Alma Mater Studiorum – Università di Bologna

DOTTORATO DI RICERCA

Georisorse e Geotecnologie

Ciclo XX

Settore/i scientifico disciplinari di afferenza: ING-IND/30
IDROCARBURI E FLUIDI
DEL SOTTOSUOLO

TITOLO TESI

EVALUATION OF ALKALI FLOODING COMBINED WITH INTERMITTENT FLOW IN CARBONATE RESERVOIR

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Esame finale anno 2008

EVALUATION OF ALKALI FLOODING COMBINED WITH INTERMITTENT FLOW IN CARBONATE RERSERVOIR

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A Thesis Submitted is Partial Fulfillment of Requirements
for the Doctor of Philosophy in Georesources and Geotechnology
Department of Chemical, Mining and Environmental Engineering
(DICMA) Faculty of Engineering, University of Bologna
Academic Year 2007/2008
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Thesis Title	EVALUATION OF ALKALI FLOODING COMBINED WITH INTERMITTENT FLOW IN CARBONATE RESERVOIR
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Accepted by Department of Chemical, Mining, and Environmental Engineering (DICMA), University of Bologna in Partial Fulfillment of Requirements for the Doctor of Philosophy

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ABSTRACT

The majority of carbonate reservoir is oil-wet, which is an unfavorable condition for oil production. Generally, the total oil recovery after both primary and secondary recovery in an oil-wet reservoir is low. The amount of producible oil by enhanced oil recovery techniques is still large. Alkali substances are proven to be able to reverse rock wettability from oil-wet to water-wet, which is a favorable condition for oil production. However, the wettability reversal mechanism would require a non-economical aging period to reach the maximum reversal condition. An intermittent flow with the optimum pausing period is then combined with alkali flooding (combination technique) to increase the wettability reversal mechanism and as a consequence, oil recovery is improved.

The aims of this study are to evaluate the efficiency of the combination technique and to study the parameters that affect this method. In order to implement alkali flooding, reservoir rock and fluid properties were gathered, e.g. interfacial tension of fluids, rock wettability, etc. The flooding efficiency curves are obtained from core flooding and used as a major criterion for evaluation the performance of technique.

The combination technique improves oil recovery when the alkali concentration is lower than 1% wt. (where the wettability reversal mechanism is dominant). The soap plug (that appears when high alkali concentration is used) is absent in this combination as seen from no drop of production rate. Moreover, the use of low alkali concentration limits alkali loss. This combination probably improves oil recovery also in the fractured carbonate reservoirs in which oil is uneconomically produced.

The results from the current study indicate that the combination technique is an option that can improve the production of carbonate reservoirs. And a less quantity of alkali is consumed in the process.

Key words: / Enhanced oil recovery/ Alkali flooding/ Wettability reversal/

ACKNOWLEDGEMENTS

My first acknowledgements go to Professor Guido Gottardi and Villiam Bortolotti (my adviser and co-adviser) for the opportunity given to me to complete this doctorate program.

I would like to thank Celso Vescogni, Fausto Peddis, Barbara Ravaglia, and Mirko Gombia for all their technical advice and assistance. My thanks also go out to Miklós Kázmér from Eotvos University, Budapest, Hungary for his advice in rock analysis. My heartfelt appreciation goes to Chevron Phillips Chemical CO. LP., for the artificial oil sample sponsorship, without which my thesis could not have been completed.

Besides the technical support, my very special thanks go to Lorenzo Alessandrini and the Paoletti family for your moral support, the warmness given to me, and for being my second family.

I would like to give a million thanks to Pundaree Bunkerd (Fern), Tomislav Jonjic (Tommy), Sukanya Kerngfak (Yaya-Yui), Rassamin Pomsantia (Rassy), Stefano Biella (Stefino), and Massimo Grassilli (Massi) for sharing all the good moments and the sincere friendship given me during my stay in Bologna. My thanks also go out to Christopher Smith for his friendship and especially for his help with my English grammar.

Last but not least, to my dearest family: Boonsom (dad), Yuwadee (mom), Feaunglap (sister), and Lekkla (brother) Srisuriyachai for all the best things that you have all given and fulfilled for me, thank you so very much.

This thesis is dedicated to you all.

Falan Srisuriyachai

CONTENTS

CONTENTS (continued)

CHAPTER **Page**

CONTENTS (continued)

CHAPTER **Page**

CONTENTS (continued)

CHAPTER **Page**

CONTENTS (continued)

CHAPTER **Page**

CONTENTS (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

FIGURE **Page**

LIST OF FIGURES (continue)

LIST OF FIGURES (continue)

FIGURE **Page**

LIST OF FIGURES (continue)

NOMENCLATURE

A	Crossectional area of core sample
A_1	Area under oil-drive curve
A_2	Area under water-drive curve
AN	Acid Number
ASP	Alkali-Surfactant-Polymer flooding
B_o	Formation volume factor of oil
C_{eff}	Alkali concentration if the effluent
C_{int}	Initial alkali concentration
CMC	Critical Micelle Concentration
$C_{o,eq}$	Concentration of fatty acid in the oil phase at equilibrium
$C_{o,i}$	Initial concentration of acid in oil phase
$C_{w,eq}$	Concentration of fatty acid in the water phase at equilibrium
E_H	Redox Potential
EOR	Enhanced Oil Recovery
I	Amott wettability index
IFT	Interfacial Tension
IWS	Irreducible Water Saturation
k	Absolute permeability
K	Partition coefficient
K_b	Base ionization time
k_r	Relative permeability
k_{ro}	Relative permeability to oil
LPG	Liquid Petroleum Gas
M	Mobility of fluid
MEOR	Microbial Enhanced Oil Recovery
m_l	Liquid mass
M_o	Mobility of oil
M_r	Relative mobility
MRI	Magnetic Resonance Imaging
m_t	Total liquid mass
M_w	Mobility of water

NMR	Nuclear Magnetic Resonance
OOIP	Original Oil in Place
p.z.c.	Point of zero charge
PAC	Polyacrylate Copolymer
PAM	Polyacryleamide
p_c	Capillary pressure
p_{NW}	Pressure of non-wetting fluid
p_o	Pressure of oil
ppm	Part per million
ppt	Part per thousand
psi	Pound per square inch
PV	Pore Volume
p_w	Pressure of water
p_{WET}	Pressure of wetting fluid
q	Liquid flow rate
ROS	Residual Oil Saturation
RPM	Round per minute
SE	Spin Echo
SR	Saturation Recovery
T_1	Longitudinal relaxation time
T_2	Transverse relaxation time
V_l	Liquid volume
V_o	Volume of oil
V_{osp}	Volume of oil displaced by spontaneous imbibition
V_{ot}	Total volume of oil displaced
V_t	Total liquid volume
V_w	Volume of water
V_{wsp}	Volume of water displaced by spontaneous imbibition
V_{wt}	Total volume of water displaced
W	The USBM wettability index
w/w	Weight by weight
WAG	Water Alternated with Gas
w_h	Hydrostatic weight of core

WOR	Water-Oil Ration
w_s	Dry core weight
w_{sat}	Water-saturated core weight
XG	Xanthan Gum

Greek

ΔL	Length of core sample
δ_o	Displacement-by-oil ratio
Δp	Pressure difference between inlet and outlet
δ_w	Displacement-by-water ratio
θ_{adv}	Water advancing contact angle
θ_c	Contact angle at the oil-water-solid interface
θ_{rec}	Water receding contact angle
μ	Fluid viscosity
μ_l	Dynamic viscosity of liquid
ρ_{ave}	Average liquid density
ρ_l	Liquid density
ρ_o	Oil density
ρ_s	Relative core density
ρ_w	Water density
σ_{os}	Interfacial energy between oil and solid
σ_{ow}	Interfacial energy between oil and water
σ_{ws}	Interfacial energy between water and solid
υ_l	Kinematic viscosity of liquid
Φ	Porosity

CHAPTER 1

INTRODUCTION

In the oil filed production, oil is first produced by primary recovery by means of natural drive mechanisms. After a certain period of oil production, the natural drive decreases and large amount of oil is left inside the reservoir formation. Prolonging the production will not yield further economical results. Secondary recovery and Enhanced Oil Recovery (EOR) are then utilized to extend the production life of reservoir.

Secondary recovery or waterflood is simply performed by injecting water (mostly refers to sea brine) into an injection well. Oil is released from reservoir formation from waterflood pressure that overcomes the oil-entrapped capillary force. Mobilized oil then moves toward a production well. Some reservoirs may not respond to waterflood because of the unfavorable reservoir characteristics and conditions. The ultimate oil recovery after primary and secondary recovery can be less than 40% of the original oil in place (OOIP) in some reservoirs (Donaldson *et al.,* 1985). EOR may then be chosen to improve oil recovery.

EOR, also called tertiary recovery, is the oil recovery by injecting the materials that are absent in the reservoir (Lake, 1989). It is not necessarily to perform an EOR after water flooding. An EOR method can be chosen after primary recovery in cases that waterflood is expected to give uneconomical results. Several conventional EOR methods are steam flooding, miscible flooding (e.g. carbon dioxide injection), and immiscible flooding (injection of polymer, surfactant, alkali, gel, and foam). Nowadays, each method has been modified to suit the requirements of specific reservoir conditions.

The wettability, one of the petrophisical properties, is defined as the tendency of one fluid to adhere onto solid surfaces in the presence of other immiscible fluids. Wettability directly affects the oil recovery by controlling the location, flow and distribution of fluids in the reservoir. In the oil-wet reservoirs, oil tends to spread onto the reservoir rock instead of being produced, causing generally low oil recovery. Anderson (1986) stated that 80% of carbonate reservoirs are naturally oil-wet and less than half of oil in place can be produced by primary and secondary recovery. These reservoirs need an EOR method to improve oil recovery by reversing the rock wettability. Alkali substances have been proven to be an appropriate means to improve the oil recovery from oil-wet reservoirs by reversing the rock wettability to a more favorable condition and by reducing the Interfacial Tension (IFT) between fluid phases to an ultra-low level. The combination of alkali with surfactant and polymer gives the mixture of chemical that can increase and optimize oil production.

Generally, carbonate surface is positively charged at moderate pH condition. This facilitates the adsorption of negatively-charged carboxylic acids which are dissolved in oil phase, rendering the rock surface an oil-wet condition. Wettability reversal by adsorption–desorption mechanisms of adsorbed materials occurs slowly, requiring a long period to reach the wettability equilibrium (Craig, 1993). Likewise, Hirasaki et al. (2004) concluded that wettability reversal in the positively-charged calcite to negative is dependant from the aging time, temperature and chemical substances. Aging time allows the wettability reversal mechanism to reach a more favorable condition (less strongly oil-wet) in the presence of alkali substances.

Intermittent flow (Hyne, 1991), which is a non-continuous process consisting of an alternation between production and non-production periods, is combined with alkali flooding in this study, allowing the hydroxide ions to reverse the wettability of rock surface and to allow the interface to reach the wettability equilibrium. However, aging alkali in the reservoir formation unavoidably creates a drawback. It is well known that alkali substances react with divalent ions (calcium ion (Ca^{2+}) and magnesium ion (Mg^{2+})) in the brine phase to form the water soluble compounds that do not affect oil recovery improvement. Moreover, the alkali consumption increases proportionally with time and temperature (Donaldson *et al.,* 1985). This results in a loss of alkali without recovery improvement. Surprisingly, the wettability alteration function is predominant at alkali concentration lower than 1% w/w, whereas IFT reduction is oppositely predominant at higher concentration than 1 %w/w (Arihara *et al.,* 1999). Therefore, the alkali consumption can be limited by the use of low alkali concentration during the aging alkali injection.

The aims of this study are to evaluate the efficiency of the combination between alkali flooding and intermittent flow and to study the parameters that affect this combination exploited in carbonate reservoir. Limestone is chosen in this study because it does not cause non-deleterious problems from reaction between rock and alkali substance. The results are compared with continuous alkali flooding which is a conventional method. The subjects studied in this research are alkali concentration, type of alkali substance, acid number of oil, type of acid, and interstitial water saturation. Part of experiments is dedicated for Alkali-Surfactant-Polymer (ASP) flooding combined with intermittent flow, in order to improve the efficiency of the previous alkali flooding. The flooding performance curve is chosen as a major criterion for efficiency judgment. The wettability index related to ultimate oil recovery is taken in consideration. Dynamic alkali consumption is unavoidable and could reach a maximum loss for aging cases. However, dynamic alkali consumption is studied and included in this research.

CHAPTER 2
WETTABILITY

Wettability is defined as the tendency of a fluid to spread or adhere onto the solid surface in the presence of other immiscible fluids (Anderson, 1986). Wettability is considered as an important factor that controls the location, flow, and distribution of fluids in the reservoir. Therefore, wettability affects most of the petrophysical properties including capillary pressure, relative permeability, waterflood behavior, electrical properties, and simulated tertiary recovery.

Basically, wettability of solid surface can be classified in three types: water-wet, oil-wet, and neutral-wet. Water-wet describes a surface that prefers to adhere by water when there is a presence of oil phase, while oil-wet surface is opposite, tending to attach with oil in a presence of water. Neutral–wet (so called intermediate-wet) terms for a surface having either water-wet and oil-wet characters or a surface without wettability preference. Theoretically, some parameters are directly used to indicate the type of surface wettability such as contact angle and wettability index. Some petrophysical-related data can also indirectly indicate the wettability preference, for example, the relative permeability curve, capillary pressure curve, and flooding performance curve (Craig, 1993). Basic knowledge of wettability and wettability measurement are reviewed in this chapter.

2.1 Wettability of Reservoir Rock

In wettability literatures, sandstone and carbonate rocks are mostly studied. The wettability of both rocks is affected from the surface molecular property which is different in chemical, structural, and molecule orientation aspects.

2.1.1 Sandstone Reservoir Rock

Sandstone is a classic, sedimentary rock composed primarily of sand-sized particles. Chemically, the composition of sandstone is silicon dioxide (SiO_2 or silica) oriented in the crystalline form. One silica molecule is represented by a tetrahedral structure formed by one silicon atom at the center and surrounded by four atoms of oxygen. These oxygen atoms are linked with other silicon atoms from adjacent molecules, resulting in a continuous network of structure. However, this continuous structure represents only for the bulk molecules. At the surface, the discontinuity is present; two oxygen atoms from each silica molecule are not bonded, yielding negative charges on the surface. Figure 2.1 depicts the structure of silica crystalline.

Initially, sandstone is a strongly water-wet since the rock is deposited in the aqueous environment. After that, oil migrated through the formation and is consecutively trapped. The connate water prevents the attachment of oil which causes the wettability reversal in sandstone. However, some authors have shown that sandstone rocks can be neutral or oil-wet.

The point of zero charge (p.z.c), the point at which the surface charge density changes from positive to negative or vice versa, corresponds to the pH of 2.5 for silica surface. At the pH above this value, silica surface is negatively charged. Decreasing pH (increasing of hydrogen ion (H^+)) will reverse the surface charge by protonation of hydrogen ion on the surface-oxygen atoms.

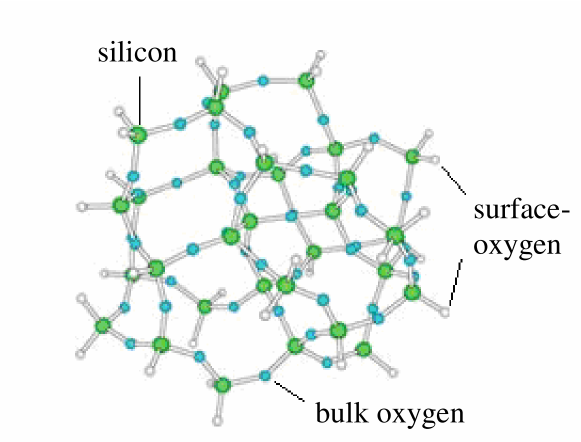


Fig. 2.1: Three dimension structure of Silicon dioxide.

2.1.2 Carbonate Reservoir Rock

Carbonate rock is a potential reservoir rock composed primarily of calcium carbonate. Figure 2.2a shows the three dimensional structure of calcium carbonate which explains only bulk structure. Likely to sandstone, surface structure of carbonate rock is different from bulk structure. Oxygen atoms are the key to determine the surface charge of carbonate rock. Mao and Siders (1997) used the Hartree-Fock model to describe surface structure and charge of calcium carbonate dimers. In the Hartree-Fock model, oxygen atoms can be categorized in two types: non-bridging oxygen atoms (bonding with one calcium atom) and bridging oxygen atoms (bonding with two calcium atoms). According to the stabilized structure, the non-bridging oxygen atoms represent the edge of the surface (or surface structure). The protonation of hydrogen ion occurs at the non-bridging oxygen atoms resulting in the positive charge at surface. The stabilized rotation of calcium carbonate dimers is shown in figure 2.2b.

In the environment with pH value lower than 9 which is the p.z.c for carbonate surface (Anderson, 1986), the protonation of hydrogen ion is predominant and carbonate surface charge remains positive. As the pH value increases (increasing of OH^-), negative charges exceed in the solution and the protonated-hydrogen bonds are broken. This results in negatively-charged surface from the un-bonded oxygen atoms on carbonate surface.

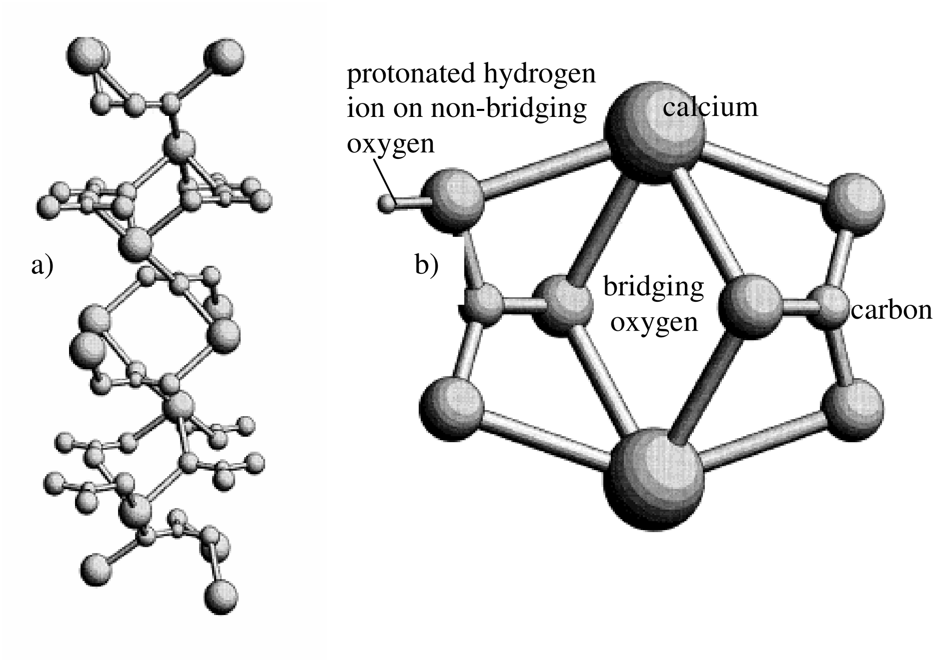


Fig. 2.2: a) lattice molecular of calcium carbonate and b) surface structure of calcium carbon.

When carbonate surface is positively charged, carboxylic acids, the wettability reversal materials which are normally found in crude oil can be adsorbed onto carbonate surface by their negative site (hydroxide part). This results in the orientation of carboxylic molecule, exposing the non-polar part outward from rock skin and yielding a more oil-wet surface (Hamauda and Gomari., 2006). Evidentially, 80% of carbonate reservoirs are naturally oil-wet (Anderson, 1986).

2.2 Wettability Reversal Mechanism in the Reservoir

Initially, all petroleum reservoir rocks were believed to have a strongly water-wet condition. Sandstone reservoirs were deposited in an aqueous environment. Connate water would prevent sandstone surface from attaching with oil and other wettability material. The reversal of wettability from water-wet to oil-wet occurs during oil migration, oil trapping, and during production phases since the rock surface exposes to the reversal potential compounds and reaches the wettability equilibrium over a long aging period. Buckley et al. (1997) summarized the four wettability alteration mechanisms induced by crude oil: polar interaction, surface precipitation, acid/base interaction, and ion binding.

2.2.1 Polar Interaction

Polar interaction is a direct interaction between the charges from rock surface and the opposite charges of chemicals in crude oil. The interaction occurs when water film (brine film) between rock surface and oil phase is absent. In the moderate pH (pH around 7) environment, sandstone surface, which is negatively charged, interacts with the positively-charged compounds, while carbonate surface interacts with the negative ones. However, the polar compounds found in crude oil generally have a non-polar part which is normally a long chain of hydrocarbon. This un-interacted long chain of hydrocarbon exposes outward from rock surface, causing monolayer of the non-polar compounds and yielding the surface an oil-wet condition.

2.2.2 Surface Precipitation

Surface precipitation depends primarily from the solvent property of crude oil itself to asphaltene compounds which are considered as solutes. Asphaltenes are high molecular weight compounds (around 500-1500) and composed mainly of carbon and hydrogen with lesser amounts of nitrogen, sulfur, and oxygen. The wettability alteration mechanism occurs when crude oil is a poor solvent for its asphaltenes. Consequently, asphaltenes cannot be properly dissolved and they then precipitate onto the reservoir rock. Asphaltene compounds reverses rock surface to oil-wet condition by exposing its non-polar part to stick with oil phase. Yan et al., (1997) induced an oil-wet condition with sandstone rock by the asphaltene precipitation and concluded that the reversal of wettability occurs significantly at low temperature. Moreover, the cation in brine phase promotes the asphaltene precipitation while anion has a relatively minor effect.

2.2.3 Acid/Base Interaction

In the presence of water phase (brine), acid or base compounds can be fully or partially ionized through water phase as same as atoms on the surface of sandstone and carbonate rocks. In sandstone case, the negative surface charges tend to interact with the positive charges from ionized base. In the opposite, the positive surface charges of carbonate rock interact with ionized acid. However, bonding between surface charges and ionized acid/base occurs through water film. In the stabilized water film case, a water-wet condition will be maintained. On the other hand, this water film collapses in the un-stabilized water film case, allowing acid or base to interact directly with the surface charges and hence, causing the wettability reversal to an oil-wet condition.

Madsen and Lind (1997) concluded that the chain length of acid molecules strongly affects the wettability reversal in both sandstone and carbonate rocks. The size of acid chain determines the solubility of the acid in water and oil phases. The value of solubility of acid is represented by the partition coefficient (Hamauda *et al.,* 2006)

$$K = C_{o,eq} / C_{w,eq} \qquad (2.1)$$

where $C_{o,eq}$ and $C_{w,eq}$ are the concentration of fatty acids in the oil and water phases at equilibrium. In the close system, if acid firstly dissolves in oil phase the concentration of acid in water at equilibrium can be determined from

$$C_{w,eq} = C_{o,i} - C_{o,eq} \qquad (2.2)$$

where $C_{o,i}$ is the initial concentration of acid in the oil phase.

The short-chain fatty acids are preferentially dissolved in water phase (high partition coefficient), while the long-chain acids with a non-polar part mostly remain in oil phase (low partition coefficient). Therefore, the short-chain fatty acids control the wettability reversal in sandstone since surface primarily contacts with water phase. Oppositely, the long-chain fatty acids control the wettability reversal of carbonate rock in cases that rock surface directly contacts with oil phase or the water film layer is unstable and collapsed.

2.2.4 Ion Binding

Ion binding plays a major roll in the wettability reversal of sandstone. The ions in this mechanism primarily refer to the most-found divalent ions in brine phase which are calcium and magnesium ions (Ca^{2+} and Mg^{2+}). Divalent ions act as the linking bridge between the negative charges of sandstone surface and the negative charges of ionized acid from oil phase. The bridging occurs in water phase as same as the acid/base interaction. The presence of divalent ions does not potentially affect the wettability reversal in carbonate surface because of the repulsion between rock surface and divalent ions. Figure 2.3 summarizes the four mechanisms of wettability alteration by crude oil.

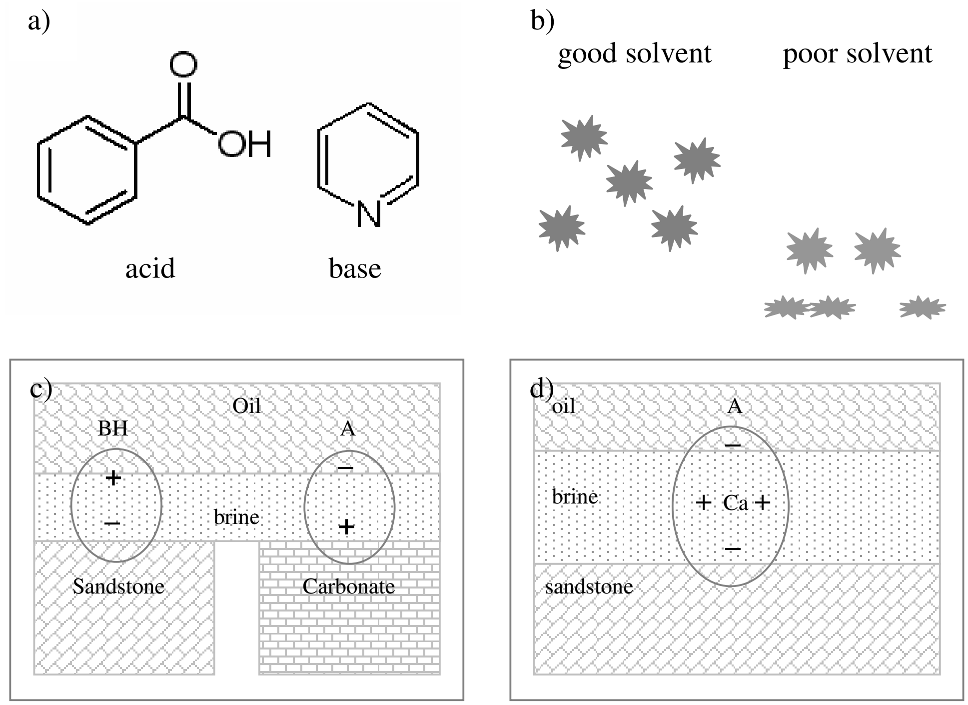


Fig. 2.3: Four mechanisms of wettability alteration by crude oil:
a) polar components in crude oil, b) surface precipitation,
c) acid/base interaction, and d) ion binding.

2.3 Parameters Affecting the Wettability Reversal in Carbonate Reservoir

2.3.1 Chemical Substances

The presence of proper chemical substances is very important for the wettability reversal condition. Naturally, carboxylic acid compounds reverse wettability from a water-wet to an oil-wet condition. This section describes the some chemicals that can reverse the induced oil-wet surface back to a water-wet condition. The induced oil-wet surface is caused by interaction between different surface charges of rock surface and adsorbed material. The chemicals having an ability to reverse the induced oil-wet back to a water-wet condition principally must have the ability to reverse the former surface charge to the opposite charge. Alkali substances, which provide strong negative charges, are well known as an injected material for the EOR process in order to reverse the positively-charged surface to a negative one. This results in the releasing of adsorbed molecules by repulsing the same negative charge of the inducing molecules and as a consequence, the rock returns to have a less oil-wet condition.

In brine phase, sulfate ion (SO_4^{2-}) and magnesium ion (Mg^{2+}) are found to have an ability to reverse rock wettability from oil- to water-wet. Gomari et al. (2006) discovered that sulfate and magnesium ions displace the pre-adsorbed molecules from calcite surface, resulting in the change of zeta potential value from -0.67 mV to -2.06 and +3.62 for sulfate and magnesium ions respectively.

Surfactant can also reverse rock wettability. Cationic surfactants reverse the oil-wet calcite surface to a water-wet condition by removing the adsorbed molecules. Differently, nonionic and anionic surfactants do not remove the adsorbed molecules but instead, these surfactants co-adsorb onto carbonate surface. This co-adsorption is also known as *"bilayer adsorption"*: the hydrophobic part of a surfactant interacts with the hydrophobic part of an adsorbed molecule, leaving the hydrophilic part of a surfactant to stick into bulk solution and yielding a water-wet condition (Wu *et al.,* 2006).

2.3.2 Temperature

Reservoir temperature indirectly affects the wettability of carbonate surface. Naturally, carboxylic acids which are the most commonly adsorbed materials can be degraded to alkenes in the presence of calcium carbonate that functions as a catalyst (Zhang and Austad*.,* 2005). This decarboxylation mechanism increases with temperature. However, the rate of decarboxylation is extremely low and it normally occurs during geological period.

Hamouda and Gomari (2006) concluded that at an elevated temperature, the modified calcite surface by carboxylic acids is less oil-wet because the calcium ion (Ca^{2+}) sites are reduced and hence, surfaces are less occupied by the adsorbed materials. Eventually, the surface becomes more water-wet.

2.3.3 Aging Time

Rock wettability requires a hundred or even thousands of hours of aging time to achieve the adsorption equilibrium. Similarly, the desorption of the adsorbed materials in the flow system could require a corresponding period of time (Craig, 1993). Carbonate reservoirs where 80 percents of them are neutral- to oil-wet (Seethepalli *et al.,* 2004) yield an uneconomical oil recovery. Moreover, it is often reported that the fractured formations are usually observed in carbonate reservoirs, making the result from waterflood insignificant and ineffective. By the use of several chemicals that have an ability to reverse rock wettability from oil- to water-wet condition, the spontaneous imbibition can occur slowly (Hirasaki and Zhang,, 2004).

