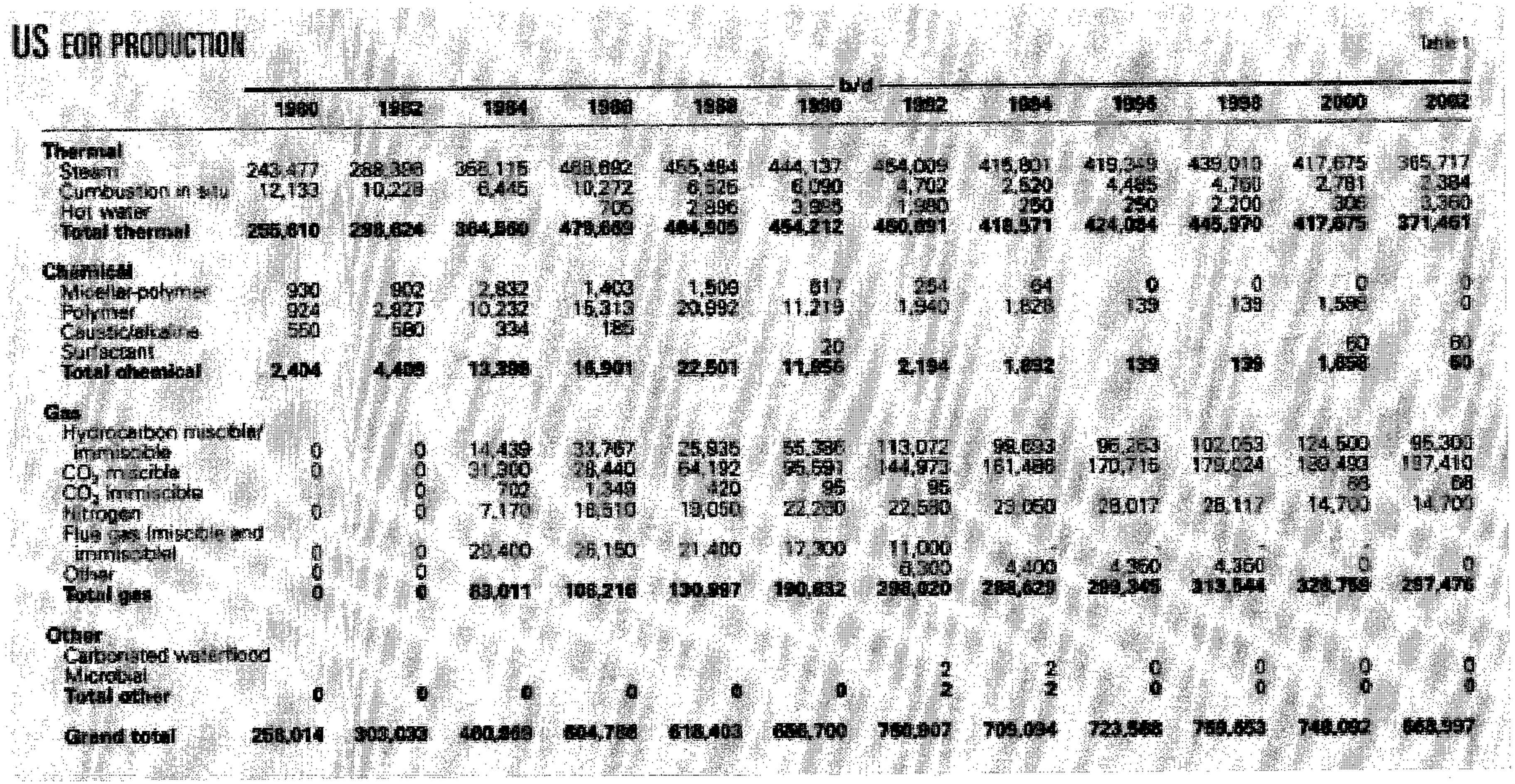
Figure A.1 Project Methodology

Appendix II

Research materials

Table A.1:US EOR Production

(Taken From:S.M. Farouq Ali. "The unfulfilled promise of Enhanced Oil recovery", Society of Petroleum Engineers, [25])