Therefore, carbonate surface which is normally positively charged, oil-wet surface, and uneconomical oil source can be reversed to negatively-charged water-wet surface by the use of proper chemical substances combined with an adequate aging period.

2.4 Effect of Core Handling on Wettability

Wettability of fresh cores can be unintentionally varied during the handling steps. Basically, core samples can be categorized in three groups according to surrounding conditions and petrophysical properties.

2.4.1 Native-State Core

Native-state core terms for the core with petrophysical properties as measured downhole at the reservoir conditions. Practically, it is difficult to preserve the properties of core from the disturbances after the cores are brought up to surface. It is noticed that during drilling phase, the use of oil-based-emulsion mud and other mud containing surfactants, caustics, mud thinners, organic corrosion inhibitors, and lignosulfonates can disturb the original reservoir wettability. In order to preserve the native-state wettability of core, these chemicals should be avoided during the drilling and coring phases. Some recommended fluids can be used during coring: 1) synthetic formation brine, 2) unoxidized lease crude oil, or 3) a water-based mud with a minimum of additives. Several researchers have attempted unsuccessfully to find a suitable available oil-based mud in order to obtain the native-state core. All of the oil-based drilling mud made water-wet cores more oil-wet.

Core packing and preservation are also considered as very important steps. Since core is brought up to surface, it must be protected from the wettability alteration caused by the loss of light ends and the oxidation of heavy ends. Some substances in crude oil can be rapidly oxidized with air to form the surfactants that can alter wettability. To prevent the wettability alteration, two core packaging procedures are recommended (Bobek *et al.,* 1958). The first method is to wrap core at the well-site in polyethylene or polyvinylidene film and then wrapped again in aluminum foil. The wrapped core is then sealed with paraffin or a special sealer designed to exclude oxygen and to prevent the evaporation of light ends. The second method is to immerse core in the deoxygenated formation or the synthetic brine in glass-lined steel or a plastic tube, which is then sealed to prevent the entrance of oxygen. For the second method, core can also be stored in their wetting fluid, either formation brine or crude oil.

2.4.2 Cleaned Core

Core is usually cleaned in order to use in multiphase flow investigations. The first reason to clean core is to remove all liquids from core. So, true porosity, permeability, and fluid saturation can be measured. The second reason is to obtain a water-wet condition which is generally the first step to restore the wettability of contaminated core. One commonly used method to clean core is the reflux extraction (Dean-Stark or Soxhlet) with a solvent such as toluene. However, many researchers have found that the use of toluene alone in the reflux extraction is ineffective. Toluene is effective in removing hydrocarbons, asphaltenes, and some weakly polar compounds. In order to remove the strongly polar compounds, which are often responsible for the wettability alteration, the combination of toluene with methanol or ethanol yields the more effective result. In addition of toluene/methanol or toluene/ethanol, chloroform/acetone, and chloroform/methanol are also reported in many successful core cleaning cases. However, the best choice of refluxing solvents depends on crude components, mineral surface, and a presence of some contaminated surfactants from drilling mud.

2.4.3 Restored-State Core

According to the reversal of original wettability during the core handling steps, restoring core is an alternative choice to reproduce the wettability of the native state. Three simple steps to restore core are: 1) clean core by removing all compounds from rock surface (by reflux extraction), 2) flow the reservoir fluid into core, and 3) age core at the reservoir temperature for a sufficient time to establish the adsorption equilibrium. Core cleaning is considered as one of the most difficult step. In order to remove all compounds from the rock surface, it is important to use the proper solvents as described in the previous section. The second step is performed by flowing the deoxygenated synthetic or the formation brine through core and then core is flooded again with crude oil. The final step is to age core at the reservoir temperature. Generally, core should be aged at the reservoir temperature for more than 1,000 hours (40 days). Many researchers have demonstrated that rock surfaces require up to 1,000 hours to reach their adsorption equilibriums (Wendel *et al.,* 1985).

Lorenz et al. (1974) and Cuiec (1977) found the method to speed up core to reach the adsorption equilibrium by saturating core solely in oil phase. By this way, polar compounds can have an interaction directly with the rock surface molecules without diffusing across the brine film and the wettability equilibrium can be reached in a few days. Likewise, Clementz (1982) showed that dry core saturation in oil phase created the formation of a very stable oil-wet condition.

Normally, core is more water-wet at the reservoir conditions than it is at room temperature and pressure. Changing temperature causes two effects to the core restoration. First, as temperature increases the adsorbed materials tend to have more solubility. This results in the desorption of the adsorbed materials, and as a consequence the surface is more water-wet compared with the lower temperature case. Second, the interfacial tension (IFT) decreases as temperature increases. Therefore, the wetting phase can be released from surface in a form of a small droplet or emulsion, rendering surface more water-wet. Pressure has less effect to wettability than temperature. However, some researchers noticed that at lower pressure or room pressure, the light ends in crude can evaporate. This changes the property of crude oil by increasing the concentration of heavy ends and hence, there is more chance to alter the wettability of rock surface to an oil-wet condition by the precipitation of heavy ends.

2.5 Artificial Variation of Wettability

Experimentally, an oil-wet condition is required for several wettability reversal tests. After the core sample from the investigated reservoir is cleaned (after the cleaning step, wettability is theoretically a strongly water-wet), some chemicals can be used to prepare the artificial oil-wet condition. The artificial variation of wettability is normally performed with sandstone rocks which are originally water-wet. Organochlorosilanes are substances that are widely used to vary water- to an oil-wet condition. Some examples of organochlorosilanes are shown in figure 2.4.

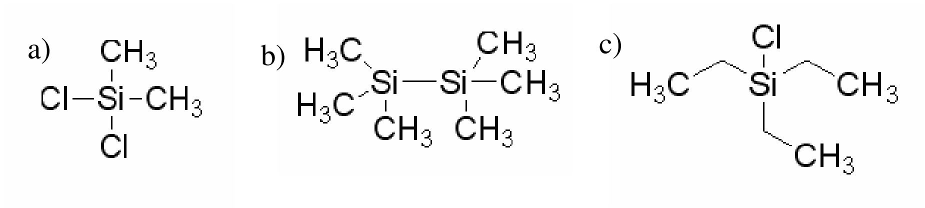


Fig. 2.4: Some frequent used organochlorosilane substances for artificial variation of sandstone surface: a) dichlorodimethylsilane, b) hexamethyldisilane, and c) triethylchlorosilane.

The sample preparation with organochlorosilane is simple. Organochlorosilane is dissolved in tetrahydrofuran and flowed through core sample. After that, sample is aged with a sufficient period to complete the reaction between organochlorosilane and surface molecules. Finally, sample is flushed by the un-reacted compounds to remove solvent (Anderson, 1986).

The reversal of wettability by organochlorosilane in sandstone samples is caused by the reaction of organochlorosilane molecule with hydroxide group attaching with silicon atoms at surface. Chlorine ion from organochlorosilane bides with hydrogen ion to form hydrochloric acid (HCl) which is suddenly dissolved in aqueous phase. Silicon atoms of rock surface are then bided with silicon atoms of organosilane via oxygen atoms. Consequently, the hydrophobic parts of organosilane molecules expose outward from the reacted surface, resulting in an oil-wet condition.

However, the wettability obtained from the use of organochlorosilane can be maximally reversed to a neutral-wet or a mildly oil-wet condition, instead of a strongly oil-wet. Figure 2.5 depicts the reaction between dichlorodimethylsilane and sandstone surface.

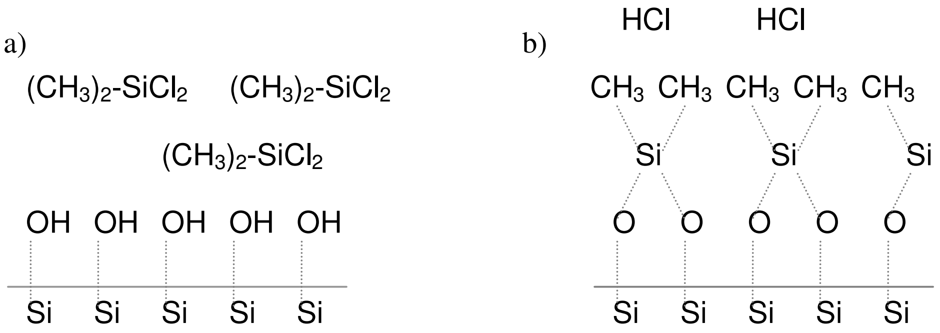


Fig. 2.5: The wettability alteration by organochlorosilane on sandstone surface: a) before reaction and b) after reaction.

For carbonate rocks, a direct adsorption by carboxylic acid onto rock surfaces is commonly used and noticed. Basically, carboxylic acid contains polar and non-polar part inside the same molecule. The size of the hydrocarbon part, which is non-polar, determines the solubility of that acid in any solvent. Short–chain hydrocarbon induces molecule itself to have a slight polarity and so, this acid can primarily dissolve in water which is a polar solvent. Oppositely, the structure of long-chain hydrocarbon obstructs the polarization of molecule. Therefore, the long-chain acids dissolve only in oil phase. Wu et al. (2006) modified calcite surfaces with several naphthenic acids dissolved in decane. Some examples of naphthenic acid used in the calcite modification are demonstrated in figure 2.6. Wu noticed that the reversal of calcite surface to an oil-wet condition does not depend on the quantity of the adsorbed acid molecules but strongly depends on the structure of acid; branched-molecule acids are more potential in the wettability reversal of calcite to an oil-wet condition more than straight-molecule acids.

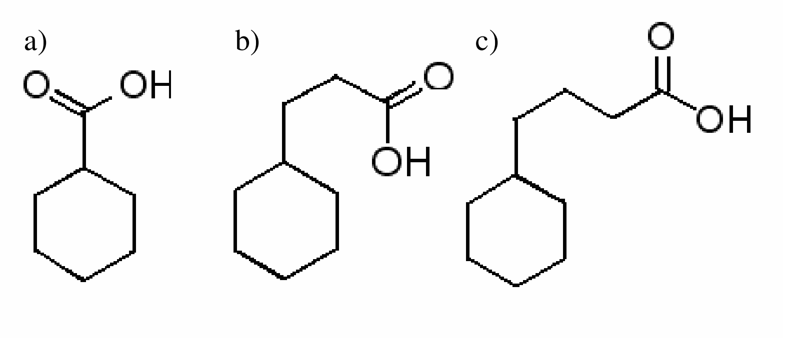


Fig. 2.6: The examples of naphthenic acid used in wettability reversal of carbonate rock: a) cyclohexanecarboxylic, b) cyclohexanepropionic, and c) cyclohexanebutyric.

Amine compounds (R-NH_2) are also used in the wettability alteration of sandstone rock samples. The pH-sensitive characteristic of amines leads to the switching of wettability by changing pH value of solvent. In the alkali pH (pH from 7 to 14), amine groups are adsorbed onto rock surfaces, exposing hydrocarbon chain to make surfaces oil-wet. On the other hand, amines rapidly desorb from surfaces and form the water-soluble salt in the acidic environment (pH below 7), leaving rock surfaces more water-wet. The most commonly used amines in the wettability alteration are hexylamine and octylamine which are shown in figure 2.7.

$CH_3(CH_2)_4CH_2NH_2$

a)

$CH_3(CH_2)_6CH_2NH_2$

b)

Fig. 2.7: The most commonly used amines in wettability alteration:
a) hexylamine and b) octylamine.

2.6 Mixed Wet and Fractional Wet Rock

The terms water-wet, oil-wet and neutral-wet (intermediate-wet or no preference of wettability) generally refer to the rock with the same wettability for all massive portion (homogeneous rock). On the other hand, heterogeneous rock can have both water- and oil-wet together. This leads to the other two additional terms for wettability condition: mixed and fractional wettability.

2.6.1 Mixed Wettability

Salathiel (1973) termed *"a mixed-wet rock"* as the rock contains oil-wet surfaces which form the continuously paths through larger pores, while smaller pores remain water-wet and contain no oil. A mixed-wet condition can be naturally generated during oil migration to an original water-wet reservoir. Oil displaces water in larger pores according to the adequate capillary pressure. Small pores remain water-wet because oil does not have enough pressure to displace water. A mixed-wet rock requires the extra condition; the formation oil has to contain the organic material that can reverse rock wettability. However, the thin layer of water or brine phase prevents the attachment of oil and organic materials onto rock surfaces. Therefore, a mixed wettability needs also a sufficient aging period to allow the wettability reversal material to diffuse through the brine layer, to rupture the brine layer, and to reach the wettability equilibrium after adhering onto rock surfaces.

Experimentally, a mixed-wet rock can be prepared. After the cleaned rock sample is saturated with formation brine, it is then flooded with the oil containing the wettability reversal materials such as carboxylic acids. The flooded oil enters core and flows through the high permeability channels; therefore, the use of heterogeneous rock samples foresees high possibility to obtain a mixed-wet condition. Finally, rock sample is aged at the reservoir temperature for a sufficient period to allow the completion of the wettability alteration to an oil-wet condition.

2.6.2 Fractional Wettability

Generally, rock is composed of many minerals with different surface chemistry and adsorption properties. This leads to the variation of wettability. Fractional wettability can be also called heterogeneous, spotted or dalmation wettability (Brown and Fatt*.,* 1956). In a fractional-wet rock, the wettability reversal materials are adsorbed in a certain area of rock. So, a certain area of rock is strongly oil-wet, while the rest remains water-wet.

Fractional-wet sample can be artificially prepared in laboratory. Sand grains, which are naturally water-wet, are treated with several wettability reversal chemicals such as organochlorosilane or Drifilm to render them oil-wet. A certain ratio of untreated and treated sand grains are then mixed together and finally packed.

2.7 Wettability Measurement

In the presence of oil, water, and solid phases, the ideal definition of wettability is derived from Young's equation (Adamson, 1982)

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos\theta_c \qquad (2.3)$$

In this equation, σ_{os} is interfacial energy between oil and solid (dynes/cm), σ_{ws} is interfacial energy between water and solid (dynes/cm), σ_{ow} is interfacial tension between oil and water (dynes/cm), and θ_c is angle at the oil-water-solid interface measured through the water (degree).

The contact angle (θ_c), obtained from the equation above, represents the wettability of an oil-water-solid system. The value of contact angle varies from zero to 180 degrees. The contact angles measured through water (water-advancing contact angle) less than 90 degrees indicates a preferentially water-wet condition, whereas the contact angle greater than 90 degrees indicates a preferentially oil-wet condition. The contact angle close to zero and 180 degrees are considered as a *"strongly water-wet"* and a *"strongly oil-wet"* respectively. The contact angle close to 90 grades covers the range termed an *"intermediate wettability"* (Craig, 1993). Figure 2.8 illustrated contact angle in an oil-water-solid system.

Several wettability measurements have been reviewed in the wettability literatures. Three quantitative methods are widely used in the petrophisical field: contact angle, Amott method, and U.S. Bureau of mines (USBM) method. The qualitative methods can also be used to distinguish the wettability preferential such as relative permeability curves, capillary curves, and water flooding performance curves.

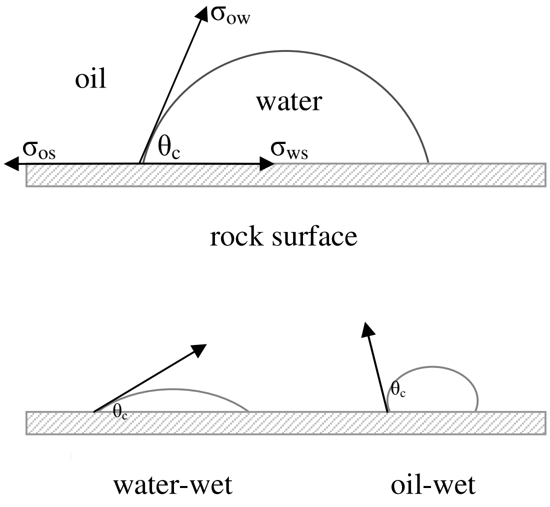


Fig. 2.8: Wettability of oil-water-solid system.

2.7.1 Quantitative or Direct Methods

2.7.1.1 Contact angle

Contact angle measurement is a direct method to measure the specific pure solid surface (uncontaminated sample) in a pure liquid. The measurement called *"sessile drop method"* (Anderson, 1986) is performed in the contact angle cell containing two flats polished crystal of the mineral that is predominant in rock surfaces (quartz and calcite are used to represent sandstone and carbonate rock respectively). The mineral plates are immersed in the formation water. A drop of formation oil is then placed between two crystal plates which are then moved in the opposite direction, allowing water to form an advance contact angle onto the crystal plates. Before measuring contact angle, the oil drop on crystal surface is aged for a few days, allowing the system to reach equilibrium. In several literatures, contact angles refer to *"water advancing"* (θ_{adv}) which are measured by pulling the periphery of a drop over a surface, while the term *"water receding"* (θ_{rec}) is the measurement by pulling it back. Figure 2.9 shows the contact angle measurement.

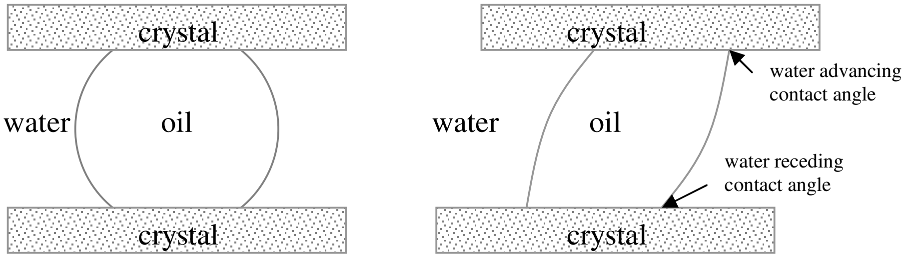


Fig. 2.9: Contact angle measurement by sessile method.

It is confirmed by a number of investigators that contact angles increase with time. An adequate aging period allows the wettability alteration to reach the equilibrium, allowing the adsorbed materials to interact with rock surfaces. The wettability equilibrium generally requires hundreds or even thousands of hours of aging time (Brown and Fatt, 1956).

2.7.1.2 Amott Method

This method is principally based on the fact that the wetting fluid imbibes spontaneously into core, displacing the non-wetting phase. The value is represented by wettability index (*I*) which is the ratio of spontaneous imbibition to the forced imbibition. The Amott method is started by saturating core sample with the formation oil and centrifuging in the formation brine until the Residual Oil Saturation (ROS) is reached. The measurement can be performed by these following four steps.

- Immerse core sample in the formation oil and measure the volume of brine displaced by spontaneous imbibition of the formation oil after 20 hours.

- Centrifuge core sample in the formation oil until it reaches the Irreducible Water Saturation (IWS) and measure the total amount of water displaced, including the brine displaced by spontaneous imbibition in the previous step.

- Immerse core sample in the formation brine and measure the volume of oil displaced by spontaneous imbibitions of the formation brine after 20 hours.

- Centrifuge core sample in the formation brine until it reaches ROS and measure the total amount of oil displaced, including the oil displaced by spontaneous imbibition in the previous step.

From the first and second steps, the ratio of the formation brine displaced by spontaneous imbibition (V_{wsp}) to the total water displaced by imbibition and centrifugal displacement (V_{wt}) is defined as *"displacement-by-oil ratio"*.

$$\delta_o = V_{wsp} / V_{wt} \qquad (2.4)$$

Similarly, *"displacement-by-water ratio"* can be obtained from the third and fourth steps, dividing the formation oil displaced by spontaneous imbibition (V_{osp}) by the total oil displaced by imbibition and centrifugal displacement, (V_{ot}).

$$\delta_w = V_{osp} / V_{ot} \qquad (2.5)$$

The difference between the displacement-by-water ratio and the displacement-by-oil ratio is called 'Amott-Harvy wettability index (I) (Amott, 1959).

$$I = \delta_w - \delta_o \qquad (2.6)$$

The Amott-Harvey wettability index ranges from -1.0 to 1.0. Generally, the value ranging from -1.0 to -0.3 indicates an oil-wet condition, -0.3 to 0.3 indicates a neutral-wet condition (no wettability preference), and from 0.3 to 1.0 indicates a water-wet condition. Similarly to contact angle, the values approaching -1.0 and 1.0 represent strongly oil- and water-wet respectively.

2.7.1.3 USMB Method

The USBM method is developed by Donaldson et al. (1969). This method is used to determine the average wettability of core (as same as the Amott method). A major advantage over the Amott method is its sensitivity near the neutral wettability zone. The measurement is performed over the capillary pressure curves, composing of brine and oil drive capillary curves. The area under the driving curves represents work that is required to displace another immiscible fluid. When the core is water-wet, the area under brine drive capillary pressure curve (when water displaces oil) is smaller than oil drive capillary. On the other hand, the area under oil drive curve is smaller than the brine drive in oil-wet rock.

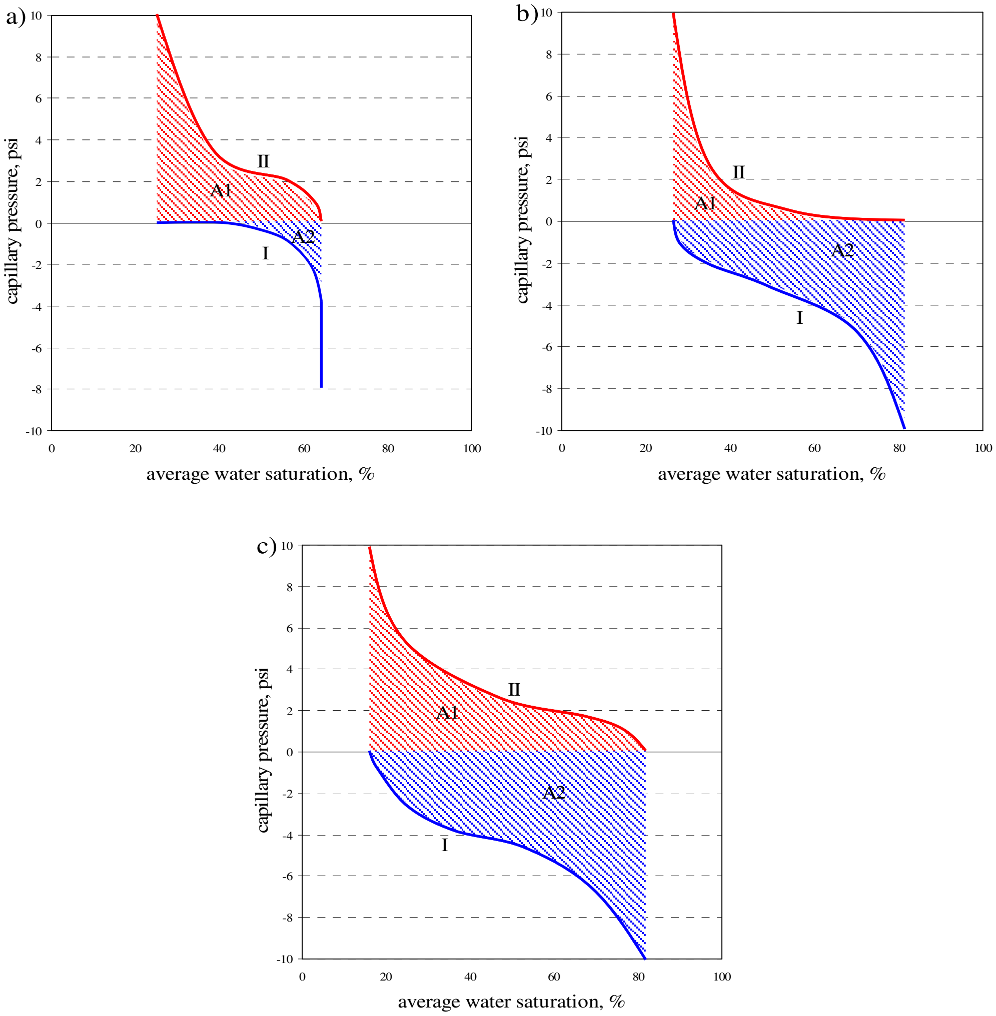


Fig. 2.10: Centrifugal capillary pressure curves for USBM wettability:

a) water-wet, b) oil-wet, and c) neutral-wet.

Before starting the test, sample is saturated with brine and then centrifuged at high speed in oil in order to reach the IWS. During the test, the centrifugal capillary pressure is measured based on water saturation. First, core sample is placed in brine and centrifuged at incremental speeds until the centrifugal capillary pressure reaches -10 psi. At each incremental gap, the average water saturation is calculated from the volume of expelled oil. In the second step, core is placed in oil and centrifuged with incremental speeds until the centrifugal capillary pressure reaches 10 psi. Figure 2.10

shows the centrifugal capillary pressure curves from three types of wettability: strongly water-wet, strongly oil-wet, and neutral-wet.

The USMB wettability index (*W*) is calculated from the ratio of areas under two centrifugal capillary pressure curves as

$$W = \log(A_1/A_2) \qquad (2.7)$$

where A_1 and A_2 are respectively the areas under the oil and brine-drive curves. The value of *W* indicates type of wettability. When *W* is higher than zero, core is water-wet and when *W* is lower than zero, core is oil-wet. The value of *W* near zero indicates a neutral-wet condition. A larger number of *W* corresponds to a strongly wet condition.

2.7.2 Qualitative or Indirect Method

In an oil-brine system, relative permeability curves, capillary pressure curves, and flooding efficiency curves can also indicate type of rock wettability. However, these curves can distinguish qualitatively between oil- and water-wet. The difference can be obviously seen between strongly wet conditions.

2.7.2.1 Relative Permeability Curve

Relative permeability terms for an ability of a porous media to conduct one fluid when one or more fluids are present. The relative permeability is normally represented by two curves: relative permeability to oil and water. Basically, relative permeability is a direct function of fluid saturation. The values of relative permeability at each saturation point is divided by the reference which is mostly the permeability to oil at the reservoir connate water saturation; therefore, the value of relative permeability to oil at connate water saturation is unity. Typical relative permeability for strongly oil- and water-wet rocks is illustrated in figure 2.11. The curves are plotted as a function of water saturation representing the displacing phase.

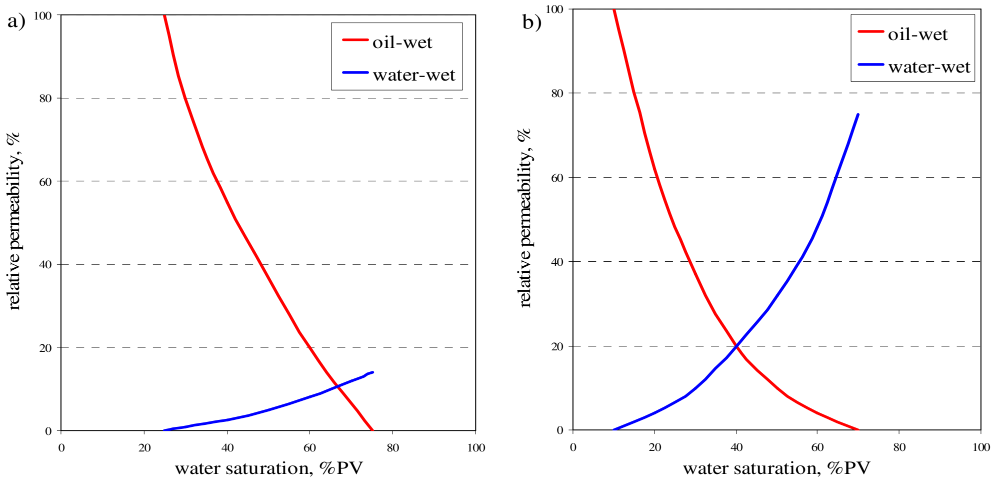


Fig. 2.11: Typical relative permeability curves for: a) water- rock and b) oil-wet rock.

In a strongly water-wet rock, the relative permeability to oil is relatively high at IWS because water is mostly located in small pores which have very little effect to the oil flow paths. In contrast, the relative permeability to water is extremely low at ROS because oil forms the globules in the center of large pores and these globules block the water flow paths.

In a strongly oil-wet rock, IWS is lower than that of a water-wet rock. The relative permeability to oil is unity since it is at the reference. The water saturation at ROS is smaller than that of a water-wet rock because oil tends to adhere onto surfaces. So, water can flow easily, resulting in high relative permeability to water.

The point at which relative permeability curves across each other is called *"cross over"* Craig (1993) summarized the rule of thumb that the cross over for a water-wet rock is usually greater than 50% of water saturation, whereas in an oil-wet rock is normally lower than 50% of water saturation. Table 2.1 summarizes Craig's rule of thumb for determining wettability between strongly oil- and water-wet rocks.

Table 2.1: Craig's rule of thumb for determining wettability.

Property	Water-wet	Oil-wet
Interstitial water saturation	Usually greater than 20 to 25% PV	Generally less than 15% PV
Cross over saturation	Greater than 50% water saturation	Less than 50% water saturation
Relative permeability to water at ROS	Generally less than 30%	Greater than 50% and can approach 100%

2.7.2.2 Capillary Pressure Curve

Capillary pressure is defined as a difference between pressures existing across the interface separating two immiscible fluids, one of which wets rock surfaces in a presence of other. The capillary pressure of an oil-water system is defined as

$$p_c = p_o - p_w \tag{2.8}$$

where p_o and p_w represent the pressure of oil and water respectively. Thus, capillary pressure can be either positive or negative value, depending upon the wettability preference. In the presence of other phases which are neither oil nor water, the capillary pressure is usually defined as

$$p_c = p_{NW} - p_{WET} \tag{2.9}$$

where p_{NW} is the pressure in the non-wetting fluid and p_{WET} is the pressure of wetting fluid.

Capillary pressure is a direct function of fluid saturation. The two-lines plotted of capillary hysteresis, which is composed of drainage and imbibition lines, are commonly recommended. The term hysteresis in petrophysical aspect is defined as the difference in multiphase rock properties that depends upon the direction of saturation change. The drainage process is termed for a process that the saturation of wetting phases is reduced, while imbibition process is opposite; defining a process of which the wetting phase saturation is increased. The capillary pressure measurement is conducted by starting from a sample saturated with the wetting fluid. The saturated sample is displaced by the non-wetting fluid (drainage) until capillary pressure does not change. After that, sample is re-displaced by wetting fluid (imbibition) until capillary pressure reaches zero.

In a strongly water-wet rock, oil pressure is higher than water pressure. At the entrance point of drainage process, this pressure is called *"threshold pressure"* or *"displacement pressure"*. As the drainage process is kept continuing, water saturation decreases while capillary pressure which is expressed by equation 2.8 increases. At IWS, oil cannot further displace water, resulting in the highest capillary pressure. The imbibition is conducted by re-displacement with water. The imbibition process terminates at ROS where capillary pressure equals to zero.

In a strongly oil-wet rock, water pressure is higher than oil phase but the threshold pressure is negative since the capillary pressure definition is defined as the equation 2.8. As the drainage process is kept continuing, oil saturation decreases as same as capillary pressure. Capillary pressure decreases until ROS at which water cannot further displace oil and at this point capillary pressure is the lowest. The imbibition process is then followed by re-displacement with oil. Again, the imbibition process terminates at IWS where capillary pressure is zero. Figure 2.12 illustrates the difference between hysteresis in strongly water- and oil-wet rock.

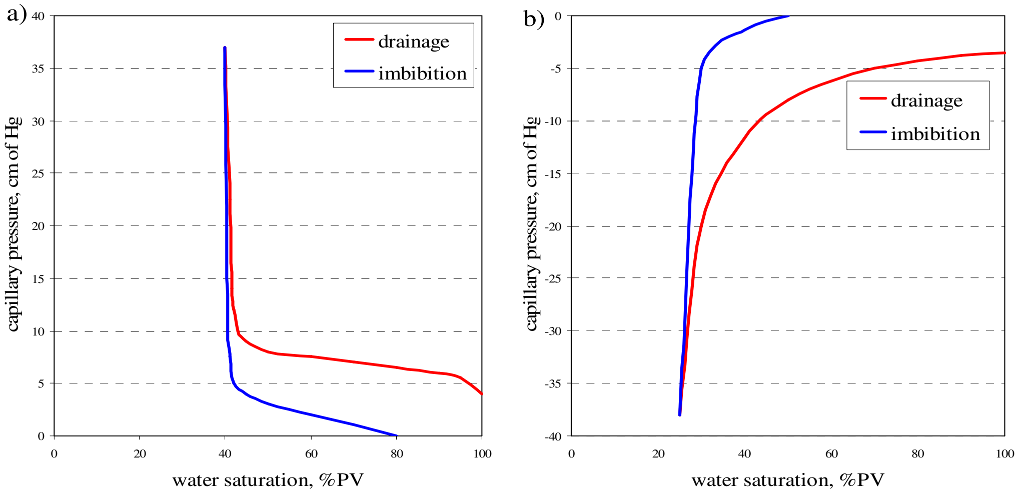


Fig. 2.12: Capillary pressure curves for; a) water- wet rock and b) oil-wet rock.

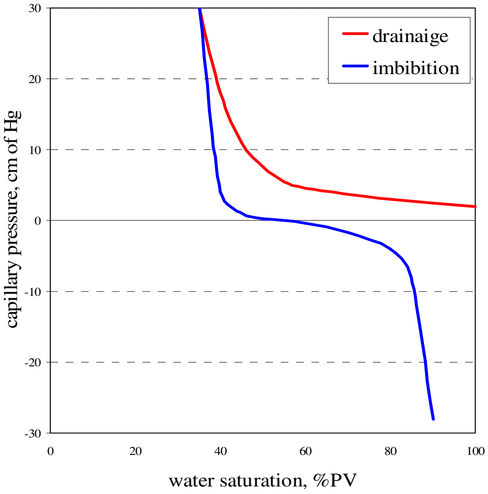


Fig 2.13: Capillary pressure curves of intermediate-wet rock

For an intermediate-wet rock, which the rock does not show any preference in wetting property, the capillary pressure curves are shown in figure 2.13. Capillary pressure of an intermediate-wet rock has both characters of strongly water- and oil-wet rocks. The drainage curve is similar to a strongly water-wet rock (as the curve is plotted with water saturation) but demonstrates the lower threshold pressure (represents moderately wet rock). The imbibition curve reaches a capillary pressure value of zero at early water saturation than that of strongly-wet case. The imbibition is further preceded and the curve enters in the negative value zone which means rock is oil-wet.

2.7.2.3 Flooding Performance Curve

The flooding performance is normally referred to the performance of waterflood. Water (brine) represents the displacing phase, whereas oil is displaced phase. In a strongly water-wet rock, water displaces oil by the imbibition process into small, medium, and large pores. After waterflood front passes, most of the remaining oil is immobile. Therefore, the addition oil recovery after the water breakthrough is small. Residual oil in this case can be found in two forms: 1) spherical globules in the center of large pores (blobs), and 2) larger patches of oil extending over many pores that are completely surrounded by water. Figure 2.14 shows the water displacement in strongly water-wet rock.

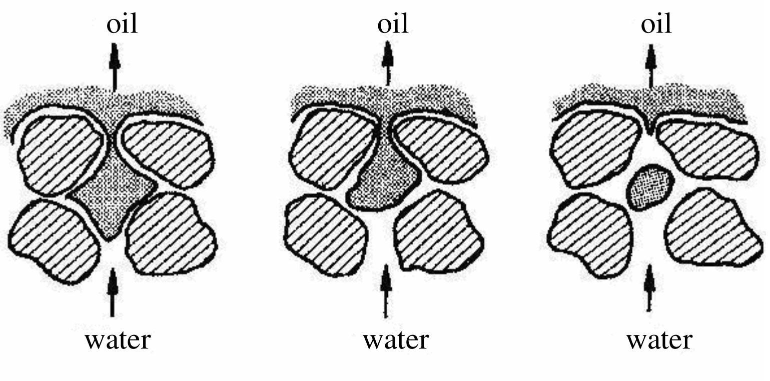


Fig. 2.14: Water displacing oil from a water-wet pore during waterflood process.

In a strongly oil-wet rock, the location of fluids is reversed from a water-wet rock. Oil is generally found in small pores and as thin films. Water is located in the centers of larger pores. Waterflood in an oil-wet rock is less efficient compared to a water-wet case. Water moves through the center of large pores, leaving a big amount of oil in smaller pores. After the warerflood front passes, oil can be found as a continuous film over pore surfaces or a larger-trapped pocket surrounded by water. The additional oil recovery proportionally increases with a number of pore volumes of injected water. Figure 2.15 depicts the steps of waterflood in a strongly oil-wet rock.

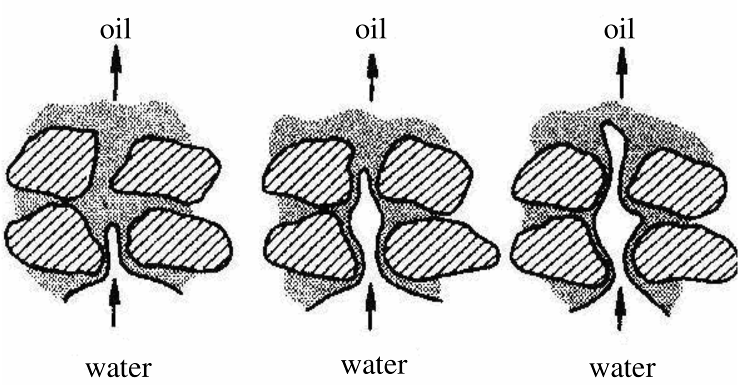


Fig. 2.15: Water displacing oil from an oil-wet pore during waterflood process.

The flooding efficiency curve is a plot between the recovery of displaced phase and the ratio of displacing to displaced phases. Generally, the curves are plotted under oil recovery and water-oil ratio (WOR) as x and y axis respectively. The difference of waterflood performance in oil- and water-rock is demonstrated in figure 2.16.

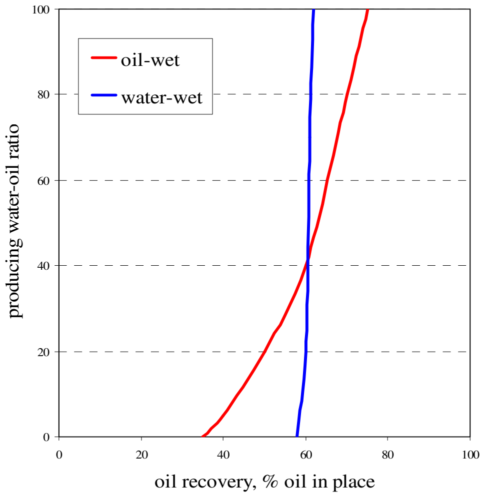


Fig. 2.16: Waterflood performance curve of water- and oil-wet rocks.

From the curves, the breakthrough of oil-wet rock is early (low oil recovery percent) and an additional oil is produced after a large number of water is injected. Differently, oil recovery at the breakthrough in water-wet rock is relatively high compared with that of oil-wet rock and no remarkable amount of oil is further produced.

Other petrophysical properties can also approximately indicate the wettability of rock sample such as imbibition test, microscope examination, and flotation test.

2.8 The Effect of Wettability on Water Injection Process

Wettability controls the location, flow, and distribution of fluids in the rock. Wettability directly affects waterflood behavior, relative permeability, capillary pressure, IWS, ROS, simulated tertiary recovery, and electrical properties. Water injection or waterflood is a frequently used secondary recovery method in which water is injected into the reservoir, displacing oil in front of it. Finally, oil is produced in the production well. Waterflood in different wettability system renders different results. The literatures of waterflood in two major wettability categories which are sub-divided in four systems are reviewed here.

2.8.1 Uniformly Wetted System

2.8.1.1 Water-Wet Systems

Considering a strongly water-wet rock at IWS, water, which is the wetting phase, occupies small pores and forms a thin layer over rock surfaces, whereas oil occupies the centers of large pores. During the horizontal waterflood at the moderate oil/water viscosity ratio, water moves through rock with a uniform flood front. Water imbibes oil from small, medium pores into large pores. So, only oil that moves in front of the flood front. After the waterflood front passes, no further oil or only a little amount of oil can be produced. This non-producible oil is left as small spherical globules in the centers of large pores or larger patches of oil extending over many pores that are completely surrounded by water. Because a little amount of oil is produced after the breakthrough, the ultimate oil recovery is independent from a number of injected water.

2.8.1.2 Oil-Wet Systems

In a strongly oil-wet rock, surfaces are preferentially adhered by oil. The location of fluids is reversed from a strongly water-wet rock; oil occupies small pores and covers rock skin as layers, whereas water occupies the centers of large pores. The waterflood in a strongly oil-wet system is much less efficient than a strongly water-wet case. During the waterflood, water forms continuous channels or fingers through the centers of large pores where water is located, and pushes oil in front of it. Most oil is left in small pores. As a number of injected water increases, water invades small and medium pores, pushing oil into larger pores and hence, the oil recovery slightly increases. Comparing a number of injected water from a strongly water-wet case, more water is required to be injected in a strongly oil-wet rock in order to recover a given amount of oil. The non-producible oil remains in small pores, as a continuous film over pore surface, and as larger pockets of oil trapped surrounded by water.

Figure 2.17 illustrates the waterflood performance in a strongly water- and an oil-wet rock. The water breakthrough is clearly noticed in a water-wet case which is the point at which the curve changes its tendency (around 1 PV of water injected). On the other hand, the breakthrough in an oil-wet case is not remarkable. The oil recovery increases proportionally with a number of further injected water and the ultimate ROS cannot be determined at low PV of injected water.

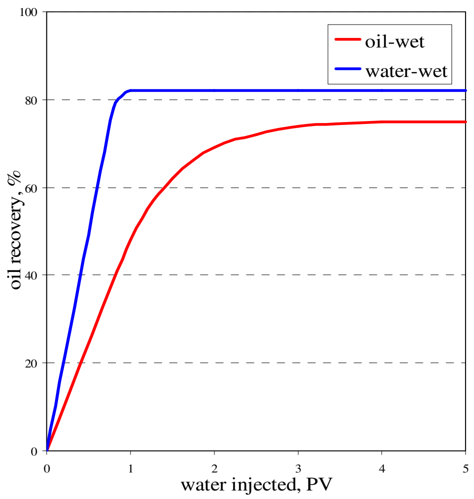


Fig. 2.17: Typical water flood performance in water- and oil-wet rock.

In a uniformly wet system, the ROS reaches the minimum value when the wettability of rock ranges from neutrally to weakly oil-wet because at this range capillary forces are small. ROS increases when rock becomes more water-wet because part of oil tends to be trapped as globules in larger pores. Similarly, the ROS increases as rock becomes strongly oil-wet because capillary forces trap oil in small pores.

2.8.2 Non-uniformly Wetted System

2.8.2.1 Mixed-Wet Systems

In a mixed-wet rock, large pores are occupied by oil that forms oil-wet paths, while smaller pores are occupied by water. These conditions represent the best aspects of water- and oil-wet system in waterflood behavior. The oil trapping in large pores as globules is reduced (since large pore is oil-wet) and since small pores are water-wet, there is not a presence of oil. Therefore, the ROS reaches very low value and the waterflood is very efficient.

2.8.2.2 Fractional-Wet Systems

The results from several experiments conducted with artificial fractional-wet samples have shown that the practical residual saturation of a fluid increases as the percent of sand grains wetted by that fluid increases. For example, the ROS increases as the fraction of oil-wet surface increases (oil-wet sand grains) while the residual water saturation decreases as the fraction of oil-wet sand increases. This result is similar to the change that occurs in a uniformly wetted system (when water-wet rock becomes more oil-wet). Thus, the preferential oil recovery is obtained when sample contains more water-wet sand grains as the water-wet condition is predominant. The waterflood behavior curves of a fractional-wet rock lie between the curves of 100% water-wet and 100% oil-wet sand packs. Relative permeability and capillary pressure are also varied with the ratio of water-wet and oil-wet sand grains.

CHAPTER 3

ENHANCED OIL RECOVERY, ALKALI FLOODING, AND RELAVANT RESEARCH

Enhanced oil recovery (EOR) is an oil recovery by means of injecting the materials that are absent in the reservoir (Lake, 1989). Initially, the reservoir is exploited by primary recovery, the recovery by natural drive mechanisms which are solution gas, water influx, gas cap drive, or gravity drainage. The secondary recovery generally refers to water or gas injection. Water injection or waterflood is simply performed by injecting water (normally refers to brine) into an injection well, sweeping oil forwardly into a production well. Gas injection is performed to maintain the reservoir pressure in order to prolong the production period. After the reservoir exploitation by primary and secondary recovery does not give an economical result, EOR is then considered as a solution.

3.1 Introduction to EOR

Nowadays, several EOR methods are performed according to the specific requirements of each reservoir. Commonly used EOR methods excluded alkali flooding is reviewed in this section. A brief concept of each flooding technique is explained.

3.1.1 Miscible Flooding

Miscible flooding is a recovery method by injecting a fluid that is miscible with reservoir fluids at the reservoir conditions (reservoir pressure and temperature) in order to improve the mobility reservoir fluid. Miscible flooding normally refers to gas or liquid petroleum gas (LPG) injection. The miscibility of fluids can be determined from the pseudo-ternary composition diagram (Clark *et al.,* 1958), representing the composition in percent of three components in the system. Figure 3.1 illustrates the pseudo-ternary phase diagram of hydrocarbon at fixed temperature and pressure.

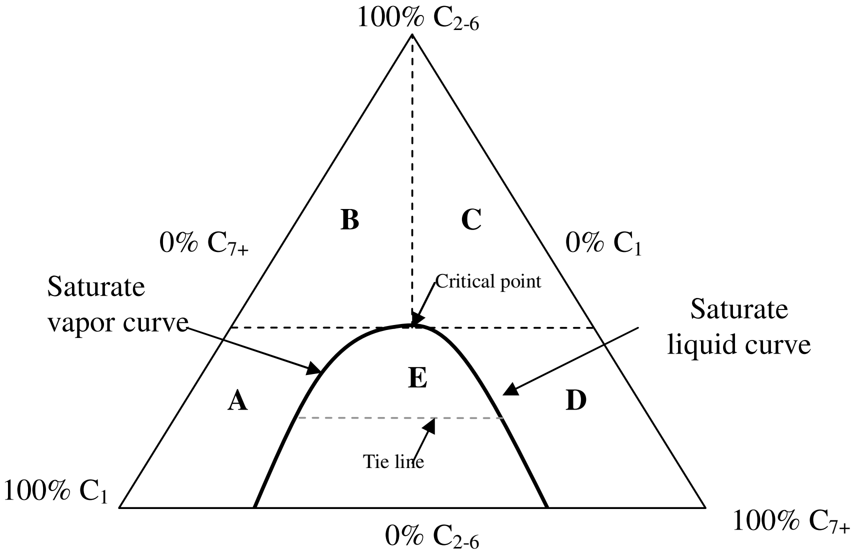


Fig. 3.1: Pseudo-ternary phase diagram of hydrocarbon.

From figure 3.1, the hydrocarbon system consists of methane (C_1), the intermediates (C_2-C_6), and heaver hydrocarbon than C_6 (C_{7+}). Any point in the area of triangle represents the composition of these three components. At the apex of each side, the composition is 100 percent for each component (pure component). The edge lines represent the systems without the component on the opposite side. For example, the line that links between C_1 and C_{7+} is the system without C_{2-6}. The region A represents the composition of all-gas phase, whereas region D is totally oil phase. The critical regions are represented by B and C in which is contained both of gas and liquid. In region B, the components are miscible with the mixtures in the dry-gas region while in region C are contained the mixtures that are miscible with the mixture in oil region. Region E is the zone where the compositions are immiscible. Tie lines terminate at the points represented a saturated gas and saturated oil which are in equilibrium. At the location where the saturated curve passes, the system is saturated. For example, over the saturate vapor curve, gas is saturated by oil vapor. Moving the composition from region A to the left (through C_{7+} apex) yields the appearance of the condensate and the system becomes two-phases. On the other hand, liquid in the region of two-phase becomes gas phase when the components pass the saturate vapor curve.

3.1.1.1 Carbon Dioxide Flooding

Carbon dioxide (CO_2) flooding is a good example for miscible flooding technique. Downhole pressure and temperature play major roles in carbon dioxide flooding because these variables control the miscibility of injected carbon dioxide in the reservoir. The reservoir candidate has to have reservoir temperature above the critical temperature of carbon dioxide ($31^{o}C$) (Gardner *et.al*., 1981) Thus, carbon dioxide can be formed only a single-phase fluid through out the flooding process.

Sources of carbon dioxide can be collected naturally and industrially. Carbon dioxide can be found in natural gas and it is needed to remove. Therefore this carbon dioxide can be sold for the carbon dioxide injection unit.

The most severe problem from the use of carbon dioxide injection is the corrosion. To prevent this corrosion problem, dehydration of carbon dioxide is necessary. Nowadays, pipeline, tubing, and pump system can be coated by inhibitors preventing corrosion from acid. Other problems can be caused by the use of carbon dioxide are the early breakthrough and viscous fingering effect (figure 3.2). Some methods are used to modify the mobility of carbon dioxide slug. One commonly used method is to alternate the carbon dioxide slug with the water slug (water alternated with gas or WAG) (Rowe *et al.,* 1981). This WAG method seems to work best in a non-strongly water-wet reservoir. Another method is to produce a CO_2-foam which has much higher effective viscosity than carbon dioxide and thus, the foam slug would tend to inhibit the viscous fingering.

Three restrictions for carbon dioxide flooding are noticed. First, the candidate reservoir should be located at the depth lower than 2500 ft without fractures in the reservoir in order to have an adequate pressure and temperature to create the miscibility. Second, oil gravity has to be higher than 27^{o}API in order to avoid the high miscibility pressure requirement. Third, the severe reservoir heterogeneity can cause the channeling and bypassing of injected gas. Therefore, the heterogeneity reservoir should be avoided by the use this technique.

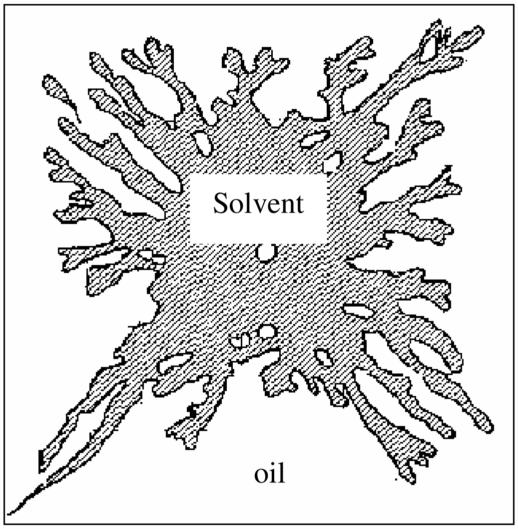


Fig.3.2: Swept zone at solvent breakthrough for a five-spot, showing a viscous fingering effect.

3.1.2 Immiscible Flooding

Immiscible flooding is the EOR technique to improve oil recovery by means of injecting fluid that is immiscible with the displaced phase. In this case, oil is displaced and the displacing phase is normally modified by some chemicals. Therefore, immiscible flooding is normally referred to the chemical injection. Most commonly used chemical injections are alkali, surfactant, and polymer injection. These chemical can be mixed together in order to yield a more-functional injected fluid. Foam and micellar are also the derived techniques by the modification of surfactant and polymer flooding, respectively. Alkali flooding is however not included in this section.

3.1.2.1 Surfactant Flooding

Surfactant flooding is the method to improve oil recovery by adding surfactant into an injected fluid. Surfactant drastically reduces the IFT between oil and aqueous phases, therefore; oil can be released as small droplets or emulsions and these particles are entrained with the injected phase. A typical surfactant monomer is composed of a non-polar portion (lypophile) and a polar portion (hydrophile). The entire monomer is sometimes called an amphiphile because of this dual nature.

Surfactant is classified into four groups depending on their containing polar. Figure 3.3 summarizes the classification of surfactants.

- Anionic surfactant. The anionic surfactant molecule is uncharged with an inorganic metal cation (usually sodium) associated with monomers. In the aqueous solution, the surfactant molecules ionize to free the cations and the anionic monomers Anionic surfactant is the most commonly used in surfactant flooding because they have the resistant to the retention time, stable, and relatively cheap compared with other types. However, this kind of surfactant is not recommended for the carbonate reservoir because the high depletion rate according to the positively-charged surface. The most common surfactants in this group are sulfonates, sulfates, carboxylates, and phosphates.

- Cationic surfactant. Cationic surfactant acts oppositely from anionic surfactant. The molecule is associated with inorganic anion to balance the charge and in the aqueous solution, the surfactant molecules ionize to free anions and the cationic monomers. Cationic surfactant is not widely used because they are highly adsorbed onto the rock surface especially sandstone surface and interstitial clays which are negatively charged. The examples of cationic surfactant are quaternary ammonium organics, pyrinum, and imidazolinium, piperidinium, and sulfononium compounds.

- Nonionic surfactant. Nonionic surfactants are widely used as surfactants and co surfactants. These surfactants do not form the ionic bonds but, when they are dissolved in aqueous solutions and then exhibit surfactant properties by electro negativity contrast between their constituents. Nonionic surfactants are much more tolerant from high salinity than anionic acid. The examples of non-ionic surfactants are alkyl-, alkyl-aryl-, aryl-, acryl-, acylamindo-, acyl-aminepolyglycol, and polyol ethers alkanoamides.

- Amphoteric surfactant. Amphoteric surfactant contains aspects of two or more of other classes. For example, an amphoteric may contain both an anionic group and a non polar group. These surfactants have not been used in oil recovery. The example of surfactant in this group is amino carboxylic acid.

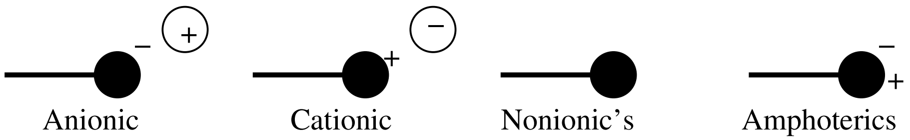


Fig. 3.3: Classification of surfactants.

Surfactant works in IFT reduction by sticking hydrophile in the aqueous phase and the lyphophile in the oil phase. Therefore, surfactant acts like a bridge between two phases. Surfactant drastically reduces the IFT between oil and aqueous phases in the low surfactant concentration range because monomers can move freely and most of them reach the interface and reduce IFT immediately. The presence of salt ions also drives the surfactant to the interface, thus; the IFT reduction is more effective. The IFT is reduced until the point at which is called "*Critical Micelle Concentration"* (CMC). At this point, surfactant monomers are getting crowded and start to rearrange themselves to form particles call "*aggregates"* or "*micelles"*. This rearrangement causes the reduction in efficiency of surfactant and as a consequence, the IFT is raised beyond the CMC. As the concentration of surfactant increases, the new phase appears. This phase appears as a film layer between oil and aqueous phase. This is caused by accumulation of the particles called "*swollen micelle"*. Swollen micelle can be generated in both water and aqueous phases by the association of oil or water droplets and some monomers of surfactant. This film layer is sometimes called "*middle-phase microemulsion"* (Lake, 1989) and this causes a great reduction of IFT at the high surfactant concentration. The low IFT condition which is a more favorable condition for surfactant flooding then normally appears twice for the use of any surfactant. The use of surfactant at CMC is more favorable because less quantity of surfactant is required to obtain an ultra-low IFT. However, the depletion of surfactant plays a major roll in the decision for surfactant concentration: in the reservoir with high surfactant depletion rate, a more quantity of surfactant is needed to be injected in order to keep the concentration at the optimal condition.

The reasons causing failure of surfactant flooding is the loss of surfactant during the retention in the reservoir. Surfactant is rapidly adsorbed onto the rock surface in case that the surface charge is opposite with the charge of ionized surfactant. For example, anionic surfactant can be depleted by the adsorption onto carbonate surface, whereas cationic surfactant is attracted by negative-charged sandstone surface. The precipitation of surfactant can occur in the presence of high concentration of divalent ions (calcium and magnesium ions). High reservoir temperature also causes the degradation of surfactant and as a consequence, surfactant flooding is ineffective. The use of high surfactant concentration is not recommended because high surfactant concentration facilitates the partitioning of surfactant in oil phase and this partially causes the surfactant depletion without the oil recovery improvement (Chan and Shah, 1980).

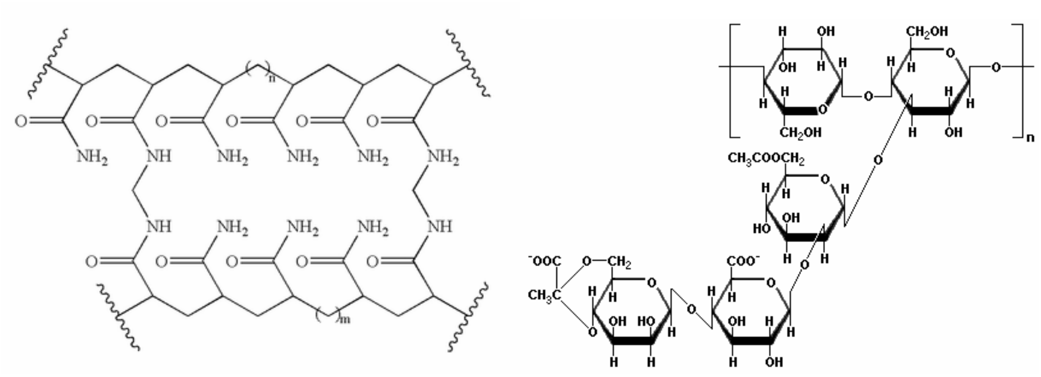
Thus, surfactant flooding is not recommended for the reservoir with high reservoir temperature (normally the temperature of 200^{o}C is believed to make surfactant degraded) (Wang *et al.,* 1982), reservoir containing the rock with the opposite charge of surfactant, and reservoir containing brine with high salinity and divalent ions.