US EOR PRODUCTION

Table 1

	b/d											
	1980	1982	1984	1986	1988	1990	1992	1994	1996	1998	2000	2002
Thermal												
Steam	243,477	288,396	358,115	468,692	455,484	444,137	454,009	415,801	419,349	439,010	417,675	365,717
Combustion in situ	12,133	10,228	6,445	10,272	6,525	6,090	4,702	2,520	4,485	4,760	2,781	2,384
Hot water				705	2,896	3,985	1,980	250	250	2,200	305	3,360
Total thermal	255,610	298,624	364,560	479,669	464,905	454,212	460,691	418,571	424,084	445,970	417,675	371,461
Chemical												
Micellar-polymer	930	902	2,832	1,403	1,509	617	254	64	0	0	0	0
Polymer	924	2,927	10,232	15,313	20,992	11,219	1,940	1,828	139	139	1,598	0
Caustic/alkaline	550	580	334	185								
Surfactant						20					60	60
Total chemical	2,404	4,409	13,398	16,901	22,501	11,856	2,194	1,892	139	139	1,658	60
Gas												
Hydrocarbon miscible/ immiscible	0	0	14,439	33,767	25,935	55,386	113,072	99,693	96,263	102,053	124,500	95,300
CO$_2$ miscible	0	0	31,300	28,440	64,192	95,591	144,973	161,486	170,715	179,024	189,493	187,410
CO$_2$ immiscible		0	702	1,349	420	95	95				66	66
Nitrogen	0	0	7,170	18,510	19,050	22,260	22,580	23,050	28,017	28,117	14,700	14,700
Flue gas (miscible and immiscible)	0	0	29,400	26,150	21,400	17,300	11,000					
Other	0	0					6,300	4,400	4,350	4,350	0	0
Total gas	0	0	83,011	108,216	130,997	190,632	298,020	288,629	299,345	313,644	328,759	297,476
Other												
Carbonated waterflood												
Microbial							2	2	0	0	0	0
Total other	0	0	0	0	0	0	2	2	0	0	0	0
Grand total	258,014	303,033	460,969	604,786	618,403	656,700	760,907	709,094	723,568	759,653	748,092	668,997

Table A2: Screening Parameters for Reservoir Characterization for Enhanced Oil Recovery

(Taken from: Donaldson, E.C., Chilingarian, G.V., Yen, T.F., Enhanced Oil Recovery I – Fundamental and analysis [30])

TABLE 6-11

Screening parameters for reservoir characterization for enhanced oil recovery by steam injection, in-situ combustion, surfactant—polymer flooding, polymer flood, caustic waterflood, and hydrocarbon miscible flooding

Screening parameters	Steam injection	In-situ combustion	CO_2 flood	Surfactant—polymer	Polymer	Alkaline waterflood	Hydrocarbon miscible
1. Oil viscosity, cp	n.c.	n.c.	< 12	< 20	< 200	< 200	< 5
2. Oil gravity, °API	10—25	10—45	> 30 (Calif. > 26)	> 25	> 18	15—35	> 30
3. Depth, ft	200—5000	> 500	> 2300	< 8500	< 8500	n.c.	n.c.
4. Reservoir temperature, °F	n.c.	n.c.	n.c.	< 250	< 200	< 200	n.c.
5. Initial reservoir pressure, psig	n.c.	n.c.	> 1200	n.c.	n.c.	n.c.	n.c.
6. Net pay, ft	> 20	> 10	n.c.	n.c.	n.c.	n.c.	n.c.
7. Permeability, md	n.c.	n.c.	n.c.	> 20	> 20	> 50	n.c.
8. Residual oil saturation, %	50	50	25	> 25	> 50	> 25	> 25
9. (kh/μ) transmissibility, md ft/cp	> 100	> 20	n.c.	n.c.	n.c.	n.c.	n.c.
10. Porosity, %	> 10	> 10	n.c.	n.c.	n.c.	n.c.	n.c.
11. Salinity (TDS), ppm	n.c.	n.c.	n.c.	< 50,000	n.c.	< 2500	n.c.
12. Hardness (Ca and Mg), ppm	n.c.	n.c.	n.c.	< 1000	n.c.		n.c.
13. Operating pressure, psi	< 2500	n.c.	> 1100	n.c.	n.c.	n.c.	> 1300
14. Target oil, bbl/acre-ft	> 500	> 400	n.c.	n.c.	n.c.	n.c.	n.c.
15. Lithology	n.c.	n.c.	n.c.	sandstone	n.c.	sandstone preferred	n.c.
16. Gas cap	none to minor	none to minor	none to minor	none to minor	none to minor	none to minor	n.c.
17. Natural water drive	none to weak	none to weak	none to weak	none to minor	none to minor	none to minor	
18. Fractures	none to minor n.c. unless extreme	none to minor	none to minor	none to minor	none to minor	none to minor	
19. Well spacing	⩽ 10	⩽ 20	n.c.	n.c.	n.c.	n.c.	n.c.
20. Comments	porosity and thickness (high) economic fresh water available economic fuel available high net to gross pay low clay content	high dip preferred porosity and thickness (high) low vertical permeability preferred temperature > 150°F preferred high net to gross pay	thin pay preferred high dip preferred homogeneous formation preferred porosity and thickness (low) natural CO_2 available; low vertical permeability	homogeneous formation preferred low clay content $\phi \times h$ (high) waterflood sweep > 50%	use with or prior to waterflood low-calcium clay content $\phi \times h$ (high)		

n.c. = not critical.