3.1.2.2 Polymer Flooding

Polymer flooding is the EOR technique by the use of water-soluble polymers. These water-soluble polymers improve the sweep efficiency by reducing the mobility ratio at the flood front. Polymer is a chemical that is composed of a number of individual molecules that are attached in same manner (Donaldson, 1989). These units are usually associated in the pattern that repeats itself throughout the length of each polymer. These repeating units are called "*monomers*" and the polymer can be either a *"homopolymer"* (only one type of monomer) or a *"dimer"* (two types of polymer, etc). Another type of polymer called "*copolymer*" representing a polymer that joins two different monomers.

Polymer molecules are large and hence, the molecular weight of polymer is correspondingly high. These large molecules are soluble in water because of the hydrogen bonding between water molecule and the polymer's polar side chains. The commonly used polymers in EOR are 1) polyacrylamides (PAM): synthetic, usually anionic, dry powder, water solution, emulsion gel; 2) xanthan gum (XG): natural biopolymer, anionic, water solution, dry powder; 3) cellulosic's: semi-synthetic, nonionic or anionic, dry powder; and 4) polyacrylate copolymer (PAC): synthetic, anionic, dry powder, water solution.

Polyacrylamides and xanthan gum are most commonly used polymer in EOR because their stabilities and resistances. Polyacrylamides are synthetic polymers. The molecule of polyacrylamide creates a very strong hydrogen bond with water molecules when it is poured in water. Generally, polyacrylamides can be soluble in water at the highest concentration of 35 %w/w. The viscosity of polyacrylamide solution decreases as the degree of and water solubility increases. In another word, the solution becomes more viscous when polymer concentration is raised. Xanthan gum is a high-molecular-weight, natural carbohydrate. It is a polysaccharide manufactured by a bacterial fermentation process. The viscosity of xanthan gum decreases slightly when the temperature is raised. Therefore, this makes xanthan gum a preferred material in the EOR process. The molecular structures of polyacrylamide and xanthan gum are illustrated in figure 3.4.



a) Polyacrylamide

b) xanthan gum

Fig. 3.4: Molecular structure of commonly used polymers:
a) polyacrylamide and b) xanthan gum.

Both polyacrylamide and xanthan gum give high viscosities at relatively low concentrations. However, their viscosities are directly affected by salinity and the presence of divalent ions which cause the difficulty in polymer hydration. The use of dry polymer powder to prepare the polymer solution can causes the formation of *"fish-eyes"* (dry powder surrounded by wetted polymer). This formation occurs when the dry powders are rapidly mixed with water. Nowadays, polyacrylamide and xanthan gum can be supplied as liquid of water based-product which prevents the formation of undesired particles.

The viscosity of polymer solution decreases as temperature is raised. The loss of viscosity is reversible unless thermal degradation occurs. In the moderate reservoir temperature, the change of viscosity of polyacrylamide and xanthan gum is normally low.

A favorable polymer solution should have stabilities concerning mechanical, thermal, bacteriological, and chemical aspects. Polyacrylamides can be degraded by the mechanical sheer during the mixing step and moreover, it is less tolerant to the presence of divalent ions compared with xanthan gum. However, xanthan gum has also disadvantages. It is always recommended to use the bacterial protection in the use of xanthan gum as flooding material (Bragg *et al.,* 1983). Moreover, xanthan gum is not stable at the reservoir temperature above 110^{o}C (Ash *et al.,* 1983). Both polyacrylamide and xanthan gum can be protected from thermal degradation by the use of thermal stability compounds such as thioures, isopropyl alcohol, nitrogen purges, sulfates, propylene glycol, formal aldehyde, and acetone.

In mobility control process, polymer is normally used to alter the fractional flow characteristic of the water phase which is displacing oil. The function of polymer in EOR is to increase the viscosity of injected water and to reduce the relative permeability to water in the formation. If the flow of water in the porous media is decreased in relation to the flow of oil, then the oil's relative flow is improved.

Mobility (*M*) is a measure of a flow of fluid through a permeable formation. It is generally expressed as

$$M = k_r / \mu \tag{3.1}$$

where k_r and μ are relative permeability in mDarcy and viscosity in cPoise respectively.

Relative mobility (M_r) is the ratio of the displaced fluid's mobility to the mobility of displacing fluid. In the waterflood process, relative mobility is then expressed as

$$M_r = M_o / M_w \tag{3.2}$$

where M_o and M_w are mobility of oil and water respectively (Donaldson, 1989).

Polymer flooding is normally chosen for reservoir with high permeability channels, heterogeneous formations, and fractures. By the use of waterflood, brine which is displacing phase flows through high permeability channels and fractures, causing fingering viscous and as a consequence, the efficiency is low. Moreover, early breakthrough of injected water causes the problem to manage high quantity of water. Polymer solution increases the viscosity and hence, reduces the mobility of injected phase. The flood front is smoother and therefore, the sweep efficiency is improved. Figure 3.5a and b demonstrate the areal and vertical sweep efficiency improvement by the use of polymer respectively.

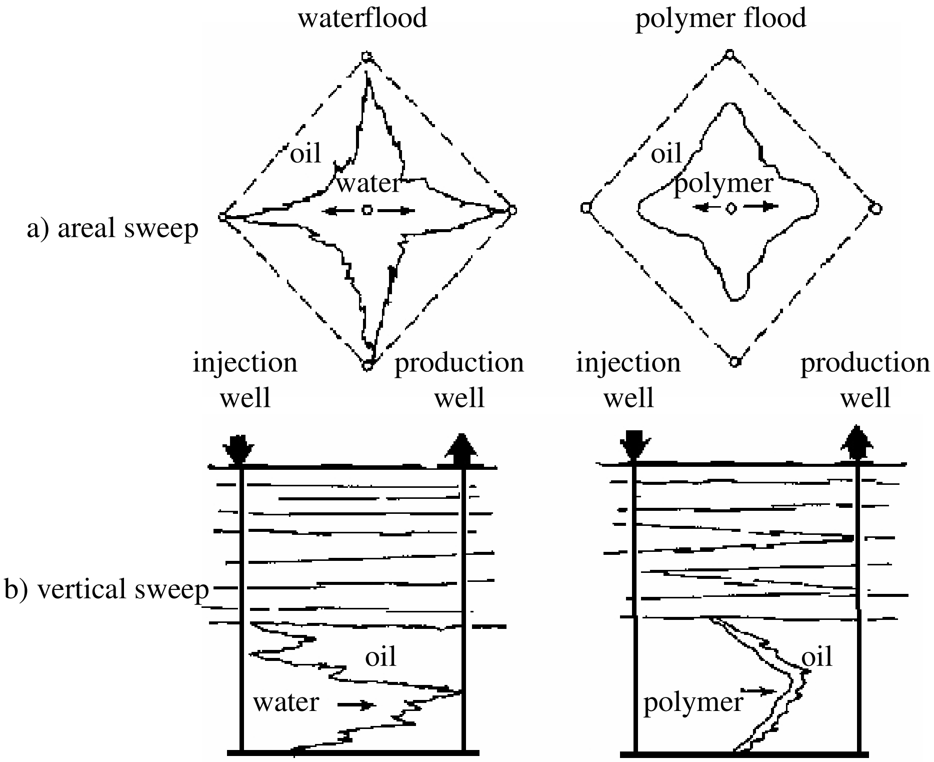


Fig. 3.5: The sweep efficiency by polymer flooding: a) areal and b) vertical.

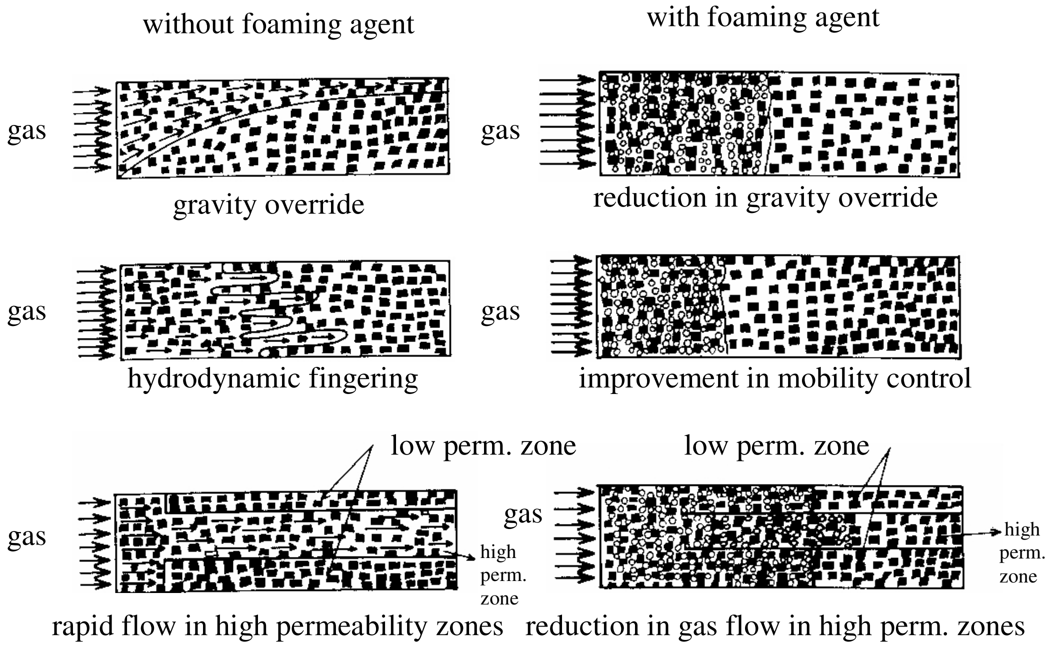
The candidate reservoirs for polymer flooding can be both sandstone and carbonate reservoirs. Sandstone is more favorable because most polymers are anionic and therefore, injected polymer will not be adsorbed onto the negatively-changed surface. The reservoir temperature less than 95^{o}C are preferred in order to avoid the polymer degradation. Thus, the depth of reservoir which correspondingly affects reservoir temperature should be less than 3000 m. Oil viscosity should be less than 100 cP because high polymer concentration is needed for high oil viscosity to achieve the desired mobility control. The presence of clay in the reservoir formation causes the loss of polymer. Therefore, reservoir containing high amount of clay should be avoided

3.1.2.3 Foam Flooding

Foam flooding is the modification of gas and surfactant flooding. In gas flooding, some problems are often reported especially in the horizontal flooding. The gravity causes the flow of gas at the top and the ride over liquid phase in the reservoir. This phenomenon is called *"gravity override"*. The second problem is the hydrodynamic fingering. The viscosities of injected gases are normally 10-100 times lower than the displaced-oil viscosity. Therefore, gas tends to flow through the high permeability channels at this unfavorable condition. In the presence of extremely high permeability zone or fractures, gas rapidly flow through this path and leave oil phase in the low permeability zone. Foam flooding is then created in order to solve these three problems by reducing the mobility of the injection gas. Figure 3.6 summarizes the improvement of foam flooding compared with gas flooding.

Foam is a relatively low-density material which can easily overcome gravitational effects and can pass through most of the heterogeneous reservoirs. Moreover, foam viscosity is greater than that of its components. In order to generate foam, a proper size of surfactant slug is injected in the reservoir formation. Gas or steam is consecutively injected at the optimal pressure to create a stable foam slug.

For the heavy oil reservoir, surfactant and steam are injected together. The ability of surfactant to generate foam increases as temperature is raised, whereas the stability decreases with an increase of temperature (Sharma *et al*., 1984). Most of nonionic surfactants cannot produce foam at the temperature above 100°C (Elson and Marsden, 1978). At a minimum steamflood temperature (177°C) the half life (time required for half of the surfactant to decompose) for most stable petroleum sulfonates (anionic surfactant), was about 11 days (Handy, 1981). The presence of salt promotes the decomposition of surfactant at high temperature. The precipitation of surfactant can occur at high temperature in sandstone reservoir (Celik *et al.*, 1979) which is caused by the interaction of surfactant and minerals in rock formation. As temperature is raised, the solubility of divalent ions from rock formation increases and this causes the precipitation with the nonionic surfactant (Reed, 1980). The steam foams are more effective in heavy oil recovery compared with air foams because steam foams effectively reduces oil viscosity and it creates a more stable foam compared with foam from air injection. In the light oil reservoir, the combination of surfactant and carbon dioxide is recommended. Anionic surfactants are widely used to improve the carbon dioxide flooding.



gravity override

reduction in gravity override

hydrodynamic fingering

improvement in mobility control

rapid flow in high permeability zones

reduction in gas flow in high perm. zones

Fig. 3.6: Comparison of flow effects between gas and foam flooding.

The restriction of foam flooding is similar to that of surfactant flooding. The loss of surfactant can occur during the flooding process by the adsorption onto rock surface, the precipitation with divalent ions, the degradation by high temperature, and the partitioning in residual oil phase. The loss from adsorption by rock surface can be avoided by choosing the same ionized charge regarding the surface charge of reservoir rock. For example, anionic surfactant is recommended for sandstone reservoir, whereas cationic is more favorable for carbonate reservoir.

3.1.3 Thermal Flooding

Thermal flooding is the technique to improve oil recovery by means of heat carriers. The most commonly used method is steam flooding because steam, which is a vapor form of water, can be simply created. Heat is transferred from super heated steams to reservoir oil and hence, the viscosity of oil is obviously reduced. Thus, less viscous oil can flow readily to the production well (Donaldson, 1989). Moreover, thermal flooding also improves oil recovery by reversing fluid-rock properties to a more favorable condition. In-situ combustion is also another thermal flooding technology and it is also included in this section.

3.1.3.1 Steam Flooding

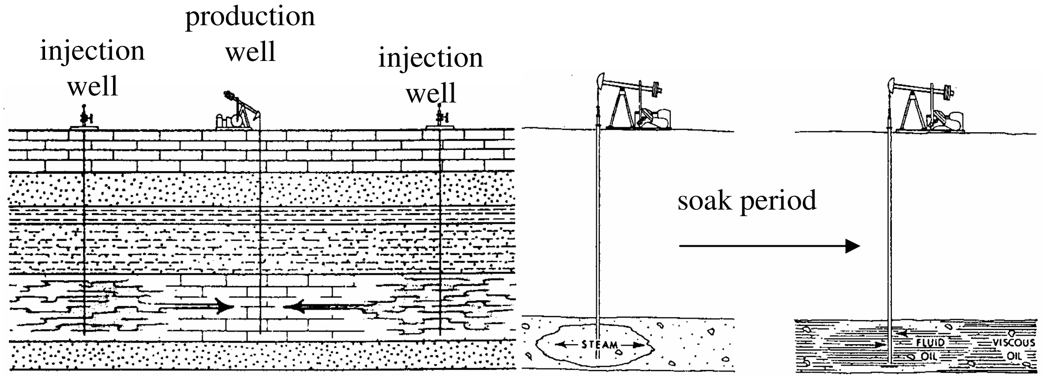
Steam is created at the surface at super heated condition (higher temperature than its boiling point) and injected to the reservoir formation. Steam injection can be accomplished continuously which is called *"steam drive"* or *"steam flooding"* (figure 3.7a) or can be injected cyclically. A cyclic steam injection is also called *"steam soak"* or *"huff and puff"* (figure 3.7b). In one cycle, steam is injected, soaked for a period, and oil is produced into the same well (steam injection well and oil production well) (Hyne, 1991).

Steam increases oil recovery by: 1) reducing oil viscosity, allowing oil to flow readily, 2) reducing residual oil saturation (ROS) and improving relative permeability to oil (k_{ro}), 3) improving sweep efficiency, 4) increasing the formation volume factor of oil (B_o), 5) vaporizing and distilling the condensable hydrocarbon, and 6) providing gas drive mechanism (Gates and Ramey, 1958). When steam is injected into the reservoir, it creates three distinct flow regimes which are

- Steam zone. In the steam zone, steam distillates the downhole hydrocarbon and as a consequence, light ends vaporize and heavy oil is left in the fluid phase. The vaporized-light compounds then flow ahead.

- Hot water zone. After steam losses the latent heat during hydrocarbon distillation and vaporization, it changes the phase to liquid at latent temperature. Plenty of viscous oil can be recovered in this zone by heat exchanging which consecutively causes the reduction of viscosity of oil and then oil can readily flow.

- Cold water zone. After heat exchanging with formation fluids, hot water loses its heat and causes the drop of temperature. Eventually, the temperature of this condensed water reaches to the reservoir temperature and the efficiency of oil recovery turns back to that of oil recovery by the normal waterflood.



a) Steam flooding

b) cyclic steam injection

Figure 3.7: Steam flooding: a) continuous steam injection and b) cyclic steam injection or huff and puff.

The restriction of steam flooding is primarily concerned the reservoir depth. The depth of reservoir affects reservoir pressure and temperature. As reservoir pressure increases, the super heated steam needs to be prepared at higher temperature in order to maintain the heat properties. Therefore, shallow depth is preferable because the reservoir pressure is correspondingly low. The depth of 120-1500 m. is proved to suit the steam flooding and steam temperature of 150-200°C is considered optimum. The viscosity of reservoir oil can be very high but not exceeds 4000 cP (Donaldson, 1989). A higher viscosity, a higher steam temperature is required.

3.1.3.2 Fire Flooding or In-Situ Combustion Technology

Fire flooding or in-situ combustion has been known since 1888. This EOR technique can be applied to a wide range or reservoir characteristics. Fire flooding is initially accomplished by creating the air relative permeability into the reservoir formation. In the reservoir with an absence of gas, high air injection pressure is required and hence, the process needs high compressor pressure. Practically, air injection rate is around 1.5-9.0 m^3/hr-m^2 (Earlougher *et.al.*, 1970). Basically, the combustion of crude oil occurs in gas phase. Light ends in crude oil vaporize and mix with air in gas phase and consecutively, the combustion occurs when the ratio of light ends vapor and air is in the range of flammability and there is a presence of ignition. The ignition can occur spontaneously after a few days of gas injection. However, in order to accelerate the spontaneous ignition (to reduce the ignition time); air is reheated before it is injected into the reservoir formation. Spontaneous ignition in the reservoir generally occurs when the temperature in gas phase reaches 55-60^{o}C. Some additive can be injected with air, such as reactive crude oil or super heated steam, in order to decrease the ignition time. In some cases, the spontaneous ignition cannot be conducted. Thus, the artificial ignition is chosen. After the air injection, the ignition is carried out by the set of downhole ignition set containing gas burner, electric heater, and catalytic igniter (Aldea and Petcovici, 1976).

The process of in-situ combustion can be divided in two types: forward and reverse combustion. Basically, air is injected into an ignition well. The ignition creates fire from the ignition well and the fire front moves forward to the production well. In the forward combustion, air is kept injected into the ignition well and the fire front keeps moving forward to the production well. On the other hand, the injection in ignition well is stopped after fire front moves for a period in the reverse combustion case. Air is injected from the adjacent well in the direction to the ignition well and the fire front moves backward.

Considering forward combustion case which is more commonly used, the flow regimes can be classified as several zones: 1) Burned region, 2) Burning front or fire front, 3) hot water zone, 4) light ends hydrocarbon, 5) oil bank zone. Figure 3.8 shows the flow regimes in a forward combustion case.

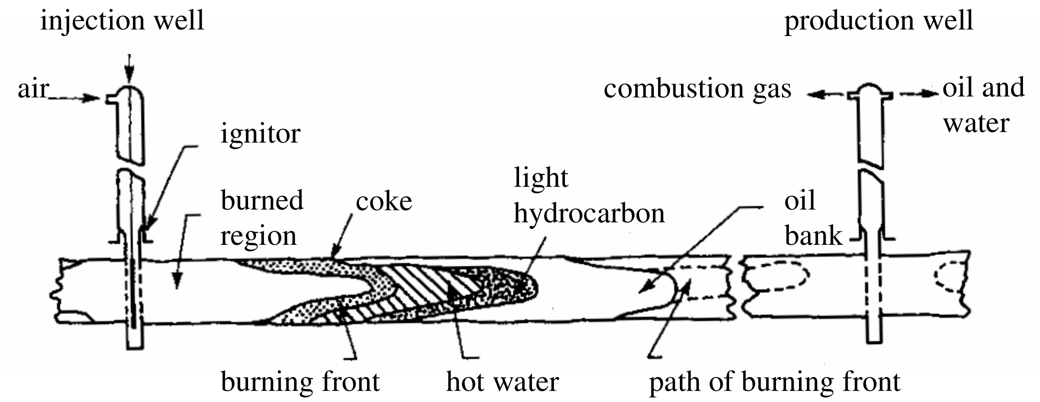


Fig. 3.8: Flow regimes in forward combustion case.

The breakthrough of fire front or combustion front at the production well can be recognized by the increment of gas production and oxygen content. The temperature of produced fluid also increases rapidly and moreover, the pH of produced water sharply decreases (acid condition) because of the presence of iron and sulfate ions.

In-situ combustion can be applied with reservoirs with the wide range of reservoir characteristic. However, some restrictions are defined. In order to create the relative permeability to air, reservoir gas is needed to be substituted by the injected air and hence, the reservoir should have already gas saturation. In the oil reservoir without the presence of gas phase, high pressure of injected gas is required.

Comparing fire flooding to steam flooding, the advantages obtained from fire flooding are that it can be utilized in thick reservoir and the long distance between injection and production well does not cause problem concerning heat loss. However, fire flooding still has several disadvantages. High cost of instrument installation is primarily considered as a major drawback. The vertical sweep efficiency is quite poor when it is applied with thick reservoir. Moreover, the use of high pressure during air injection can be risk for the explosion of compressor.

3.1.4 Microbial Flooding

Microbial flooding is the EOR method by means of injecting microorganisms, consecutively; these microorganisms metabolizes by using the petroleum crude as a raw material to produce the biochemical products. These biochemical products then improve the oil recovery by several mechanisms. The EOR process my microbial flooding is sometimes called *"MEOR"*. Widely used microorganisms are bacterium which can be generally classified as *"aerobe"* and *"anaerobe"*. Aerobe is a bacterium that needs to utilize oxygen for the metabolism, whereas anaerobe can consume other materials such as carbon dioxide instead of oxygen. However, some anaerobes cannot sustain the environment containing oxygen. The presence of few quantity of oxygen can be toxic to anaerobe because they do not have any proper enzyme. Bacterium can also grow rapidly in the optimum condition concerning temperature, pressure, salt concentration, pH and the presence of some essential chemicals for the metabolism (nitrogen, sulfate, and some minerals).

Bacterium normally has high growth rate as the temperature is raised. However, at too high temperature, the increase of temperature suppresses the growth rate and eventually the enzymes of microorganism are denaturized. Naturally, the temperature above 70°C can denaturize the enzymes of microorganisms. A few enzymes of thermophilic microbe can tolerate the temperature up too 100°C (Moses and Springham, 1982). High pressure inhibits the denaturization of some enzymes. Therefore, high reservoir pressure is preferable. High salinity is a more favorable condition for MEOR because this condition prevents the dehydration of microorganism. The presence of oxygen in the reservoir formation indicates the type of used bacterium in MEOR.

The main product from metabolism of both aerobic and anaerobic bacteria is carbon dioxide. The produced carbon dioxide improves the oil recovery by increasing the mobility of viscous reservoir oil. In the anaerobic metabolism by anaerobe, other products are produced. For example, the metabolism using sugar as the material, acid, alcohol, ketone and aldehyde, which can be solvent for reservoir oil, are produced. The extracellular products of metabolism may be extracted from cultivation at the surface and solutions of these materials may be injected into the petroleum reservoir to aid in oil recovery.

The main problem by the use of MEOR is that microbes can grow rapidly. Consequently, some of them can produce radical that can be toxic. For example, some anaerobes can consume inorganic and organic sulfate and produce hydrogen sulfide, consecutively; this gas causes the hydro sulfuric acid which is corrosive and harmful for pipeline and tubing system. Some bacterium form slime which will adhere to each other, forming a large mass. Slime can also adhere on the walls of pores, causing severe problem in core plugging.

Temperature is primary considered a restriction for MEOR. The reservoir with extremely high temperature can cause the denaturization of enzymes of microbes. The presence of some chemicals in reservoir formation is also important for the surviving of the microorganisms. On the other hand, in the proper condition, microorganisms can grow rapidly and hence, biocides are required to be injected to control the indigenous microbes. Some examples of these biocides include: formaldehyde, benzene, toluene, and several quaternary ammoniums.

3.2 Alkali Flooding

3.2.1 Introduction

Alkali substances have an ability to increase the pH of an injected slug. These chemicals are mostly inexpensive. The most commonly used alkali substances are sodium carbonate, sodium silicate, sodium hydroxide, and potassium hydroxide. The alkali flooding has been initially investigated in 1917. The alkali substances were injected to react with the acidic compounds in oil phase in order to create the in-situ surfactants. Therefore, flooding can be conducted at low IFT condition. Nowadays, it also has been proved that alkali substances also create the emulsification between oil and water phases, solubilize the rigid interfacial film which obstructs the in-situ surfactant, and reverse the rock wettability to a more favorable condition. The alkali flooding is relatively simple compared with other chemical flooding. However, the alkali flooding has also some restrictions and therefore, the confirmation from laboratory test is always required before a real application.

3.2.2 Theory

Sodium hydroxide (NaOH) is the most commonly used alkali substance. It has shown the highest efficiency among other alkali substances such as sodium orthosilicate ($2Na_2O \cdot SiO_2$), sodium carbonate (Na_2CO_3), ammonium hydroxide (NH_4OH), polyphosphate and hydroxylamine (NH_2OH).

Alkali is normally added into the injected brine in the tertially recovery. During the primary recovery, some parts of oil are trapped in the reservoir formation. Secondary recovery by waterflood is attempted to provide pressure energy to overcome the capillary force that entraps oil. However, some reservoir rock can be strongly-oil wet because the interaction between different charges, resulting in very strong force between adsorbed compounds and rock surface. The waterflood is then not adequate to overcome this entrapment force. Alkali substances have several actions to improve the oil recovery when they are injected into the reservoir formation. The most noticed mechanisms during the displacement by alkali solution are:

- To lower IFT by acid-base interaction. The injected alkali reacts with acid in oil phase to form the in-situ surfactant at the interface and causes spontaneous emulsification.

- To react with rock formation and consecutively the wettability characteristic is reversed to a more favorable condition for waterflood process.

The IFT at the interface is normally reduced to the lowest value when alkali concentration is at the optimal point. Several investigators have suggested the optimal concentration range for sodium hydroxide at about 0.01 – 0.05 molar and the optimal pH value around 12.5. The reduction of IFT results in the increment of mobility ratio. Lowering IFT is responsible for the emulsification: oil-in-water emulsion is produced and this results in the reduction of water mobility during displacement. Therefore, the sweep efficiency is improved. However, there are two mechanisms occurring after the emulsification step.

- Emulsification and entrainment. Mobilized oil is emulsified and entrained into the flowing alkali. By this combination, fine emulsion is produced. The stability of fine emulsion also depends on alkali concentration and pH value of the injected alkali. The oil improvement by these mechanisms is more preferential at lower production rate because high injection rate can leave some parts of oil behide the flood front. Low alkali concentration is also found to be more favorable to create the entrainment of the emulsion.

- Emulsification and entrapment. Emulsified oil is trapped again in the downstream in porous media at the pore throats. This causes the reduction of injected aqueous phase and hence, increases the displacement efficiency and reduces the viscous fingering.

The wettability reversal is also primarily considered as a function obtained from the used of alkali substances. Naturally, heavy components in crude oil are believed to cause the wettability alteration from water-wet to oil-wet (from favorable to unfavorable direction). These heavy components are adsorbed onto the rock surface, causing in the discontinuity of non-wetting residual oil phase and the reduction of capillary pressure that capture oil. In wettability literatures, it is known that wettability is strongly affected by the pH of aqueous solution. This pH-sensitively-changeable feature of alkali solution is the aspect that superiors surfactant substances.

Alkali substances also solubilize the rigid interfacial film. In the reservoir oil containing resins and asphaltenes, the insoluble interfacial film appears at the interface and this film obstructs the interfacial reaction (Castor *et.al.,* 1979). The presence of alkali can redissolve these materials into the oil phase and hence, the in-situ surfactant can be produced by the in-situ saponification reaction at the interface.

3.2.3 General Considerations

In order to pick up alkali flooding as the EOR technique to exploit the reservoir, several aspects have to be considered before the laboratory test.

3.2.3.1 Crude Oil Properties

Crude oil components are directly responsible for the IFT reduction. Therefore, crude oil must contain materials that can create surface active agent in the presence of alkali substances. In general, crude oil components which are essential for IFT reduction are carboxylic acids, carboxyphenols, porphyrins, and asphaltenes. However, carboxylic acid is considered as a major part of the IFT-reduction-potential material in crude oil. It is recommended that crude oil must contain acid at least 0.5 acid number or greater in order to create the in-situ surfactant.

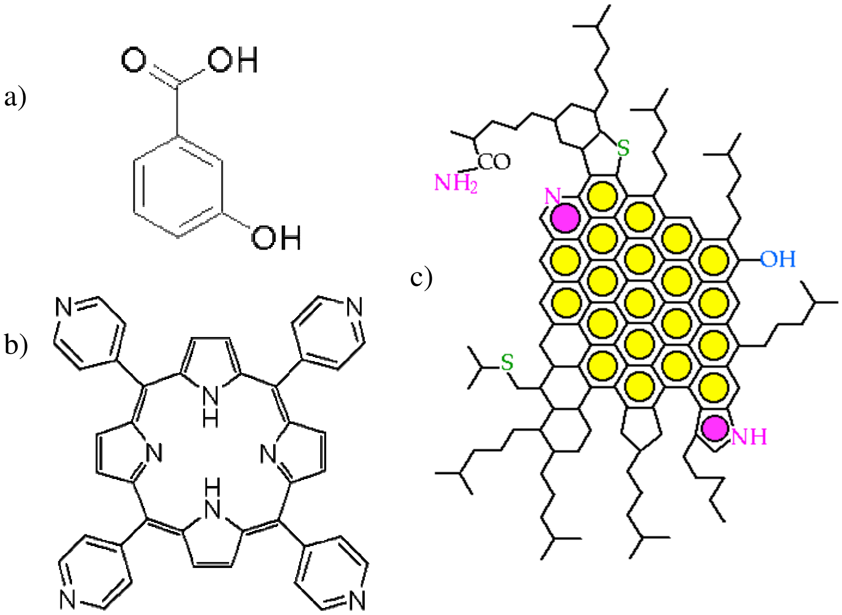


Fig. 3.9: Molecular structure of complex-wettability-induced material: a) carboxyphenol, b) porphyrin, and c) asphaltene.

3.2.3.2 Alkali Consumption

Alkali consumption is one of the most critical design parameters in alkali flooding. The loss of alkali during alkali flooding is responsible by the reactions with fluids and rock. However, it is the most significant the loss of alkali by adsorption with rock minerals. The reservoir containing high clays, tends to consume more alkali especially in case that the retention time of alkali slug increases. Nevertheless, alkali consumption is also responsible for wettability reversal of rock surface to a more favorable condition (Goyal, 1982).

Alkali consumption rate by rock increases as temperature is raised and decreases with the increase of salt concentration. The presence of anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$) causes the alkali loss. These compounds react with alkali solution to form calcium hydroxide which can be dissolved in aqueous phase and does not help in IFT reduction (calcium surfactants are not effective in IFT reduction). The reaction between anhydrite and sodium hydroxide is

$$CaSO_4\,(s) + 2NaOH \rightarrow Ca(OH)_2\,(s) + Na_2SO_4 \qquad (3.3).$$

This reaction is irreversible, therefore; the alkali is permanently consumed. Another irreversible alkali consumption reaction is the dissolution of siliceous material. The dissolution reaction between siliceous material and alkali substance can be depressed as

$$SiO_2\,(s) + H_2O \rightarrow Si(OH)_4\,(s) \qquad (3.4).$$

Clays and fines, which are relatively large surface area materials, can also consume high quantity of alkali substance and cause the pore plugging by clay swelling and migration of fines (Radke and Somerton, 1979). However, the permeability damage by clay swelling and fine migration from the alkali consumption is not considered a serious problem in general.

3.2.3.3 pH of Alkali Solution

At low pH value, the in-situ surfactant is less produced and hence, less amount of oil is mobilized. Therefore, alkali flooding should be conducted at a high pH value to create a high amount of in-situ soap. High pH value also affects the reversal of surface charge of reservoir rock surface especially in the carbonate reservoir which requires the pH value above 9 in order to reverse the surface charge. Under the pH value of 9, carbonate surface is positively charged (described in chapter 2, section 2.1.2) and thus, the surface tends to adsorb negatively-charged acid compounds and this results in the oil entrapment. Above the pH value of 9, hydroxide ions fill the carbonate surface the negative charges, rendering the repulsive force to adsorbed materials and consecutively, oil is released from the entrapment. High pH value is then more preferential in alkali flooding. A pH value of 12.5 or more is recommended.

3.2.3.4 Sodium Ion and Sodium Chloride

The presence of sodium chloride promotes the reduction of alkali concentration to achieve the low IFT. Sodium chloride ionizes in aqueous phase, becoming sodium and chloride ions. These ions supplied electrolytic charges in bulk solution and hence, create the repulsive force with the opposite charges from other compounds. Hydroxide and anionic acid (repulse with sodium ions) then can reach the interface easily. Sodium chloride thus is used to promote the ultra-low IFT condition by lower the bulk alkali concentration. However, too high concentration of sodium ion causes disadvantage because sodium ions deactivate the soap formation at the interface and this results in the increment of IFT (Chan and Yen, 1981).

3.2.3.5 Divalent Ions

Magnesium and calcium ions in formation brine interact with anionic surfactant generated by alkali-acid reaction, rendering the surfactant water-insoluble and eventually, the insoluble soap precipitates onto rock surface. The precipitation of insoluble soap causes the delay in hydroxide transportation. However, this precipitation sometimes reverses the flow and results in oil improvement (Mayer *et al.,* 1983). The reduction of divalent ion concentration results in the increment of surfactant activity. Conclusively, the effect of divalent ions depends on: 1) ion exchange isotherm, 2) divalent ion concentration, 3) pH and salinity, 4) solubility of precipitated salt.

3.2.4 Reservoir Selection

3.2.4.1 Reservoir Oil

The reservoir at least has to have residual oil saturation more than 40% (Mungan, 1981). Higher residual oil saturation is more preferential. The viscosity of reservoir oil should not exceed 100 cP and the oil gravity should be in the range of 13-35 ^{o}API. Reservoir oil must contain natural acid (carboxylic) at least 0.5 acid number in order to produce the in-situ surfactant by the reaction of injected alkali substance. Oil with dissolved gas such has hydrogen sulfide and carbon dioxide should be avoided by alkali flooding because these gases can consume high quantity of alkali (Wilson, 1976). Oil with high compressibility (containing high quantity of dissolved gas) is not preferential.

3.2.4.2 Formation Water

The connate water saturation should be less than 50% and the salinity of formation water should be in the range of optimal salinity. The salinity of 200,000 ppm (20% w/w) is the upper limit for alkali flooding. The presence of calcium and magnesium ions results in IFT increment. Some acidic ions such as hydrogen carbonate ion, sulfate ion, chloride ion, and hydrogen sulfide causes the alkali consumption. Therefore, high acidic compounds in formation should be avoided.

3.2.4.3 Rock Mineralogy

The presence of anhydrite or gypsum is undesirable because they cause the production of calcium surfactants that are not effective in IFT reduction. Carbonate rock enriched in divalent ions are unsuited because these ions can be dissolved in aqueous phase and cause in the insolubility of in-situ surfactant. This makes sandstone reservoir a more suitable as a candidate. The presence of clay minerals can cause in clay swelling which is undesirable.

3.2.4.4 Reservoir Character

The reservoir formation must not be very heterogeneous. The presence of fractures and thief zone is undesirable. The net pay zone should not be so small.

Connecting with large aquifer is not suitable. The reservoir temperature less than 95^{o}C are recommended.

3.2.5 Laboratory Test for Alkali Flooding

Some experiments are recommended before the real application of alkali flooding. This section reviews several experiments recommended by Donaldson et al. (1985,1989).

- Acid number measurement. As described before in previous section, oil must contain acid at least 0.5 acid number. The simple method to measure the amount of acid in crude oil is color titration by using potassium hydroxide (KOH) as a titrant. The gram of postassium hydroxide needed to neutralize crude oil is the concentration of that correspondingly crude, expressing in acid number.

- IFT measurement. IFT measurement is performed to find the optimal concentration of alkali substance that yields an ultra-low IFT condition. IFT can be measured as a function of alkali concentration. Moreover, the presences of other chemicals are also recommended to be included in this test such as salinity and divalent ions.

- Wettability reversal measurement. The wettability reversal can be studied from the imbibition test. In some researches, the wettability index can be calculated (describe in chapter2, section 2.7). Normally, the sample is aged in alkali solution for 200 hours in order to allow the rock surface to reach the wettability equilibrium before the wettability index measurement after the treatment by alkali substances.

- Emulsion formation. In the case of continuous flow, the emulsification and entrainment or entrapment should form. Therefore, the alkali concentration that allows the stability of emulsion is preferential. The test is simply performed by shaking the reservoir crude with alkali solution at different concentration. The viscosity of emulsion is measured and the emulsion is aged in order to observe the stability as time increases.

- Brine-crude oil interaction. In the presence of resins and asphaltenes in crude oil, the formation of rigid film can occur at the interface. The brine-crude oil interaction test is performed by measure IFT value at the different alkali concentration.

- Alkali consumption test (static test). As alkali consumption can deplete the alkali substance during the flood process and causes the ineffectiveness. The optimal concentration of alkali concerning the adsorbed amount by rock formation is compulsorily determined. This test is performed by grinding rock formation and soaks it in the known concentration of alkali substance. However, the obtained alkali consumption by this static test expresses the highest number of alkali quantity in order to complete the reaction with all amounts of rock minerals. In real, the alkali consumption also depends on the pore geometry and the formation structure. Therefore, the dynamic alkali consumption is more realistic.

- Displacement test. The displacement test is performed in the core flood cell. The test is run comparing with the conventionally waterflood in order to determine the increment of oil production by alkali flooding. The dynamic consumption can be determined by analyzing the effluent of core flood. Moreover, the core flood test is also run to determine the chemical requirement, acquaintance with operating problem, injectivity and feasibility, increment of oil recovery, residual oil, production rate, and economics.

Alkali flooding is relatively cheap compared with other EOR techniques. It is also simple and it compromises a good result (when it is chosen for a proper reservoir). The mechanisms of oil improvement by alkali flooding are fairly too well understood. Hence, it is not complicated to design proper applications for the alkali flooding. The alkali consumption is a major drawback and can be very restricted for some reservoirs. Several tests previously listed are strictly recommended to be conducted before the real application in order to avoid the undesirable results.

3.3 Relevant Research

In the last decade, many researches concerning alkali flooding have been developed. Part of them is dedicated for carbonate reservoir which was not recommended as a candidate for alkali flooding. Carbonate reservoirs were not proper candidates because of the enrichment in calcium and magnesium ions which can dissolve into aqueous phase during the fluid displacement and causes the increment of IFT value. However, the presence of these divalent ions does not have direct effect to the wettabiliy reversal function of alkali solution. Some investigators have proved that dolomites and limestones do not cause the severe problems by alkali flooding and moreover, high oil recovery can be obtained. In this section, researches concerning the EOR by alkali substance, wettability reversal in carbonate reservoir and related topics are reviewed.

Al-Hashim et al. (1996) summarized the use of alkali-surfactant-polymer flooding in Saudi Arabian carbonate reservoir. A combination of sodium hydrogen carbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) represents alkali substance. They observed that, the loss of surfactant is significantly reduced in the presence of alkali. This made the process very desirable and cost-effective. They found that divalent ions in brine phase caused the high rate of adsorption of surfactant onto rock surface. The concentration of surfactant that yielded the highest recovery appeared at its CMC where it is the point at which the lowest IFT can be obtained. The application of polymer with alkali-surfactant slug rendered some drawbacks. Polymer caused the interaction with surfactant and thus, the efficiency of surfactant in IFT reduction was reduced. Moreover, the used polymer did not have thermal stability and the thermal degradation occurred at the reservoir temperature.

The authors also recommended using sodium carbonate instead of sodium hydroxide in order to avoid the high rate of alkali consumption. Soften brine is always recommended for the chemical slug to avoid the interaction with divalent ions that can cause several severe problems.

Madsen and Lind (1997) studied the adsorption of carboxylic acid onto the reservoir minerals for both sandstone and carbonate. In this study, the term called partition coefficient played a major role in acid adsorption in sandstone and carbonate surface. In the sandstone reservoir with sufficient water saturation, short chain carboxylic acid tended to dissolve in water phase. And since sandstone surface is generally adhered by water, the short chain acid can be linked with sandstone surface by divalent ions. On the other hand, the long-chain carboxylic acid remained in oil phase. In the case where water film adhering on carbonate surface was interrupted from instability condition, the long-chain carboxylic acid in oil phase can be directly adsorbed onto the carbonate surface. Therefore, the oil-wet conditions in sandstone and carbonate surfaces were influenced by different materials.

Zou et al. (2000) investigated chemical interactions between brine and dolomite. Dolomite, which primarily contains calcium magnesium carbonate ($CaMg(CO_3)_2$), can naturally provide the pH build up by dissolution in water. As a salt of weak acid, dolomite dissolves in water by the mechanism

$$CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \qquad (3.5)$$

The products from dissolution form a CO_3^{2-}/HCO_3^{-} buffer system in the vicinity of the fluid-rock interface and control the pH of the solution. When the retention time increases, the buffer system controls the pH value and pH eventually reaches the equilibrium.

In this research, they found that the pH of effluent reached the value of 10 at equilibrium when the pH of injection brine ranges 4-10. When the pH of injection brine was greater than 10, the pH of effluent proportionally increased. The pH above 9 is enough to reverse the surface charge of carbonate from negative to positive (p.z.c). Therefore, wettability reversal can be spontaneously created when brine was injected (pH around 7) and retention time (aging) was enough to create the buffer system in the formation brine fluid. However, the dissolution was also controlled by the quantity of divalent ions in brine phase. These divalent ions depressed the dissolution process and hence, high concentration of divalent ions prohibited the spontaneous wettability reversal.

Berger and Lee (2002) investigated the alkali-surfactant-polymer flooding in sandstone and limestone. They attempted to create a new type of surfactant which was high tolerant to the divalent ions in brine phase. Therefore, normal brine can be used without the divalent ions removal. In the carbonate reservoir, the alkali substance was preferentially injected in order to reverse the surface charge and this resulted in reduction of surfactant adsorption. The ultra-low IFT was not required in carbonate sample, where as in sandstone ultra-low IFT was compulsory.

Hirasaki and Zhang (2004) studied the surface chemistry of fractured, oil-wet, carbonate formation. The oil recovery in fractured reservoir was often dependant from spontaneous imbibition. But the spontaneous imbibition in oil-wet carbonate surface was insignificant. Hirasaki and Zhang then attempted to reverse the wettability of carbonate rock to a more favorable condition by the use of sodium carbonate and anionic surfactant. They experimented with wettability reversal on calcite surface and they found that the positively-charged calcite surface can be reversed to negative through the presence of $NaHCO_3/Na_2CO_3$ in the brine. However, the wettability reversal of oil-wet calcite surface is a function of aging time, temperature, and surfactant formulation. The degree of wettability alteration observed was in the range of water-wet to intermediate-wet. In the core flood step, they concluded that oil displacement can occur by buoyancy since alkali and surfactant reduced IFT and altered wettability to a more water-wet condition.

At the room temperature the wettability of oil-wet calcite can be reversed to water-wet condition but the system that was aged at elevated temperature (80^oC), the calcite surface was reversed only to neutral- to intermediate-water wet condition, They also had purposed the future work to study a more efficient technique to recover oil from the elevated ambient temperature which was not the favorable condition for wettability reversal.

Xie et al. (2005) tried to improve the oil recovery from the carbonate reservoir by the chemical stimulation. Similar to the research of Hirasaki and Zhang, this research was attempted to reverse the wettability of fractured, oil-wet, carbonate reservoir to a more favorable condition. However, alkali substance was absent in this study. The investigators used instead cationic and nonionic surfactants at very low concentrations as wettability reversal material. Surfactant can promote oil recovery by spontaneous imbibition or by gravity segregation or by the combination of both. Cationic surfactant tended to promote oil recovery by gravity segregation, whereas nonionic surfactant improved oil recovery by increasing the rate of spontaneous imbibition. Therefore, nonionic surfactant was conclusively more potential in wettability reversal. Oil recovery from spontaneous imbibition from both surfactants ranged from 5-15 % of original oil in place (OOIP).

Seethepalli et al. (2004) investigated the wettability alteration of calcite plate by the use of alkali substance and anionic surfactant. However, investigators concluded that the wettability reversal was primarily accomplished by the effect of anionic ion instead of alkali substance. The alkali substance assisted anionic ion to depress the surfactant adsorption onto the carbonate surface. Anionic surfactant lowered the IFT and consecutively liberated oil and adsorbed molecules in droplet or emulsion form. Therefore, the carbonate surface was free from oil phase and adsorbed molecules. Nevertheless, in some researches, anionic surfactant was believed to reverse the wettability by the effect of bilayer formation (the two layer adsorption onto rock surface and the second layer expose the hydrophilic outward, sticking the hydrophilic part into aqueous phase) which does not really change the surface property. In this study, sodium carbonate was added to reduce the adsorption rate of anionic surfactant. The cooperation between anionic surfactant and alkali substance can reverse the oil-wet surface to intermediate water-wet condition. Low alkali concentration at the CMC was preferential and looked promising for fractured carbonate formations.

Zhang and Austad (2005) studied the effect of acid number and temperature on the chalk wettability. They found that, the wettability of carbonate reservoir was directly dependant on the concentration of acid concentration in the oil phase. Moreover, the wettability index to water of original chalk increased proportionally as acid number increased. Temperature played a minor role regarding chalk wettability. Reservoir temperature affected to the catalytic decarboxylation process. In another word, as temperature increased, calcium carbonate acted as the catalysts to free the adsorbed carboxylic acid and as a consequence, the surface became less oil-wet compared with surface at lower temperature.

A consecutive research of Zhang and Austad was done by Austad et al. (2005). The investigators studied the improved oil recovery in fractured chalk by the use of sea water. The presence of sulfate (SO_4^{2-}) in brine improved the spontaneous imbibition. Sulfate substitutes adsorbed material onto positive-charged carbonate surface. This results in releasing the adsorbed molecules and rock surface became less oil-wet. The pH of this process was kept constant around the pH of brine at (7-8). Therefore, the reversal of surface charge to negative was difficultly conducted. The adsorption of sulfate was found be predominant at elevated temperature. Above 100^{o}C sulfate was more poorly solvated in water due to the break of hydrogen bonding between water molecules and sulfate ions. Thus, sulfate ions tended to leave aqueous phase either by adsorption onto rock surface.

Wu et al. (2006) studied the wetting behavior and surfactant in EOR in carbonates. The mechanism of wettability reversal by anionic and cationic surfactants was demonstrated in this work. Cationic surfactant reversed the rock wettability by forming the ion-pairs with the dissociated adsorbed anion materials in the aqueous phase, and so this results in the removal of adsorbed material, yielding the surface less oil-wet. On the other hand, anionic and nonionic surfactants did not remove the adsorbed molecules but they co-adsorbed on the carbonate surface. This so-called bilayer adsorption is caused by surfactants, which have strong hydrophobic-hydrophobic, interact with the adsorbed material, leaving the polar head of surfactant sticking out into bulk solution. This polar head which is hydrophilic group then provided a water-wet layer near the surface. The cationic was more potential in wettability reversal in carbonate surface compared with anionic or anionic because it removed the adsorbed molecules and frees the surface from attachment with oil. However, surfactant did not permanently change the surface wettability. The surface charge, which played a major role in wettability control, remained positive. Therefore, the re-adsorption of carboxylic acid can occur again if the surface charge remained positive. Alkali substance was then chosen to build up a permanent condition for wettability reversal by adding the positive charge onto the surface above the p.z.c (around 9 in carbonate surface).

The investigators also concluded that the structure of carboxylic acids that were adsorbed onto carbonate surface had more effects in wettability of that surface than the quantity of adsorbed molecule.

Gomari et al. (2006) also studied the ions than can improve oil recovery. They found that not only calcium and carbonate ions that controlled the charge of carbonate surface sulfate and magnesium ions partially converted surface charge to a more favorable condition. Sulfate and magnesium ions also raised the pH of brine to approximately 9.25 and 8.48 respectively. The increase of pH may have partly contributed the wettability reversal mechanism; however, the water wetness condition in the presence of magnesium and sulfate ions was not reported in this research.

Hamouda and Gomari (2006) investigated the influence of temperature on wettability alteration of carbonate reservoirs. At the elevated temperature, carbonate surface became less oil-wet because of the modification of calcite surface. The number of available calcite site to adsorb carboxylic acid was reduced and moreover, some short acids can be dissolved more in aqueous phase when temperature increased. This resulted in less adsorbed material onto the carbonate surface and consequently, affected to a less oil-wet condition.

Other relevant researches concerning alkali flooding and wettability reversal in sandstone are also useful and reviewed in this section.

Jadhunandan and Morrow (1993) performed a laboratory test to confirm the effect of wettability on waterflood recovery for crude-oil/brine/rock system. The investigators found during the core preparation step that wettability of sandstone tended to be more oil-wet when there was a presence of divalent ions because divalent ions acted as bridges to link between negatively-charged sandstone surface and negative compounds in oil phase such as carboxylic acid. This mechanism was named after by other investigator as ion bonding (this mechanism is important in sandstone but do not have effect in carbonate reservoir). Another important conclusion from this research was that the highest oil recovery was obtained around neutral-wet instead strongly water-wet condition. In strongly water-wet, oil can be trapped through the disconnection of oil at pore throats (snap-off) to form blobs that largely fill the pore body. Therefore, the wettability condition induced by crude oil (wettability changed to neutral-wet condition) tended to inhibit the snap-off mechanism by which oil became trapped as blobs at very strongly water-wet condition. It can be concluded that, the maximum in oil recovery at neutral-wet condition was obtained because the capillary forces were minimized. The increase of reservoir temperature resulted in less water-wet condition which was opposite with carbonate rock. The decrease of initial water saturation also caused a less strong water-wet condition.

Wang and Guidry (1994) studied the effect of oxidation-reduction (redox) condition on wettability alteration. Redox condition of sedimentary material was described in term of redox potential (E_H) E_H describes electron-capturing tendency, whereas pH describes the proton-capturing tendency. The conclusion from this work was that the wettability of mixed-wettability system was not affected by difference in the redox condition, whereas strongly water-wet system tended to change to mixed wettability under aerobic conditions (oxidation state) except when iron (Fe) and other transition metals were removed from the surface. In order to maintain the mixed-wet condition, the investigators stored the sample at their ROS or connate water saturation under either anaerobic or aerobic condition and the original wettability were preserved for many months.

Wanchao et al. (1995) studied the alkali-surfactant-polymer flooding in the sandstone reservoir containing oil with high acid value. The injection of alkali (in this research, sodium hydroxide, sodium carbonate, and sodium silicate) promoted the ultra-low IFT condition at the interface. The presence of alkali decreased the loss of surfactant in porous media. About 16% of OOIP can be obtained in experiment, whereas 13.4% was obtained in the pilot test in the abandoned water flooded field of Gudong, Shandong, China.

Yan et al. (1997) studied the wettability reversal by the adsorption of asphaltenes in sandstone. They found that the precipitation of asphaltene occurred at low temperature and caused in the change of wettability to an unfavorable condition. In the presence of cation in brine, the precipitation of asphaltene can be preferentially induced, whereas anion had only a relatively minor effect. The best waterflood recovery with wettability changes induced by adsorption of asphaltenes indicated a maximum in oil recovery at very weakly water-wet condition.

Buckley et al. (1998) summarized four possible wettability alteration mechanisms by crude which were polar interactions, surface precipitation, acid/base interaction, and ion-binding. All mechanism was possible for sandstone but theoretically, only three mechanisms can explained for carbonate surface.

Polar interaction can be conducted in carbonate surface by the direct acid adsorption because carbonate surface is positively charged in neutral environment. Surface precipitation can also occur onto the carbonate surface because this is the effect of solvency property of oil. Acid-Base interaction can be occurred in carbonate reservoir by the presence of water film. Carbonate surface ionizes in water phase and acts as base side, reacting with ionized acid through the water film. Ion-binding is primarily considered for sandstone because most ions affecting the wettability reversal are divalent ions. The positive charges of divalent ion interact only with oppositely negative charge of sandstone surface, binding the sandstone surface with another negatively-charged material.

Arihara et al. (1999) concluded the oil recovery mechanisms by alkali-surfactant-polymer flooding in sandstone reservoir. Theoretically, the IFT reduction of alkali substance was predominant at alkali concentration higher than 1% w/w (equivalent to 0.25 molar for sodium hydroxide). At alkali concentration lower than this value, the wettability reversal function is favorable. In the use of high alkali concentration, the surfactant concentration can be reduced at a few percent because alkali can also reduce the IFT at very low value. However, the IFT reduction lasted only a few hours. The IFT gradually increased as aging time of interface system increased. In high surfactant concentration, alkali concentration can be reduced to a very low concentration. It was recommended that polymer slug should be injected separately as a buffer between chemicals and chase water.

In general, most literatures are concerned the use of alkali in cooperation with surfactant substance. Most authors paid attention to the surfactant as the material that reverses the wettability of carbonate surface. But, as seen in most papers, surfactant cannot work solely without the presence of alkali especially in carbonate reservoir because the surface charge remains positive. Surfactant is very effective in removal the adsorbed materials and liberate the carbonate surface but it does not have an ability to reverse the surface charge because it cannot build up the high pH value (above 9) and cannot provide the negative charges which are necessary in charge reversal. This research then emphasizes on the surface charge reversibility by alkali substance in the absence and presence of surfactant.

CHAPTER 4

EXPERIMENTS

Six categories of experiment are conducted in this research and the details are described in this chapter: rock and fluid properties measurement, interfacial tension measurement, wettability measurement, wettability alteration measurement, core flooding test, and alkali consumption test.

4.1 Rock and Fluid Properties

In general, alkali flooding is recommended for sandstone reservoirs. Carbonate reservoirs were not candidates because of the enrichment in divalent ions that can react with alkali slug, causing in increment of IFT and alkali loss without oil improvement. However, dolomites and limestones are proven to be proper candidates since most of them do not react with alkali slug to cause deleterious effect (Donaldson *et al.,* 1989). The *Lecce stone*, an Italian limestone from the south of Italy is chosen for this study. Soltrol170, a hydrocarbon solution composing of C_{12}-C_{14} represents the oil phase. Artificial brine is prepared in the laboratory and is utilized as aqueous phase. More information of rock and fluid properties are described in this chapter.

4.1.1 Rock Properties

Lecce stone is a homogeneous limestone found in the south of Italy (province of Lecce). It is sometimes called *"la pietra del Salento"* which is named for the location of quarry. Geologically, Lecce stone was deposited in the Miocene age. Fossil fragments in the rock are from planktonic and benthonic species. Some of fossil evidences are conserved in their entirety. By a petrographic test, Lecce stone appears to compose from granular components (microfossil, fragment of fossil, intraclasts, and pellets) embedded by calcite cement. The more details of microfacies study is reviewed in appendix A. Figure 4.1 illustrates Lecce stone as seen in thin section. Planktonic foraminifers (probably *Globigerina*) of various sizes are distributed irregularly in a micritic matrix partly re-crystallized to sparite (microsparite). Chambers of a few foraminifera are empty (blue tint of dyed Araldite resin visible), while others are filled by micrite or glauconite (dark material). Round dark spots with white centre are bubbles within Araldite resulting from imperfect removal of air by vacuum. Foraminifera in lower centre of picture is 500 micrometer long.

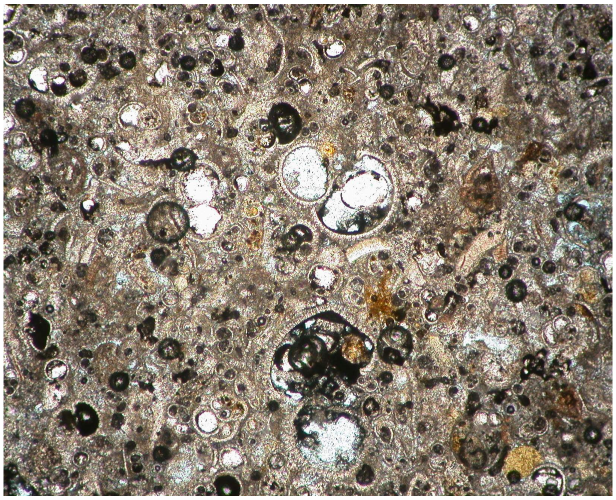


Fig. 4.1: Thin section of Lecce stone.

Chemically, Lecce stone contains calcium carbonate in a range of 93-97 % (Bossio *et al.,* 1988). A few percents of glauconite, quartz, feldspar, muscovite, phosphate, and clay minerals are responsible for variation of its character. For example, Lecce stone can be hard or soft or can be brittle or ductile. Consequently, Lecce stone is classified in many varieties characterized by color, grain size, homogeneity, and compaction.

Visually, Lecce stone appears to have pale brown color and smooth surface (Fig 4.2). Lecce stone is cut into two size: 5.4cm×5.5cm and 2.5cm×5.5cm (diameter×thickness). More details from the thin section show the homogeneity required for alkali flooding (Donaldson *et al*., 1989). The physical properties provided by the official website *(www.roselli.it)* of Lecce stone are reviewed in table.4.1.

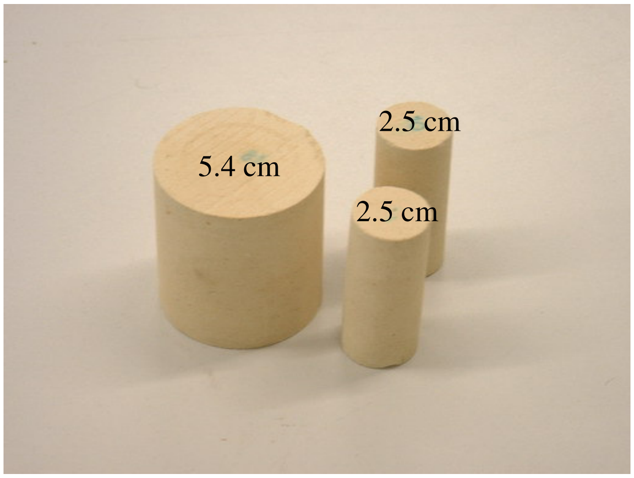


Fig 4.2: Lecce stone in two different cut 5.4cm and 2.5cm diameter.

Table 4.1: Physical properties of Lecce stone.

Property	**Value**	**Unit**
True density	2710-2770	kg/m^3
Apparent density	1572-1861	kg/m^3
Gravitational compaction	55-69	%
Porosity	31.3-44.8	%
Imbibitions coefficient	11.6-20.7	%

4.1.1.1 Porosity and Relative Density

The precise value of porosity is verified for core samples in order to calculate the saturation of fluids. Relative density was calculated from measured porosity values. Porosity and relative density are simply verified by measuring dry core weight (w_s), water saturated weight (w_{sat}), and hydrostatic weight (w_h). It is important that a core sample has to be fully saturated. The recommended method is to saturate core under vacuum. Porosity (Φ) and relative density (ρ_s) of Lecce stone are calculated from equations 4.1 and 4.2 respectively.

$$\Phi = (w_{sat} - w_s) / (w_{sat} - w_h) \quad (4.1)$$

$$\rho_s = w_s / (w_s - w_h) \quad (4.2)$$

From the measurement, porosity and relative density of Lecce stone correspond to 0.31 and 2.7 respectively. A porosity of 0.31 determines a potential reservoir rock able to capture high volumes of fluids. However, to determine that Lecce stone is a good porous media, rock permeability needs to be evaluated.

4.1.1.2 Absolute Permeability

Absolute permeability (k) is a measurement of the ease in which a single fluid can flow through the pores of a rock when only that fluid is present in the pores. (Hyne, 1991). The absolute permeability of Lecce stone is performed in a core flood cell (details in section 4.5). Any fluid can be used in absolute permeability measurement since absolute permeability is the rock property (not rock-fluid property) and thus, it is independent from fluid viscosity. However, distilled water is recommended. Initially, Lecce stone is cut into a size of 5.4cm×5.5cm by diameter and length respectively. Cut core is then saturated with distilled water under vacuum. Saturated sample is placed in the core flood cell. The water displacement is performed from by injecting water at the top and draining out water at the bottom of the core flood cell. The measurement of the exit water flow rate fulfills the left hand side of Darcy's equation (equation 4.3) and thus, the absolute permeability can be calculated from equation 4.4.

$$q = (kA\Delta p) / \mu\Delta L \qquad (4.3)$$

$$k = (q\mu\Delta L) / A\Delta p \quad . \qquad (4.4)$$

In these equations, k is absolute permeability (mDarcy), q is liquid flow rate (cm^3/s), A is cross-sectional area of core sample (cm^2), Δp is pressure difference between inlet and outlet (atm), ΔL is length of core sample (cm), and μ is fluid dynamic viscosity (cPoise).

The absolute permeability of Lecce stone obtained from equations 4.3 and 4.4 ranges between 4.5 - 4.9 mDarcy.

After the rock is cut into proper sizes, the cut samples are cleaned by the reflux extraction with toluene. The reflux extraction by toluene renders rock samples a strongly water-wet condition which is believed to be an initial condition for any deposit rock reservoir. The extraction can be applied for the used samples which are contaminated with hydrocarbon and other chemical substances. The reflux extraction set called *“Soxhlet”* is utilized in this study and the picture of this equipment set is shown in figure 4.3.

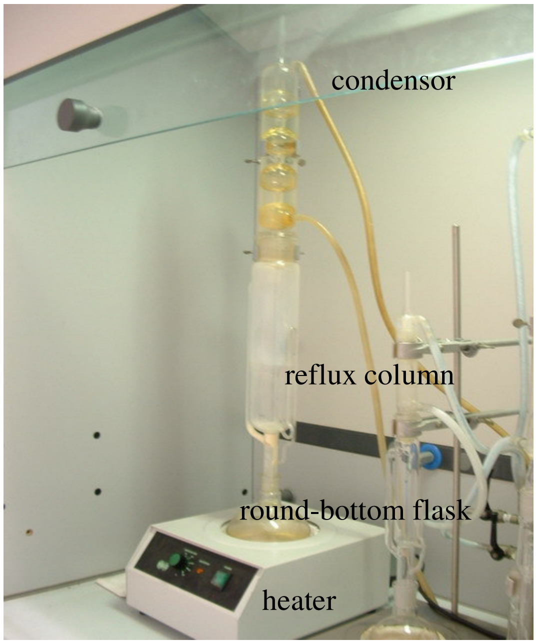


Fig. 4.3: Soxhlet reflux extraction set.

The Soxhlet reflux extraction set composes of a heater, a round-bottom flask, a reflux column, a condenser, and a holder. Samples are initially placed in a reflux column and half liter of toluene is poured into a round-bottom flask. Then, the instruments are assembled as in figure 4.3. The temperature of heater is set at 200^{o}C which is higher than the boiling point of toluene (110-111^{o}C) and it is lower than the boiling point of present hydrocarbon (soltrol170) in the used samples (initial boiling point 233.3^{o}C). Cold water is circulated in a condenser, exchanging heat with toluene vapors and resulting in the condensation of toluene to liquid phase. Toluene liquid at its boiling temperature drops into a reflux column and leaches the adsorbed material inside samples, rendering a cleaned core condition. The reflux of toluene liquid occurs when the level of toluene arrives to the height of the U-shaped reflux tube which is connected to the bottom of reflux column. Refluxed toluene then reenters the round-bottom flask and is reheated. Nevertheless, the samples necessarily need to be dried before placing inside a reflux column because water, which has boiling point of 100°C, can reenter in a reflux column after re-vaporization and condensation.

4.1.2 Fluid Properties

4.1.2.1 Oil Properties

Soltrol170 isoparaffin is a transparent liquid, primarily composed of paraffinic hydrocarbon $C_{12} - C_{14}$. Some properties of Soltrol170 isoparaffin, which represents oil phase in this research, are provided by the manufactured data (Chevron Phillips Chemical CO.LP) as shown below.

Table 4.2: Properties of Soltrol170 isoparaffin.

Property	**Value**	**Unit**	**Test method**
Distillation range at 1 atm			ASTM D 86
Initial boiling point	233.3	°C	
10%	225.6	°C	
50%	228.9	°C	
90%	235.0	°C	
End point	244.4	°C	
Color	+30	saybolt	ASTM D 156
Flash point	88.9	°C	ASTM D 56
Copper corrosion at 100 °C	1	-	ASTM D 130
Aromatic content	300	ppm	UV spectroscopy
Specific gravity at 15/15 °C	0.78		ASTM D 1298
Density of liquid	0.784	g/cm^3	ASTM D 1250
Sulfur	2	ppm	ASTM D 3120
Aniline point	91.1	°C	ASTM D 611
Kauri-Butanol value	24.6	-	ASTM D 1133
Bromine number	0.8	-	ASTM D 1492
Kinematic viscosity at 37.8 °C	2.6	cSt	ASTM D 445

Liquid density of Soltrol170 (ρ_l) is needed to verify again at a certain temperature because it is important for the liquid saturation calculation in core samples. The dynamic viscosity (μ_l) is calculated for the absolute permeability calculation. Acid content is necessarily to be tested before the modification of acid number in order to obtain the desired acid number.

4.1.2.1.1 Density and Viscosity

Density of Soltrol170 is measured in laboratory by measuring liquid volume (V_l) and liquid mass (m_l). Liquid density is then calculated by the equation 4.5. The average value measured in laboratory at ambient temperature (25 ^oC) is 0.7695 g/cm^3.

$$\rho_l \quad = \quad m_l / V_l \qquad (4.5)$$

Dynamic viscosity in centipoises (cPoise) can be calculated from kinematic viscosity (v_l) provided by the manufactured company by using the equation 4.6. Fluid viscosity from this calculation is 2.0 cP.

$$v_l \quad = \quad \mu_l / \rho_l \qquad (4.6)$$

4.1.2.1.2 Acid Content and Acid Number Modification

Acid number is defined as a quantity of potassium hydroxide (KOH) in milligram needed to react with acid in one gram of oil sample. (IP139/98). Acid number is a very important key for alkali flooding. It is noticed that, the candidate reservoir for an alkali flooding should have formation oil with an acid number greater than 0.5 (Donaldson *et al*., 1989).

Acid number determination can be performed by two methods: color indicator titration and petentiometric titration. Color indicator titration is chosen in this research according to its simplicity. The fine details of acid number determination by color indicator titration are reviewed in appendix B. Color indicator titration (IP139/69, ASTM D974-64) is a measurement of acid number by detecting the end point, the point at which base and acid compounds are completely reacted and hence, there is no basic or acidic compounds left in the rest of solution. At this point, the color indicator remarkably changes its color from one to another. The color indicator in this research is *p*-naphtholbenzein. This indicator has dark orange color itself and also in the acidic solution. At the end point, it changes the color from orange to dark green which means the solution changes to have basic compound. Chemical structure of *p*-naphtholbenzein is illustrated in figure 4.4.

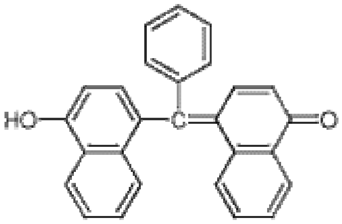


Fig. 4.4: Molecular structure of *p*-naphtholbenzein.

The color indicator titration of Soltrol170 indicates that there is no acid compound in this liquid hydrocarbon. Hence, the desired acid number can be modified by adding correspondingly an amount of acid. The calculation of acid number modification is described in appendix C. Oleic acid is used as an acid number modifier. The range of acid number varies between 0.5 -5.0 which is a possible range can be found in oil reservoirs.

4.1.2.2 Brine Properties

Brine, representing aqueous phase, is artificially prepared in laboratory. Salinity of seawater is usually around 35 parts per thousand (ppt). The average composition of brine is listed in table 4.3 (*www.biosbcc.net*).

Table 4.3: Composition of average sea brine.

Chemical Ion	**Concentration (ppt)**	**Mass Percent**
Chlorine	19.345	55.03
Sodium	10.752	30.59
Sulfate	2.701	7.68
Magnesium	1.295	3.68
Calcium	0.416	1.18
Potassium	0.390	1.11
Bicarbonate	0.145	0.41
Bromide	0.066	0.19
Borate	0.027	0.08
Strontium	0.013	0.04
Fluoride	0.001	0.003
Other	less than 0.001	less than 0.001

However, the trace elements are neglected in this research (bromine, borate, strontium, and fluoride). From the ion-mole balance, the mass ratio of following chemicals shown in table 4.4 is used for the brine preparation.

Table 4.4: Mass ratio of chemicals used for the brine preparation.

Chemical	**Molecular Weight**	**Mass Ratio**
$MaCl_2$	95.21	0.147
$CaCl_2$	110.98	0.033
KCl	74.55	0.021
NaCl	58.44	0.679
Na_2SO_4	142.04	0.114
$NaHCO_3$	84.00	0.006

From table 4.4, $MaCl_2$, $CaCl_2$, KCl, NaCl, Na_2SO_4, and $NaHCO_3$ stand for magnesium chloride, calcium chloride, potassium chloride, sodium chloride, sodium sulfate and sodium hydrogen carbonate, respectively. From the mass ratio, brine can be prepared by multiplying each element to the mass concentration. For example, one liter of brine with the salinity of 35 ppt contains chemicals as shown in table 4.5.

Table 4.5: Mass of chemicals for one liter of brine with the salinity of 35 ppt.

Chemical	**Mass (gram)**
$MaCl_2$	5.145
$CaCl_2$	1.155
KCl	0.735
NaCl	23.765
Na_2SO_4	3.990
$NaHCO_3$	0.210

Soften brine can be prepared by removing divalent ion compounds which are $MgCl_2$ and $CaCl_2$. Therefore, the salinity of soften brine is less than that of the normal brine (around 28 ppt).

4.2 Interfacial Tension Measurement

Interfacial tension (IFT) plays a major role in waterflood performed in viscous-oil reservoir. Primarily, the IFT evaluation is conducted before performing alkali or surfactant flooding in order to evaluate proper amount of chemical dosage. Generally, the oil recovery by alkali flooding is expected from two mechanisms (which are the main features of alkali): IFT reduction and wettability alteration. In this research, IFT reduction is minor expected from the intermittent flow case (The research is attempted to recover oil by wettability reversal ability of alkali substance). Therefore, the IFT evaluation is approximately performed in coarse scale equipment. A platinum-iridium ring tensiometer is used in this study. For a fine scale investigation such as surfactant flooding (IFT is expected to be an ultra-low value), the measurement should be performed by a spinning drop tensiometer.

4.2.1 Apparatus

The tensiometer, (as shown in figure 4.5) called *“Fisher Surface Tensiomat model 21”*, including a platinum-iridium ring with the mean circumstance of 5.995cm, is used in this study. Soltrol170 isoparaffin, representing the oil phase, is mixed with oleic acid at a desired concentration. According to a minimum acid number require, acid number of 0.5 is prepared in this phase. Sodium hydroxide (NaOH) and dodecylbenzenesulfonic acid sodium salt represent alkaline and surfactant substances respectively. Brine and distilled water are used as the aqueous phase. Chemical structures of acids and surfactant are shown in figure 4.6.

Fig.4.5: Tensiometer and platinum-iridium ring.

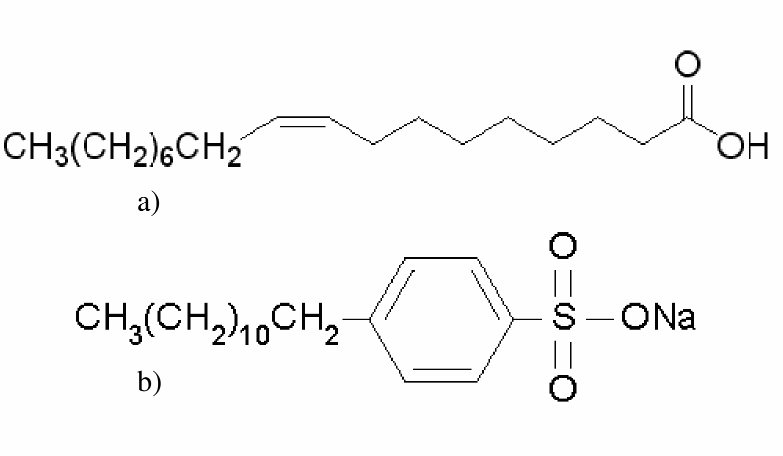


Fig.4.6 Structural formula of represented chemicals: a) oleic acid and b) dodecylbenzenesulfonic acid (sodium salt).

4.2.2 Methodology

The measurement of IFT from more dense liquid to less dense liquid is made by exerting an upward force on the ring. The ring and sample container are cleaned and dried. The more dense liquid (water phase) is poured into the glass vessel and placed on the sample table, and the table moved beneath the platinum-iridium ring. The sample table is then raised until the ring is immersed about 1/8 inch and wetted by the heavier liquid. The torsion arm is now released and the instrument adjusted to a zero reading. Adjust the knob on the right side of the case until the index and its image are exactly in the line with the reference mark on the mirror.

Pour the lighter liquid onto the surface of the heavier liquid to a depth of about 1/4 to 1/2 inch. The layer of lighter liquid should be deep enough so that the ring will not break through the upper surface of the lighter liquid before the interface film ruptures. Lower the sample table until the ring is interface between the two liquids, while at the same time adjusting the knob to keep the index lined up with the reference mark on the mirror. The interface between the liquids will become distended, but the index must be kept at the reference. Continue the two simultaneous adjustments until the distended film at the interface ruptures. The scale reading at the breaking point of the interfacial film is the *"apparent interfacial tension"*.

The measurements are divided in four groups to study the effects of these chemical on IFT value: alkali concentration, surfactant concentration without the presence of alkali, surfactant concentration on IFT value with the presence of alkali, and salinity.

4.2.2.1 The Effect of Alkali Concentration

Soltrol170 isoparaffin which is prepared at acid number of 0.5 is poured onto sodium hydroxide solution with the varied concentrations of 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 molar. The blank solution (without sodium hydroxide) is additional tested. The IFT values are measured at the mixing moment and then, are re-measured again after the two-phase system is aged for 24 hours, 48 hours, and 1 week. The obtained data is plotted between sodium hydroxide concentration and IFT value in linear scale.

4.2.2.2 The Effect of Surfactant Concentration

Dodecylbenzenesulfonic acid sodium salt (anionic surfactant) is dissolved in distilled water at varied concentrations of 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 % w/w. Again, the measurements are performed at the different times as same as the previous test (the effect of alkali concentration). The obtained data is plotted on semi-log scale between surfactant concentration and IFT value.

4.2.2.3 The Effect of Surfactant and Alkali Concentration

Only two concentrations of dodecylbenzenesulfonic are chosen and tested: 0.05 and 0.10 % w/w according to the optimum concentration obtained from the previous section. Those two surfactant solutions are sub-prepared by dissolving with sodium hydroxide at the varied concentration of 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 molar.

4.2.2.4 The Effect of Salinity

The effect of salinity is studied for three alkali concentrations: 0.15, 0.20, and 0.25 molar. These concentrations are chosen after the effect of alkali concentration test is conducted. Salinity is varied from 0 – 30 ppt. The measurements are performed at the mixing time, after aging for 24 hours, 48 hours, and one week, respectively.

The results from IFT measurement are illustrated by the plots between concentrations of each substance and IFT values. The optimum concentrations chemical substances are then identified in the analyzing step. The optimal concentrations obtained in this step are also used in the rest of experiments.

4.3 Wettability Measurement

The Amott-Harvey wettability index is chosen for the wettability measurement. The theoretical procedure of Amott method is already explained in the chapter2 (section 2.7.1.2). In this section, the technical procedure concerning apparatus, materials, and additional techniques are reviewed.

4.3.1 Apparatus

The most important equipment in this study is a centrifugal machine. A centrifuge model CRU-5000 manufactured by the International Equipment company, is used in this study. Main parts of centrifuge are rotor and bottle holders. The rotor speed can be adjusted from 0 – 6200 RPM. Four bottle holders are connected with rotor. However, the centrifuged bottles must have the same weight (total weight included sample) in order to balance the rotor while it rotates at high speed.

Temperature of centrifuge chamber can also be adjusted. Figure 4.7 shows the centrifuge machine and sample bottles. The operating conditions of rotation speed and chamber temperature are set at 3600 RPM and 25°C respectively.

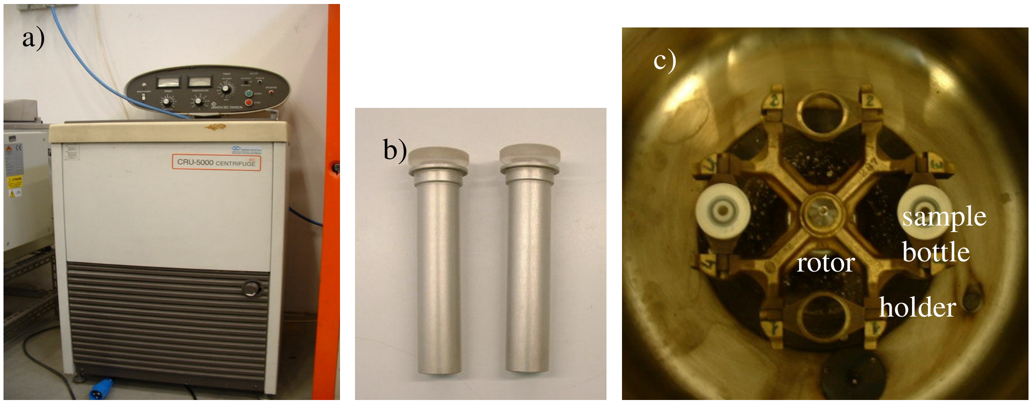


Fig. 4.7: a) a centrifuge machine, b) sample bottles. and c) inside the centrifuge chamber.

4.3.2 Methodology

Lecce stone is cut into a size of 2.5cm×5.5cm by diameter and length of sample respectively. Samples are dried in oven for 24 hours in order to eliminate humidity from the core cutting phase. After that, samples are cleaned by reflux extraction. Samples are divided in two groups according to the different preparation procedures. The first group, samples are initially saturated with distilled water while the second group, samples are primarily saturated in soltrol 170.

The samples firstly saturated with distilled water are placed in bottles (centrifuge cell), submerging in soltrol170, and centrifuged for two hours. At this point, the samples are labeled as Irreducible Water Saturation (IWS). On the other hand, the samples firstly saturated with soltrol170 are centrifuged in distilled water for two hours and labeled as Residual Oil Saturation (ROS). Table 4.6 summarizes the measurement for both groups of sample.

Table 4.6: Essential measurement for the wettability index for samples starting with IWS and ROS conditions.

IWS samples	**ROS samples**
1) Immerse samples in water for 24 hours, measure oil expelled (V_{osp})	1) immerse samples in oil for 24 hours, measure water expelled (V_{wsp})
2) Centrifuge samples in water for 2 hours, measure total oil expelled (V_{ot})	2) centrifuge samples in oil for 2 hours, measure total water expelled (V_{wt})
3) Calculate $\delta_w = V_{osp} / V_{ot}$	3) calculate $\delta_o = V_{wsp} / V_{wt}$
4) Immerse samples in oil for 24 hours, measure water expelled (V_{wsp})	4) immerse samples in water for 24 hours, measure oil expelled (V_{osp})
5) Centrifuge samples in oil for 2 hours, measure total water expelled (V_{wt})	5) centrifuge samples in water for 2 hours, measure total oil expelled (V_{ot})
6) Calculate $\delta_o = V_{wsp} / V_{wt}$	6) calculate $\delta_w = V_{osp} / V_{ot}$
7) calculate $I = \delta_w - \delta_o$	7) calculate $I = \delta_w - \delta_o$

The expelled liquid volume can be indirectly measured by mass balance equation. When a sample contains water and oil phase, the average density is expressed by

$$\rho_{ave} = (V_o / V_t) \times\rho_o + (V_w / V_t) \times\rho_w \qquad (4.7)$$

where ρ_{ave}, ρ_w, ρ_o, V_w, V_o, V_t are average density, water density, oil density, water volume, oil volume, and total liquid volume respectively. From equation 4.7, substituting the terms V_o by $V_t - V_w$ and ρ_{ave} by m_t/V_t ,results in the arrangement as

$$m_t/V_t = [(V_t-V_w)/V_t] \times\rho_o + (V_w / V_t) \times\rho_w \qquad (4.8)$$

where m_t is total liquid mass and then

$$m_t = (V_t-V_w) \times\rho_o + V_w\times\rho_w \qquad (4.9)$$

so that, water and oil volume can be calculated from

$$V_w = [m_t - (V_t \times \rho_o)] / (\rho_w - \rho_o) \qquad (4.10) \text{ and}$$

$$V_o = V_t - V_w \qquad (4.11).$$

Physically, the wettability index obtained from sample initially saturated with water is different from sample initially saturated by oil. The samples initially saturated with water (IWS samples) have water layer adhering rock surface and this water layer prevents the attachment of the wettability alteration materials; as a consequence, these samples are less oil-wet compared with samples that are firstly saturated with oil (Hirasaki *et al.,* 2004).

Distilled water and soltrol170 are utilized for the Amott-Harvey wettability index of natural samples. However, a strongly oil-wet condition is needed for this research. Therefore, samples are treated with carboxylic acid (dissolved in Soltrol170) to create a direct acid adsorption onto the surface, rendering oil-wet condition. The wettability indexes of treated samples are then measured by the procedure previously described. Oleic acid dissolved in Soltrol170 with the concentration of 2.0 acid numbers is used as the oil phase, whereas brine represents aqueous phase. At this step, only ROS samples are prepared according to several previous studies concluding that a direct acid adsorption onto rock surface without water layer will cause the stronger oil-wet condition in shorter aging period.

However, the adsorption of acid has to occur homogeneously in the entire sample. Basically, Nuclear Magnetic Resonance (NMR) is a powerful, non-invasive, and non-destructive technique used for the analysis of reservoir rock characteristics. In particular, Magnetic Resonance Imaging (MRI) is used to monitor the process of wettability reversal. Preliminary measurement tests have clearly shown that the longitudinal relaxation time (T_1) could be used to characterize the kind of fluid saturating the sample (pure soltrol170 or acid-soltrol). Therefore, by means of MRI images that emphasize the T_1 differences (T_1-weighted images) it is possible to follow up the process of wettability variation. Also analysis with T_2-weighted images was done (T_2 is transverse relaxation time). The main apparatus is the ARTOSCAN™ tomograph (Esaote S.p.A., Genoa, Italy, shown in figure 4.8), an instrument with a 0.2 T permanent magnet and which operates about 8 MHz for protons.

Fig 4.8: MRI tomograph.

Two-dimensional images were obtained by using multi-slice spin echo (SE) pulse sequences for T_2-weighted images, and saturation recovery (SR) pulse sequences for T_1-weighted images. All images were then processed with the in-house software ARTS (Borgia *et al.,* 2001) and filtered to reduce the noise. In all cases the size of the voxel (pixel size × slice thickness) was about $0.5\times0.5\ \mathrm{x}\times5.0\ \mathrm{mm}^3$.

Opportunely, combining a series of images is possible to obtain a *"relaxation map"* (in T_1 or in T_2) where each pixel is proportional to the value of relaxation time (Bortolotti *et al.,* 2006). This type of analysis is another powerful tool that allows following the changes in wettability process.

Oil-saturated carbonate rock samples are then detected for the wettability change from the chemical treatment process by previously-described instrument. The application of NMR feature is primarily used to detect the completion of acid adsorption in the samples. The small samples, with a size of 2.5cm×5.5cm by diameter and length respectively, are utilized in this measurement.

4.4 Wettability Reversal Measurement

Wettability reversal measurement is a preliminary test before the alkali flooding in core flood cell. The objectives of this measurement are to verify the ability of alkali substance in wettability alteration function which is strongly dependent from aging period and to estimate the improvement by the use of the combination between alkali flooding and intermittent flow. In this research, a strongly oil-wet condition is initially required because the improvement of wettability to a favor condition (water-wet) is thus remarkably seen. Treated samples from the previous step with the known wettability index are then centrifuged in alkali solution. Sodium hydroxide is chosen for this measurement according to no gas products, which cause the unavailability of mass balance calculation, are being produced during the entirely step. Samples are divided into two groups. The first group, samples are prepared to have an ROS state and are centrifuged continuously for 14 hours. The sample weight is measured every two hours in order to calculate the fluid volume fraction. The second group, samples are flooded for two hours in centrifuge, measured weight, and aged for 24 hours before re-flooding. The intermittent finishes when the total centrifugation time reaches 14 hours which equals to 7 times of intermittent aging step. Finally, the wettability index is re-measured for every sample. Table 4.7 summarizes the details of wettability alteration experiment.

Table 4.7: Summarize of wettability alteration experiment performed by centrifuge.

Continuous flow	**Intermittent flow**
1) Surfactant flood 0.05%w/w	1) alkali flood 0.05 molar
2) Alkali flood 0.2 molar	2) alkali flood 0.2 molar
3) Alkali + surfactant flood (1 + 2)	3) Alkali flood 0.5 molar
	4) Alkali + surfactant flood (1 +3)

Solely surfactant flooding is not performed with intermittent flow because anionic surfactant does not have a surface charge reversal function. Moreover, aging anionic surfactant in carbonate rock foresees a depletion of surfactant by co-adsorption which does not cause the improvement to a more favorable wettability condition (Wu *et al.,* 2006).

The comparison of these floods is done by the plots between oil recovery improvements against time in linear scale. The wettability index of samples from every experiment which are measured after 14 hours of centrifuge period is correlated with the oil recovery improvement.

4.5 Core Flooding

Core flooding is primarily considered as the representative step of this research. It is performed in order to study the oil recovery from waterflood. Basically, water injection is normally performed in a well with the injection zone located relatively lower than the production well. Water, which is denser than oil, sweeps oil upward. Finally, oil bank reaches a production well. An upward inclined reservoir is thus a good candidate for water injection. Experimentally, it is complicated to set up the core flood cell to have an inclination according to pressure maintenance system. Therefore, a vertical injection is chosen in this study.

4.5.1 Apparatus

A Hoek triaxial cell (figure 4.9) is an instrument used in this phase of work. The cell composes of an iron body (A) which has a shape of annulated cylinder with an inner diameter of 5.5cm. The body is completed with two quick release self sealing couplings, for the introduction of the hydraulic oil and cell pressure, and for air outlet and saturation of the chamber, respectively. The inner part of the cell body is installed by rubber sealing sleeve (B) to separate the specimen from the cell fluid. The cell also composes of two end caps screwed into the cylindrical body (C). These two end caps enclose the cell body and maintain the pressure in vertical axis (via overburden pressure build up system) while the rock sample is placed inside. The bottom cylinder end cap has a small injection hole connected to liquid injection system. The top cylinder end also has the small hole but it is connected to the liquid collecting tube.

The cell is connected to four surrounded systems: vertical pressure, lateral pressure, liquid injection, and liquid collecting. The pressure system prevents the liquid by-passing problem. Vertically, the iron pad presses the cell on the top end cap, and it is manually controlled to build up the pressure. Vertical pressure is monitored by manometer and kept constant for the entire experiment. The lateral pressure system functions by the manual liquid pump that pumps oil into the iron body via one side of quick release self sealing coupling. Again, the pressure can be controlled manually and it is shown on the connected manometer. In this research, both vertical and lateral pressure is kept constant at 40 atm. Liquid injection system is connected with the bottom end cap. The system composes of air compressor, liquid container, gauge manometer, and rubber tubes. Pressure inlet varies from 1.5–3.0 atm. Liquid collecting system is simple, composing of iron tube connected with the top end cap and a cylinder with clear scale. The schematic diagram of core flooding system is illustrated in figure 4.10.

Fig. 4.9: Compositions of Hoek triaxial core flood cell.

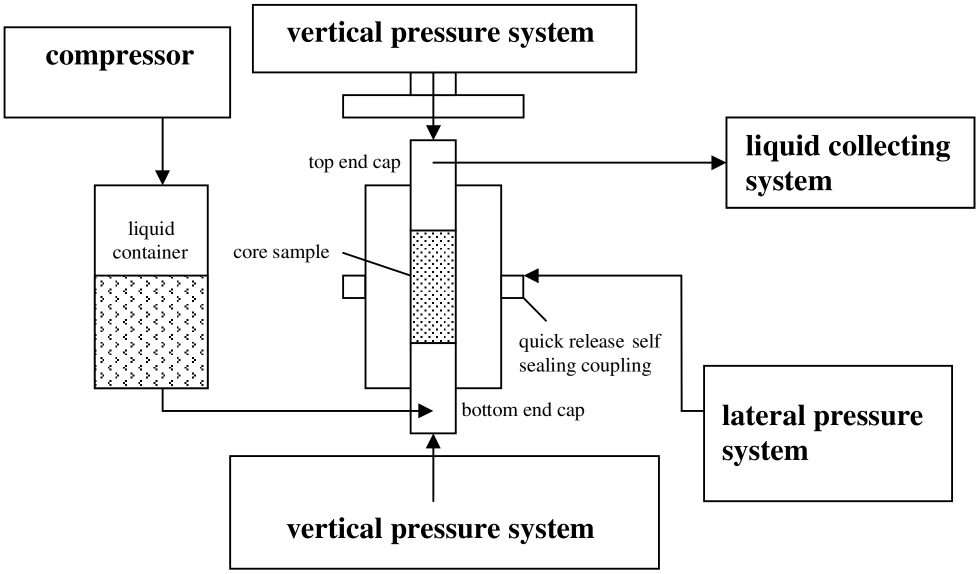


Fig. 4.10: Schematic diagram of core flooding system.

4.5.2 Methodology

Core flood test is separated into six groups according to the factor studied. The details of each test are explained in the following.

4.5.2.1 Continuous Waterflood and Brine flood

Continuous brine and waterflood is basically performed as a reference case. This test can be comparable to the secondary recovery. The result obtained from this flood shows the flooding behavior when additional materials are absent. Core samples are saturated under vacuum with oleic acid-soltrol170 with the concentration of 2.0 acid number and aged for one week. An aged core is then placed in the cell and flooded with injected fluid. The injection pressure is set at 1.5 atm. Volume of oil and water are measured at elevated time and used for the water-oil ratio (WOR) calculation. The test is run until WOR reaches 10. Three injected fluids are used in this test: distilled water, normal brine and soften brine. The result from changing these three fluids indicates the effect of brine compositions to the flooding behavior. Additional tests are run with the samples saturated with different concentration of acid in oil phase (0.5 and 5.0 acid number).

4.5.2.2 The Effect of Alkali Concentration

Sodium hydroxide is used as an alkali substance in this step. Cores are saturated in 2.0 AN oleic acid in soltrol 170 and aged for one week. An oil-wet core sample is flooded with brine until oil recovery reaches 0.65 (ROS reaches 0.35), which is the point that oil production drastically decreases. Normally, recommended ROS for starting alkali flooding is around 0.4 (Donaldson *et al.,* 1989). Then, a 0.2 PV slug of soften brine is injected to prevent the incompatibility problem between alkali slug and formation brine. Sodium hydroxide is dissolved in soften brine and a 1.0 PV slug is injected consecutively. At this point, the experiment is divided into two parts: flooding continuously and intermittently. In continuous case, a 0.2 soften brine is injected after alkali slug and followed with brine as chasing fluid. Differently, the alkali-contained sample is removed from core flood cell and aged at room temperature in the intermittent case. The core sample is wrapped by the transparent film to prevent the mass loss during aging period. The samples are aged for 200 hours (around 8 days) and then re-flooded by 0.2 PV soften brine and chasing fluid respectively.

Three concentrations of sodium hydroxide are prepared by using soften brine as a solvent: 0.05, 0.2, and 0.5 molar. Soften brine is chosen as a solvent for alkali substance because it prevents the depletion of alkali by direct contact with divalent ions (Ca^{2+} and Mg^{2+}) from previous brine flood.

4.5.2.3 The Effect of Alkalinity

The effect of alkalinity is performed by changing alkali substance. Sodium hydrogen carbonate which has much less alkalinity is chosen for this test. The procedure is the same as the previous test (the effect of alkali concentration) with the only difference which is substituting sodium hydroxide by sodium hydrogen carbonate at the same concentration.

The difference in alkalinity of sodium hydroxide and sodium hydrogen carbonate can be obviously measured by pH value. At the same concentration and same temperature, sodium hydroxide can be totally ionized in water, yielding plenty of hydroxide ion. On the other hand, sodium hydrogen carbonate which is weak base can be partially ionized, depending on ionization constant (K_b) (which is a function of temperature). Thus, pH value is very high in case of the use of sodium hydroxide (12-14) whereas, in sodium hydrogen carbonate case, pH ranges at lower values (8-9).

4.5.2.4 The Effect of Acid Concentration

The effect of acid number is performed by changing the concentration of oleic acid in soltrol170 during the core preparation phase. The additional oleic concentration in soltrol170 5.0 acid number is prepared and used for the sample saturation. Again, the saturated cores are aged for a week before the core flooding step. Cores are separated into two groups: continuous and intermittent. The procedure is the same as of the previous experiment 4.5.2.2 (the effect of alkali concentration). However, flooding efficiency is expected to be minor compared with the use of 2.0-acid-number oil. The alkali flooding is fixed to start after the oil recovery reaches 0.65.

4.5.2.5 The Effect of the Presence of Initial Water Saturation

Core samples are initially saturated with brine and flooded by oil. At the breakthrough, the average brine recovery is about 0.5 (oil saturation remains 0.5 in the sample) and no additional brine can be produced after. Therefore, the variation of water saturation cannot be performed in this study. Again, the procedure of this test is similar to the previous step in 4.5.2.2, substituting total oil saturated samples by 50 percent-oil-saturated samples. However, the oil recovery in this case is expected to be lower than the cases where samples are absent of initial water saturation. The alkali flooding therefore is performed by considering primarily the WOR value instead of oil recovery. WOR of 3.0 is set as the starting of pre-flush injection.

4.5.2.6 Advanced Combination with Surfactant and Polymer

Additional core floods are run in this phase. Five core samples are initially saturated with acid-soltrol170 at the concentration of 2.0 acid numbers. After cores are aged for a week, following five floods are performed:

- continuous flood by surfactant,
- continuous flood by alkali and surfactant,
- continuous flood by surfactant and intermittent flood by alkali,
- continuous flood by surfactant, intermittent flood by alkali and chase by polymer,
- continuous flood by polymer.

Sodium hydroxide, sodium docecylbenzene sulfonate, and polyacrylamide are used as alkali, surfactant, and polymer, respectively. The optimal concentrations of alkali and surfactant are obtained from IFT test: 0.2 molar and 0.05% w/w respectively. Polymer concentration is 1000 ppm. However, surfactant in this study is anionic type which is proved that it does not have the wettability reversal ability. Therefore, surfactant flooding is only continuously performed. Polymer has the main function to reduce the mobility of injected fluid. Hence, it is continuously injected since it does not have the wettability reversal ability. Polymer is recommended to be injected separately from other chemical slugs (Arihara *et al.,* 1999).

4.6 Alkali Consumption Test

Alkali consumption is one of the most important parameter to indicate the effectiveness of alkali flooding in carbonate reservoir. It is known that alkali consumption increases with time and temperature; however, the use of low alkali concentration limits its loss. The consumption of alkali by rock is believed to have a responsibility for surface charge reversal. Therefore, high oil recovery from low alkali consumption is preferred and indicates the ideal condition. Total alkali consumption (or static consumption) is performed by soaking grinded rock or rock powder in alkali solution. The consumption is then measured by several techniques such as color indicator titration or UV-spectroscopy. But, the consumption in porous media is different depending on the pore geometry and a presence of previous fluid. In this research, alkali consumption test is performed by alkali consumption from the porous media or the dynamic alkali consumption.

4.6.1 Apparatus

A simple titration is chosen for alkali consumption test. The equipment set shown in figure 4.11 composes of: burette 50 ml (A), burette holder (B), bottle of rinsing water (C), volumetric flask 250 ml (D), flat-bottom flask 100 ml (E), and pipette 10 ml and suction rubber (F).

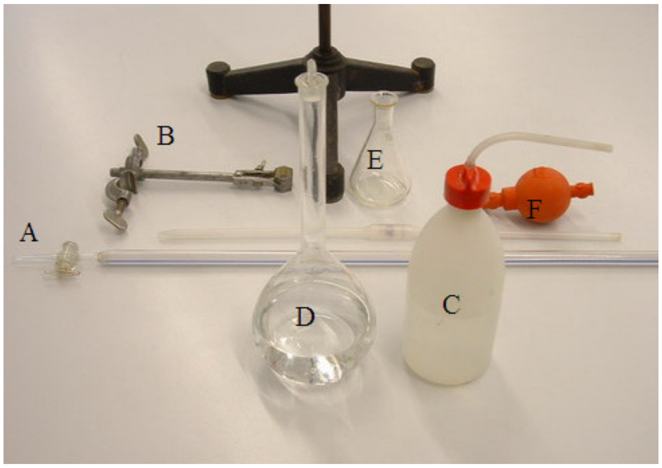


Fig.4.11: Color indicator titration set.

Hydrochloric acid, a titrant, is diluted to low concentrations (0.05-0.1 molar) in order to detect a very low quantity of alkali in the solution (the ratio of hydrochloric acid and sodium hydroxide in the acid-base equation is unity). Phenolphthalein and methyl orange are used as the color indicators. Phenolphthalein is colorless and pink in acidic and basic solutions respectively. In this test, the alkali solution turns from pink to colorless at the end point (pH around 8) where basic and acidic compounds are proportionally reacted. Phenolphthalein is used in the titration of sodium hydroxide which is strong base. Theoretically, the end point from titration between strong base and strong acid is at pH 7-10 whereas, titration between weak base and strong acid is differently at pH around 4. Therefore, the titration of sodium hydrogen carbonate which is weak base needs another indicator that changes color in that range. Methyl orange is then chosen for sodium hydrogen carbonate titration. In the basic solution, methyl orange is yellow while in acidic solution it is red. At the end point, the color changes from yellow to orange and consecutively turns to reddish level within a few drops of hydrochloric acid. The formula of phenolphthalein and methyl orange in basic and acidic solution are illustrated in figure 4.12.

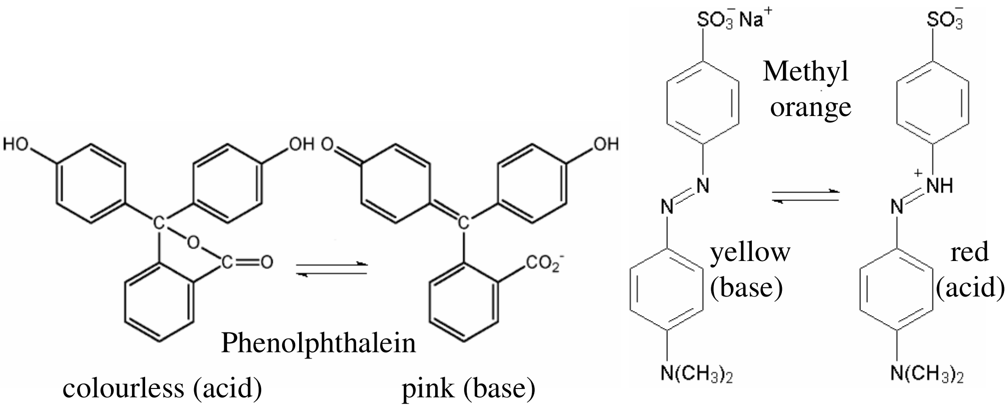


Fig.4.12: Formulation of phenolphthalein and methyl orange.

4.6.2 Methodology

Dynamic alkali consumption in porous media is measured from the collected effluent from alkali-aged samples. However, effluent should be collected only few quantity to avoid the dilution of alkali concentration from the injected brine. The effluent is extracted solely aqueous phase (the bottom phase) for the color indicator titration. Sodium hydroxide which is strong base is titrated with hydrochloric acid, using phenolphthalein as an indicator whereas; effluent with sodium hydrogen carbonate is titrated with hydrochloric acid by the use of methyl orange as an indicator.

Alkali consumption is calculated as a fraction or percentage from the loss alkali concentration divided by the initial alkali concentration which can be expressed as

$$\text{Alkali consumption} = (C_{int} - C_{eff}) / C_{int} \qquad (4.12)$$

where C_{int} and C_{eff} are the initial concentration of alkali and the alkali concentration in effluent respectively.

CHAPTER 5

RESULTS AND DISCUSSION

Results from the experiments which are described in chapter 4 are reviewed in this chapter. Rock and fluid properties are not included in this part because the details are already shown in a previous chapter. This chapter is sub-divided in five sections: interfacial tension (IFT) measurement, wettability measurement, wettability alteration measurement, core flood test, and alkali consumption test.

5.1 Interfacial Tension Measurement

Results are plotted in linear scale between the concentration of interest chemical and the IFT value. Chemical concentrations are in different units, depending on type of chemical. Alkali concentration is shown in molar, whereas weight percent is used for surfactant concentration. The unit of IFT value is in dynes/cm.

5.1.1 The Effect of Alkali Concentration on IFT

The effect of alkali concentration on IFT of the system composed of oleic acid-soltrol170 and sodium hydroxide is illustrated in figure 5.1.

The red solid line represents the IFT values at the moment that two immiscible phases are in contact. The line rapidly declines from a zero-concentration point to a concentration of about 0.20 molar. After that, the increment of alkali concentration yields a linear reduction of IFT. The reduction of IFT value is caused by products of the reaction between oleic acid in oil phase and sodium hydroxide in aqueous phase. This well known reaction is called *"saponification"* reaction. In this case, sodium oleate is produced. A molecule of sodium oleate contains two different characters: hydrophobic and hydrophilic as seen in figure 5.2.

A hydrophobic part dissolves in oil phase (non-polar), while a hydrophilic part sticks into aqueous phase. The sodium oleate therefore links oil and aqueous phases together. At very low alkali concentrations, there are a few molecules of sodium oleate at the interface. An increase of alkali concentration drastically decreases IFT value by producing sodium oleate to the interface. At alkali concentrations higher than 0.2 molar, sodium oleate molecules moderately occupy the interface. The addition of sodium oleate onto the interface is more difficult and hence, the IFT value slightly decreases as a linear function with alkali concentration.

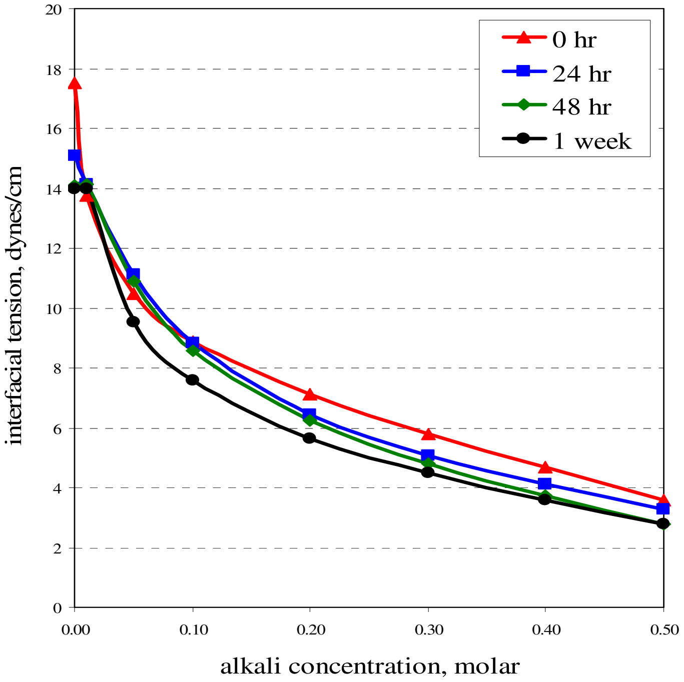


Fig. 5.1: The effect of alkali concentration on IFT.

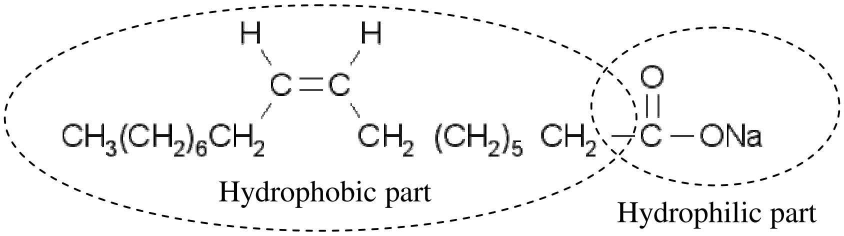


Fig.5.2: Molecular structure of sodium oleate.

IFT values are re-measured after 24 hours, 48 hours, and one week. The data are plotted in blued, green and black solid line, respectively. The IFT at no-alkali concentration slightly decreases from 17.5 to 14 dynes/cm within a week. This slightly decrease of IFT is responsible by partitioning effect (Madsen and Lind, 1997). Basically, oleic acid, which is a non-polar material, can be slightly dissolved in aqueous phase but this occurs slowly (depending on partitioning coefficient). Some molecules of oleic acid diffuse across the interface and in the same time, link the interface together. Consequently, IFT slightly decreases. At 24 and 48 hours, IFT values remain constant in a low alkali concentration zone. At the alkali concentrations higher than 0.2 molar, IFT values keep reducing as time has risen because some additional molecules of sodium oleate are generated at the interface.

Conclusively, IFT values decreases as time increases. Alkali concentration directly affects the IFT by controlling the concentration of sodium oleate at the interface. Moreover, alkali concentration also drives the two-phase system to reach the equilibrium stage: a higher alkali concentration reaches equilibrium quicker.

The alkali concentration of 0.2 molar is reasonably chosen as an optimal concentration because it is the point at which IFT reduction changes its trend. This point represents the alkali concentration that correspondingly yields an optimal quantity of in-situ soap sodium oleate at the interface.

5.1.2 The Effect of Surfactant Concentration on IFT

The behavior of surfactant in two-phase system is different from alkali substance. The effect of surfactant concentration (dodecylbenzenesulfonate or petroleum sulfonate) on IFT is illustrated in figure 5.3.

At very low surfactant concentrations, surfactant molecules dispersedly dissolve in aqueous phase as monomers. Some monomers move reach the interface and reduce the IFT by the action of hydrophilic-hydrophobic contained in the molecule of surfactant. IFT value drastically decreases as the concentration is slightly increased. The ultra-low IFT reaches in this concentration range. At the surfactant concentrations more than 0.05 %w/w, IFT values re-increase because monomers start to agglomerate, causing the particles called "*aggregates*" or "*micelles*". These particles occur by the orientation of hydrophobic tail of some monomers to associate among themselves in order to balance the charge. Thus, some active monomers deplete with monomer agglomeration and this results in a reduction of surfactant efficiency.

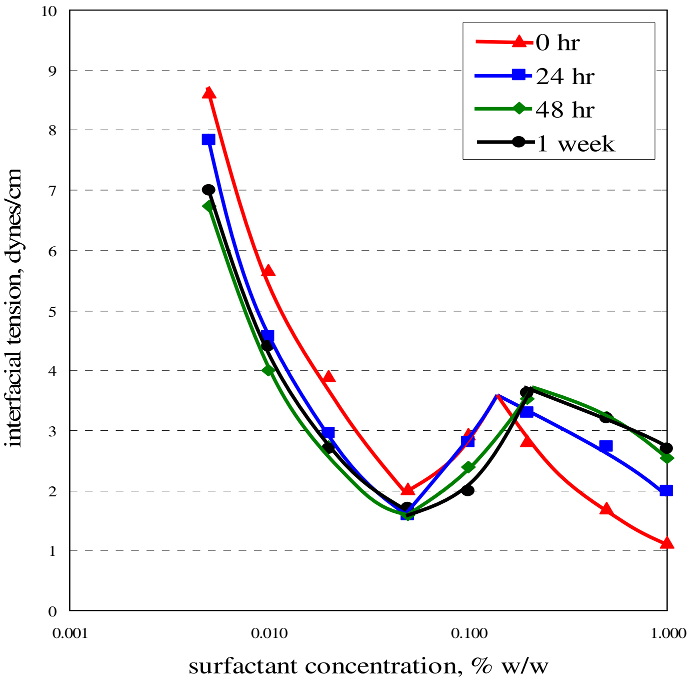


Fig. 5.3: The effect of surfactant concentration on IFT.

IFT value decreases again at surfactant concentrations higher than 0.2 %w/w. This reduction of IFT value is caused by the presence of middle phase microemulsion formed by the swollen micelles (Lake, 1989). In aqueous phase, swallow micelles cover the oil globule by sticking the hydrophobic tail inside oil and exposing hydrophilic head to the aqueous phase. Swollen micelles can also be formed in oil phase by a group of monomers sticking hydrophilic heads inside water globule and exposing hydrophobic tails to oil phase. The middle phase microemulsion is illustrated in figure 5.4.

Low IFT appears twice in this experiment. First, at the critical micelle concentration (CMC) which is the concentration micelles are initially formed. At this concentration, the quantity of monomer is maximal. In our experiment, the CMC appears at 0.05 %w/w. The second low IFT appears at the high concentration of about 0.5–1.0 %w/w in where a stable microemulsion layer is formed in the system.

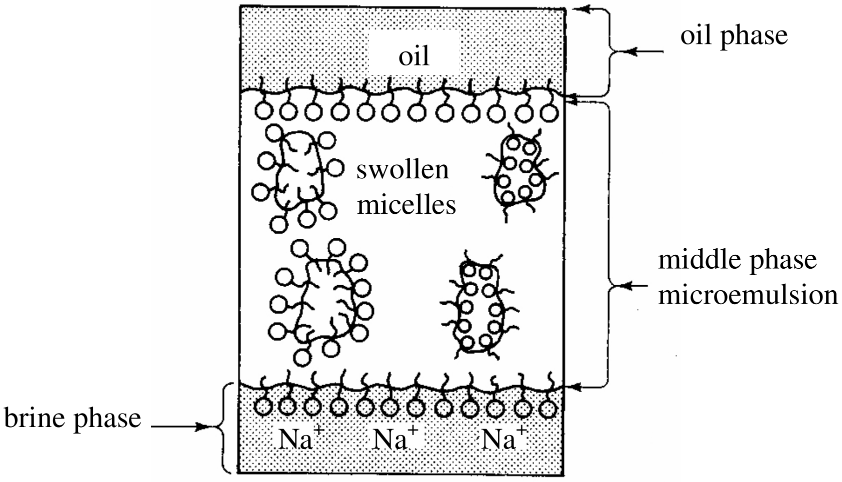


Fig. 5.4: Microemulsion between oil and aqueous phases.

As time increases, IFT slightly decreases in a low surfactant concentration zone (0–0.05 %w/w). The slight decrease of IFT is caused by the diffusion and rearrangement of monomers at the interface. In the opposite, IFT increases with time in higher concentration zone because the microemulsion becomes less stable. The lowest IFT value obtained at CMC, is more favorable because lesser amount of surfactant is required and moreover, the IFT is kept reducing as time increases.

The intensity magnitude of IFT reduction scale, obtained from the use of surfactant and the use of alkali, is obviously different. Surfactant renders the lowest IFT value around 1-1.5 dynes/cm, whereas alkali lowers IFT to the range of 2-8 dynes/cm at their optimal concentrations.

5.1.3 The Effect of Alkali-Surfactant Concentration on IFT

Figure 5.5 shows the results in the presence of both surfactant and alkali substances in the two-phase system. Solid and dash lines represent the result when 0.05 and 0.1 % w/w of surfactant is added into alkali solution respectively.

At very low alkali concentrations (around 0.001 molar), IFT increases for every time step (based on the IFT from no-alkali concentration). A trace amount of alkali is not adequate to drive the acid-base reaction at the interface. Ionized alkali molecules remain in the bulk aqueous phase and as a consequence, part of surfactant molecules, which are anionic, associate with ionized sodium. The association of surfactant and sodium ion causes the reduction of potential surfactant molecules. IFT values start to decline regularly at alkali concentration higher than 0.001 molar. An adequate of alkali concentration drives alkali molecules to reach the interface and to react with acid compounds and thus, the in-situ soap is created. The shape of curves is similar to that of the results obtained when solely alkali substance is used: sharply declines at the initial and becomes slightly-declined straight line after the alkali concentration of 0.2 molar.

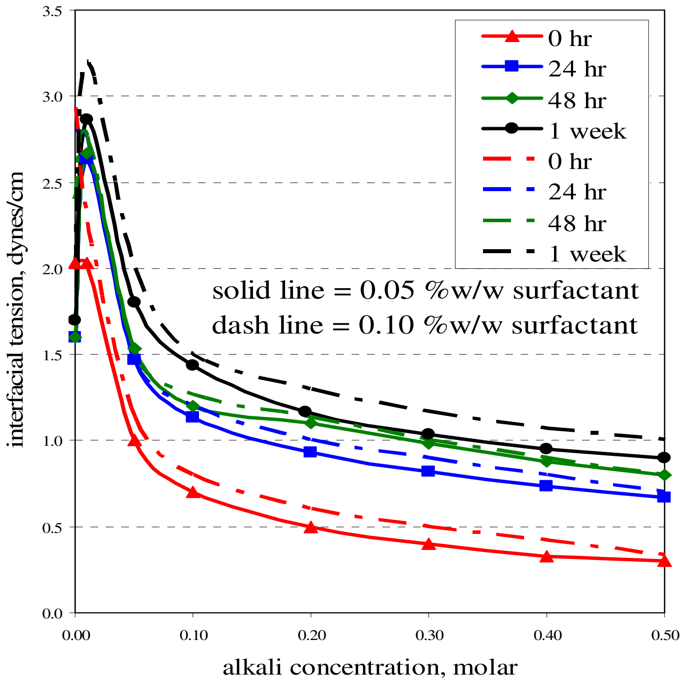


Fig. 5.5: The effect of alkali concentration on IFT in the presence of surfactant.

The IFT values obtained from the use of 0.05 % w/w surfactant (solid line) are slightly lower than the use of 0.10 % w/w surfactant (dash line). This indicates that the use of surfactant at CMC renders the lowest IFT even alkali substance is present. The association of alkali and surfactant reduces IFT to relatively low level compared with the use of solely alkali or surfactant. In this study, IFT values are lower than 1.0 dynes/cm in some alkali concentrations with the presence of surfactant at CMC. Alkali supplies ions that drive surfactant molecules to the interface and alkali itself reacts with acid in oil phase to produce the in-situ surfactant.

Figure 5.6 shows the comparison between solely alkali and surfactant-alkali solutions (0.05% w/w of surfactant). A big gap of IFT reduction is obviously seen. Surfactant is a more potential substance in IFT reduction compared with alkali substance. The combination of alkali and surfactant shows the lowest IFT result which is the most favorable condition. As time has risen, IFT values slightly increases for every alkali concentration. The decrease of surfactant molecules at the interface by agglomeration with sodium ions during the aging time causes this slight increment of IFT.

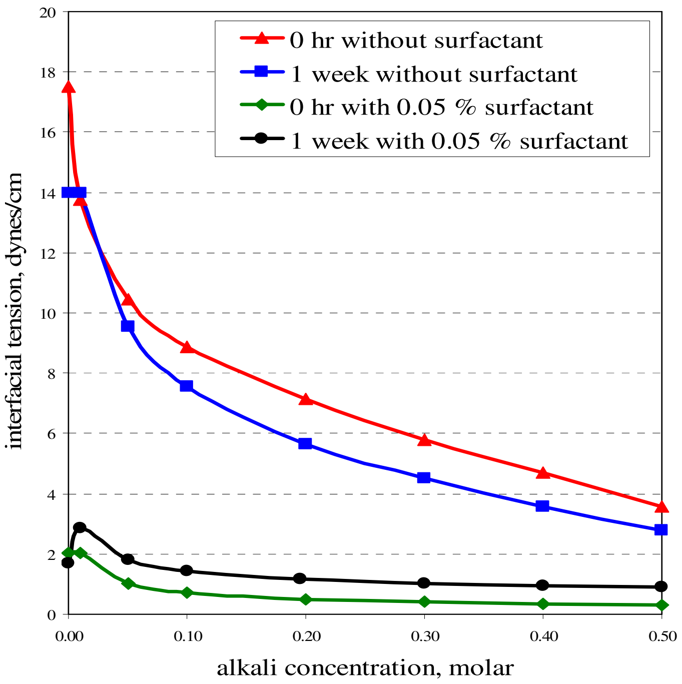


Fig. 5.6: Comparison between IFT obtained from alkali and surfactant-alkali solutions.

The IFT reduction by the use of solely alkali substance does not show the hump in a very low alkali concentration zone. This phenomenon occurs only when surfactant is present. The hump is caused by the interaction of surfactant and alkali and this causes in the reduction of available number of surfactant to reach the interface. In the absence of surfactant, there is not other different charged species that can cause the interaction with alkali substance.

5.1.4 The Effect of Salinity on IFT

In this section, distilled water is substituted by brine because brine is a commonly used alkali solvent in a field application. Brine is prepared at different concentrations. Sodium Chloride (HCl) is solely used in this test because other substances in sea brine providing divalent ions foresee an obvious interfere in IFT reduction. Thus, soften brine, in which divalent ions are absent, is generally chosen as solvent for chemical flooding. Alkali and surfactant are both present in aqueous solution. Surfactant concentration is kept constant at the CMC (0.05 %w/w), while three alkali concentrations around the optimal range (0.15, 0.20, and 0.25 molar) are chosen (according to the result in section 4.2.2.1). Figure 5.7a-d demonstrates the change of IFT values in each of the following time steps: 0 hour, 24 hours, 48 hours, and 1 week, respectively.

At initial time step (Figure 5.7a), IFT values are relatively low for every salt concentration compared with the rest time steps. The optimal salinity appears at the salt concentration of about 0.2-0.3 %w/w. The use of 0.25 molar alkali concentration yields the lowest IFT values compared with other alkali concentrations. As time increases, IFT values increases for every measurement. However, at salt concentration higher than 0.2 %w/w, IFT values changes only a bit from the initial time step. This signifies that a more stable condition can be achieved at this salinity. From figure 5.7 b, c, and d, the optimal salinity appears at 0.2 %w/w for every alkali concentration according to the lowest IFT and the stability of low IFT value.

At a time step of one week, IFT value at salinity higher than 0.2 %w/w remains at low value around 0.7 dynes/cm for every alkali concentration. The low IFT, which is favorable, can be achieved also when the salinity is higher than the optimal salinity for all chosen alkali concentrations.

Salinity indirect affects IFT value. Sodium and Chloride ions (Na^+ and Cl^-), which are primarily found in brine phase, drive surfactant molecules and hydroxide ions to the interface (Chan *et al.,* 1982). Surfactants molecules rapidly stick the hydrophobic part into oil phase, while hydroxide ions from alkali react with acid in oil phase, generating the in-situ surfactant (sodium oleate). At the salt concentration of

0.2 %w/w, surfactant and sodium oleate molecules can stably link oil and aqueous phases. High salinity can cause the deactivation of soap and surfactant at the interface, resulting in a slight increase of IFT as seen in the range of concentration higher than optimal salinity (Chan and Yen, 1981). The unstable condition in IFT reduction can be obviously seen in salt concentration lower than 0.2 %w/w where the agglomeration between anionic surfactants and sodium ions is predominant.

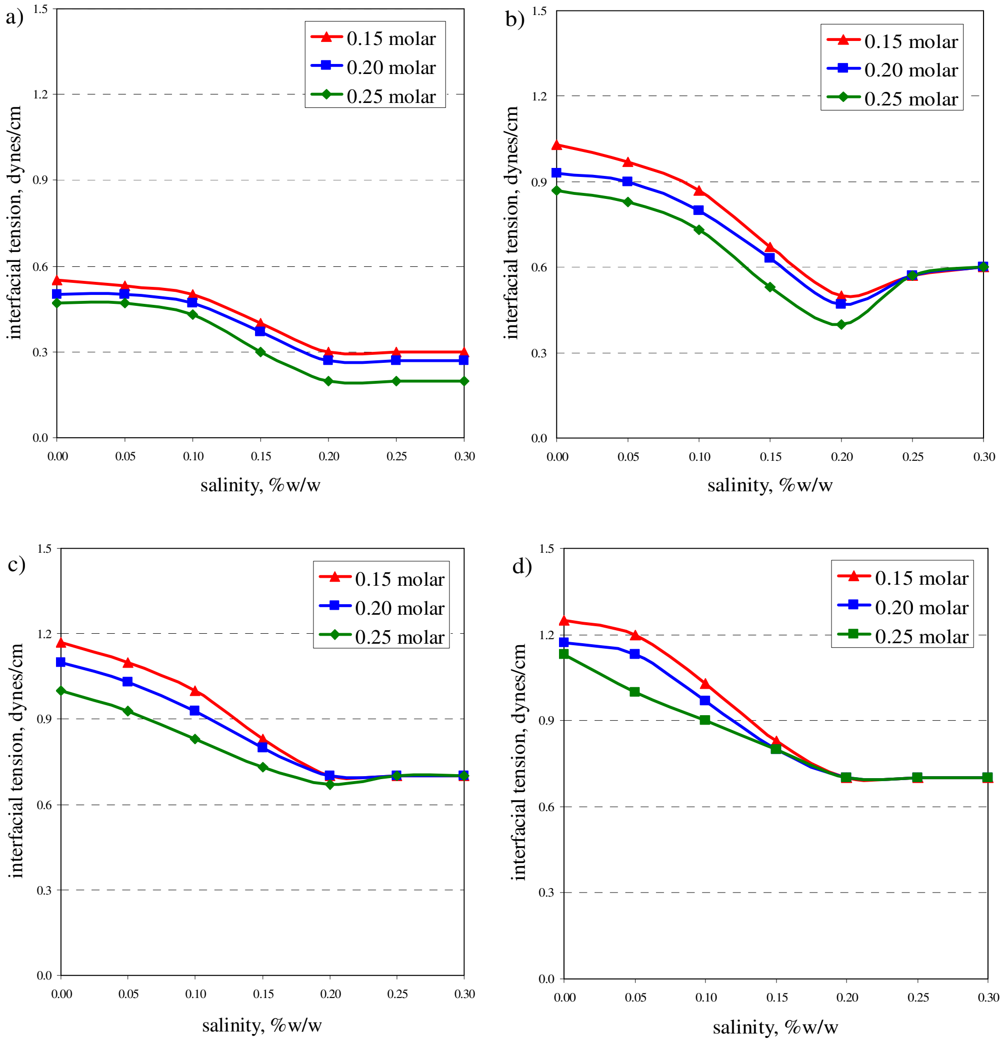


Fig. 5.7: The effect of salinity to IFT at different time step:

a) 0 hour, b) 24 hours, c) 48 hours, and d) 1 week.

The effect of salinity on each alkali concentration is shown in figure 5.8. The curves are similar for every alkali concentration in every time step. A bit lower IFT values are observed for the alkali concentration of 0.25 molar. After one week, there is not difference of IFT value among alkali concentrations especially at high salinity.

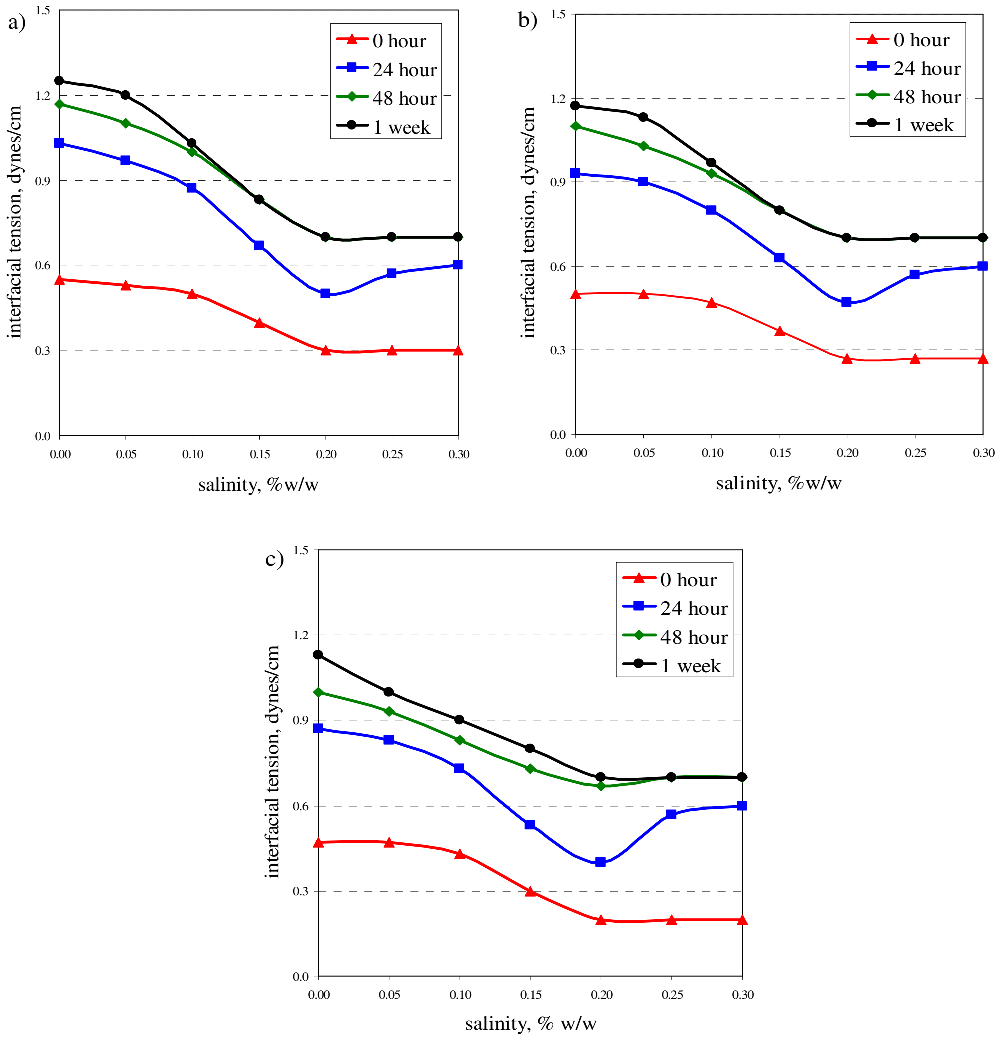


Fig. 5.8: The effect of salinity to IFT at different alkali concentration: a) 0.15 molar, b) 0.20 molar, and c) 0.25 molar.

Practically, the salinity of average sea brine is around 35 ppt which is equivalent to 0.35 %w/w. However, this concentration includes also divalent ions. Divalent ions cause the depletion of alkali and results in less effective in IFT reduction. Soften brine is frequently used for the ultra-low IFT flood instead of normal brine. Soften brine can be prepared from normal brine by removing compounds containing divalent ions. Therefore, the salinity of soften brine is lower. In this research, the salinity of soften brine is 28 ppt (equivalent to 0.28 %w/w). This obtained by removing Calcium and Magnesium Chloride ($CaCl_2$ and $MgCl_2$). The salinity of soften brine still predictably yields the lowest IFT according to data in this section.

5.1.5 Summary

IFT measurement is a compulsory test before performing a chemical flood. Alkali substance reduces IFT by producing in-situ soap from saponification reaction with acid in oil phase at the interface. From the experiment, the alkali concentration of 0.2 molar is chosen as an optimal alkali concentration. However, surfactant is a more potential substance in IFT reduction compared with alkali. The use of surfactant at the CMC, which is 0.05 %w/w, renders the lowest IFT. The combination of alkali and surfactant moreover yields better result; the IFT is further reduced lower than 1.0 dynes/cm in a proper range of alkali and surfactant. The optimal salinity appears at 0.2 %w/w. Higher salinity than the optimal value shows the tendency of IFT stability. The use of soften brine would render and stabilize an ultra-low IFT value because its salinity is not much higher than the optimal salinity and divalent ions are absent. These optimal concentrations of chemical substances are utilized in the following experiments.

5.2 Wettability Measurement

The Amott-Harvey wettability index is the method to measure an average wettability of the rock samples. The obtained index value represents the whole wettabiltiy of that sample. Thus, the homogeneity of chemical treated sample is needed to be checked before performing the wettability measurement.

5.2.1 Control of Homogeneity of Wettability

Lecce stone samples are saturated with distilled water and soltrol170. In the case where samples are saturated with distilled water, the wettability of the samples is non-doubtfully homogeneous according to the purity of distilled water. But, in the case where samples are initially saturated with soltrol170 (acid-free but with some minor natural contaminants remained from refinery process) or oleic acid-sotrol170, the heterogeneity of wettability change occurs by the adsorption of impurities and acid onto the rock surface. Therefore, it is compulsory to control the change of the wettability from acid adsorption mechanism. However, the wettability reversal by acid adsorption directly depends on aging time (Hirasaki and Zhang, 2004); thus, the wettability change control is needed to be performed at different time step.

The T_1-weighted image, which is the result of an SR MRI experiment, is utilized primarily to observe the diffusion of impurities during the sample preparation step. The ideal sample must have a homogeneous wettability in order to represent the only one value of wettability. For example, in the case where acid adsorption is expected, the adsorption has to occur homogeneously for all over the sample. The tomography images shown in figure 5.9a-f, taken every 24 hours for six days, visualize the diffusion of the acid inside an sample.

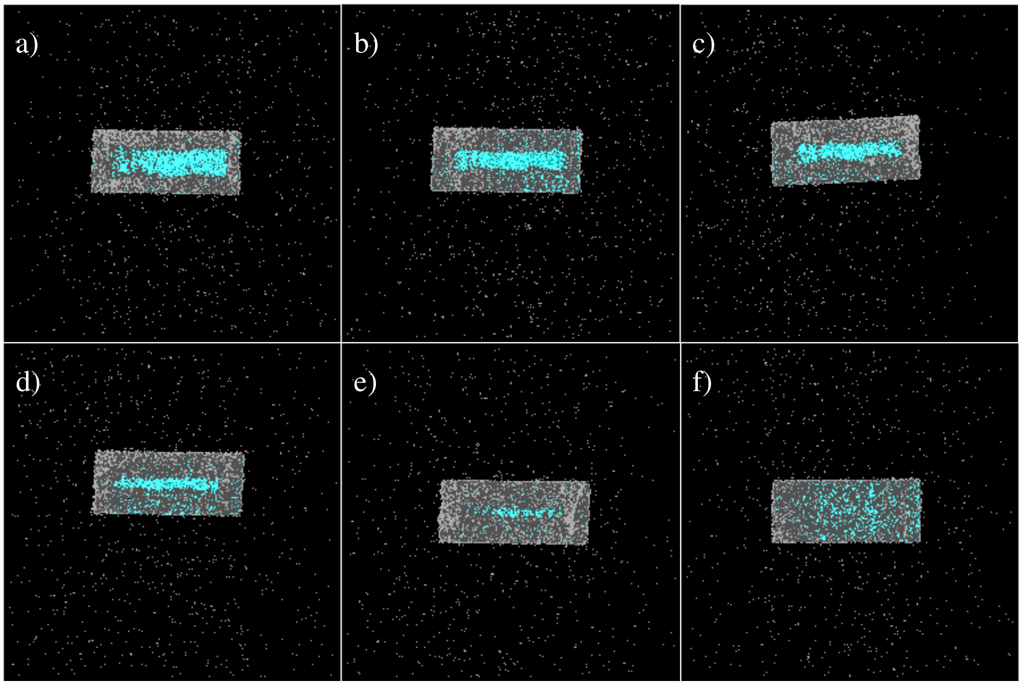


Fig. 5.9: T_1-weighted images obtained from sample saturated with acid-soltrol170 at: a) 1day, b) 2days, c) 3days, d) 4days, e) 5days, and f) 6days.

A simple description of this behavior could be the follows. During the vacuum sample saturation, soltrol170 and oleic acid enters a rock sample with different rate. Soltrol170 which is a non-polar lighter molecule enters a rock sample faster than oleic acid which is a slightly-polar heavy molecule. Oleic acid is moreover absorbed onto the rock surface during the way to reach the core of rock sample because of its negative charge which is attracted to the positive charge of carbonate surface. Therefore, the occurrence of oil-wet condition starts from the outside boundary of the sample, representing by grey color in figure 5.10 a-f. As aging time increases, the acid adsorption zone moves forward to the core zone of sample by diffusing through pores which is already saturated by soltrol170 (green color area). The use of higher acid concentration is expected to have a higher rate of acid diffusion. The size of sample also has the effect on wettability development. The thicker sample would need longer aging time to complete the wettability reversal to oil-wet condition. The adsorption of acid onto the rock surface happens rapidly in the first period and the rate of adsorption decreases during the aging period (Yan *et al.,* 1997). However, an aging period of one week is adequate in this study according to the result from tomography.

Although the relation between NMR relaxation time and wettability is known from long time (Brown and Fatt, 1956), also owing to the experimental difficulty of the subject, we have preferred to use NMR essentially only in a qualitative manner.

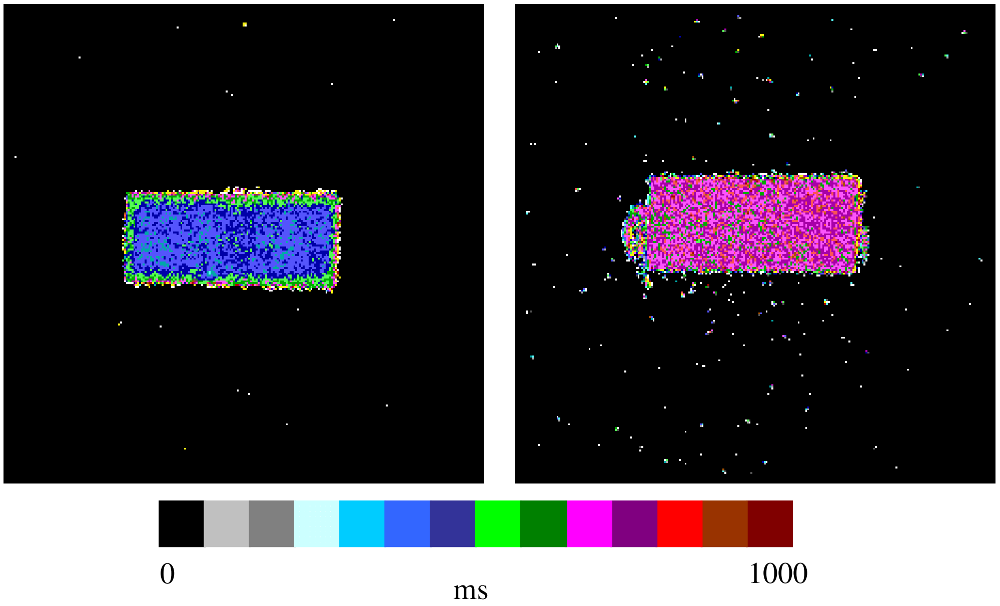


Fig. 5.10: T_1 Maps for sample saturated with:

a) pure soltrol170 and b) oleic acid soltrol170 (with 5.0 AN).

In any case, the tomograph images that we have collected induce one to make some simple analytical consideration. Figure 5.10 a and b show T_1 map (from

Saturation Recovery experiments) for samples saturated with acid-free soltrol170 and oleic acid soltrol170 (with 5.0 AN) respectively. Both samples are saturated and aged in the saturating solutions for a week before the test in order to allow the completion of wettability inversion.

As shows the figure 5.10a, the T_1 map obtained from sample saturated with pure soltrol170 is almost all represented by blue color (about 430 ms), except a thin green boundary (about 570 ms) that seems to indicate that there are some adsorbed impurities contained in soltrol170 and that these impurities have altered the wettability of the rock surface. In the case where sample is saturated with acid-soltrol170 (figure 5.10b), the signal is shown by pink color (about 710 ms) for all over the sample.

This seems to state that by means of T_1 maps one could study not only the diffusion of the impurity inside the sample, but also evaluate the value of wettability of the sample. But this analysis would need a more sophisticated set of experiments that go beyond the scope of present work.

5.2.2 Amott-Harvey Wettability Index

After samples are saturated and aged for a week, allowing sample to complete the wettability reversal mechanism, they are ready for the wettability index measurement. Three cases are studied in this section and two samples are tasted for each case in order to confirm the repeatability.

The first case, two samples are saturated with distilled water and centrifuged until they reach the Irreducible Water Saturation (IWS) stage (practically, this step takes two hours). The samples are then tested by Amott-Harvey method as described in chapter 4 (Table 4.6). Table 5.1 shows the liquid volume in samples at each step and the wettability index which is calculated from the Amott-Harvey method.

Table 5.1: Wettability index of natural sample initially saturated with distilled water.

Property	**Sample1**	**Sample2**
V_t, cm^3	12.1700	12.0327
V_{wi}, cm^3	8.4487	8.4938
V_{wsp}, cm^3	8.9938	8.7819
V_{wt}, cm^3	9.6542	9.1776
δ_w	0.4559	0.4213
V_{oi}, cm^3	2.5158	2.8550
V_{osp}, cm^3	3.1049	3.1574
V_{ot}, cm^3	3.7212	3.5389
δ_o	0.4887	0.4421
δ	-0.0328	-0.0208

The initial water volume inside the samples of 8.5 cm^3, which correspondingly equals to the IWS of 0.7, is relatively high. Naturally, any rock which is primarily deposited in water environment tends to be water-wet. However, this volume cannot definitely confirm the water wetness of rock because high IWS can be caused from the pore geometry. It is possible that oil cannot displace water occupying in micro pores even the forced displacement is applied. The volumes of water in rock samples after water imbibitions and forced displacement render a moderate wettability to water ratio (0.46 and 0.42 for sample1 and 2 respectively). After samples are forced displaced by water, ROS reaches very low value (around 0.2) which is opposite of IWS. However, the ratio of oil volumes in samples after oil imbibitions and forced displacement is not different from that of ratio obtained by water displacement (0.49 and 0.44 for sample1 and 2 respectively). The wettability index calculated by Amott-Harvey method in this case equal to -0.0328 and -0.0208 for sample 1 and 2 respectively and these values indicate that rock samples are neutral-wet.

The second case, samples are initially saturated with pure soltrol170. Table 5.2 demonstrates the liquids volumes at each step of Amott-Harvey wettability method and the wettability index which is calculated at the end.

Table 5.2: Wettability index of natural samples initially saturated with pure soltrol170.

Property	**Sample1**	**Sample2**
V_t, cm^3	11.8428	11.8474
V_{oi}, cm^3	4.6756	4.6945
V_{osp}, cm^3	4.9766	4.9933
V_{ot}, cm^3	7.0406	7.0533
δ_o	0.1273	0.1267
V_{wi}, cm^3	4.8021	4.7941
V_{wsp}, cm^3	6.1347	6.1049
V_{ot}, cm^3	7.1672	7.1530
δ_w	0.5635	0.5557
δ	0.4362	0.4290

The oil saturated samples are forced displaced until Residual Oil Saturation (ROS) is reached. The oil volumes inside samples at this step are 4.68 and 4.7 cm^3 for sample1 and 2 which are convertible to ROS of about 0.4. ROS obtained in this second case is much higher than ROS in first case. This is caused by the opposite phenomenon; micro pores are primarily occupied by oil. However, ROS by the displacement of water is much lower than the reverse mechanism; IWS by the displacement of oil (in first case). This means that, micro pores are preferentially adhered by water. It can be obviously seen that Lecce stone tends to be water-wet as seen from wettability index in this step. Wettability index to oil is much lower than the wettability to water. The value of wettability index around 0.43 signifies a moderate water-wet condition.

According to the results from these two cases, Lecce stone tends to be neutral- to moderately water-wet when the wettability induced materials are absent (the wettability is dependant from the initial phase that occupies the micro pores).

In the third case, the wettability induced material is present. Two samples are saturated by oleic acid-soltrol170. Table 5.3 shows the liquid volumes from each step according to the Amott-Harvey wettability index test.

Table 5.3: Wettability index of samples initially saturated with oleic-soltrol170.

Property	**Sample1**	**Sample2**
V_t, cm^3	12.0745	11.5096
V_{oi}, cm^3	5.0288	5.1401
V_{osp}, cm^3	7.0073	6.7190
V_{ot}, cm^3	7.0811	6.8230
δ_o	0.9601	0.9382
V_{wi}, cm^3	4.9933	4.6865
V_{wsp}, cm^3	5.0182	4.6999
V_{wt}, cm^3	6.8457	6.3695
δ_w	0.0135	0.0079
δ	-0.9467	-0.9303

The samples treated with oleic acid are strongly oil-wet. The wettability index of about -0.94 indicates that oil has a high ability to imbibe water; around 95% of expelled water is responsible by oil imbibitions. On the other hand, only a few percents (less than 1.5 %) of water can imbibe oil. This indicates that the polar interaction between oleic acid and carbonate surface yields samples a strongly oil-wet condition.

5.2.3 Summary

The strongly-oil wet condition can be artificially prepared by the polar interaction (or direct acid adsorption). A period of one week is adequate to complete the wettability reversal as seen from MRI images. The Amott-Harvey wettability index shows that Lecce stone is reversed from a moderately water-wet in natural condition to strongly oil-wet by the artificial sample preparation.

5.3 Wettability Reversal Measurement

In this study, the wettability reversal is the attempted to change the surface wettability from unfavorable to a more favorable condition or to the less oil-wet condition. The experiments are primarily divided in two parts to study the difference obtained from non-aging (continuous) and aging (intermittent) flows. Results are shown by the curves plotted between flooding time and oil recovery. The relative oil recovery is the parameter used in this step in order to compare the oil recovery from different flow method. The relative oil recovery is the additional produced oil saturation obtained from alkali flooding divided by the ultimate ROS before the starting of alkali flooding. The residual oil is also plotted with flooding time. The wettability indexes are measured at the end of flooding process (14 hours) and the obtained wettability index are plotted with corresponding ultimate oil recovery.

5.3.1 Continuous Flow

Three continuous flow cases are designed with different three flooding solutions: 1) surfactant 0.05 %w/w, 2) alkali 0.2 molar, and 3) alkali-surfactant with the concentration of 0.2 molar and 0.05% for alkali and surfactant respectively. In each case, two samples are flooded in centrifugal with flooding solution. Samples are previously flooded with distilled water until they reach ROS. Then, flooding solution is substituted distilled water and the samples are flooded with solutions continuously. Figure 5.11a and b show the results from the use of three solutions in continuous flow.

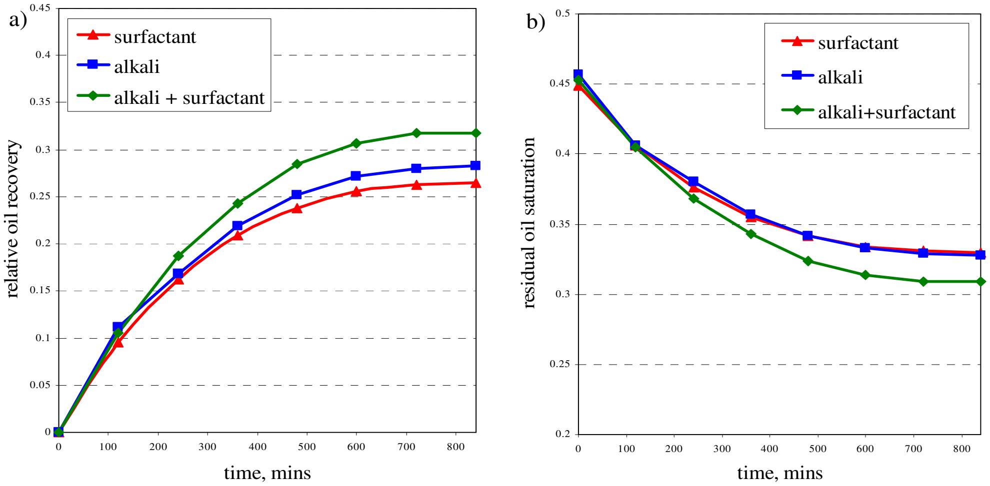


Fig. 5.11: Oil saturation of samples at different flooding time flooded continuously: a) relative oil recovery and b) residual oil recovery.

Figure 5.11a illustrates the relative oil recovery as time increases for the three solutions. The relative oil recovery obtained from alkali-surfactant solution is the highest; around 32% of ROS is further produced. Solely alkali and surfactant solutions render less relative oil recovery of 28% and 26.5% respectively. The combination of alkali and surfactant solution yields the best result in continuous flow by reducing the IFT to ultra-low condition. The use of solely alkali or surfactant does not give much different. Figure 5.11b confirms the potential of the combination between alkali and surfactant compared with the uses of solely alkali and surfactant solution. IFT strongly affects the oil recovery in the continuous flow by generating an ultra-low IFT condition and as a consequence, the emulsification and entrainment between oil and injected solution occurs simultaneously (Donaldson, 1989).

5.3.2 Intermittent Flow

In the intermittent flow cases, four flooding solutions are chosen: alkali 0.05 molar, alkali 0.2 molar, alkali 0.5 molar and the combination of alkali 0.2 molar and surfactant 0.05%. The use of solely surfactant is not included in this step because anionic surfactant does not reverse the surface charge of carbonate rock and it can be totally adsorbed onto the rock surface (Wu *et al.,* 2006). Figure 5.12a and b show the results from flooding combined with intermittent flow of four different flooding solutions.

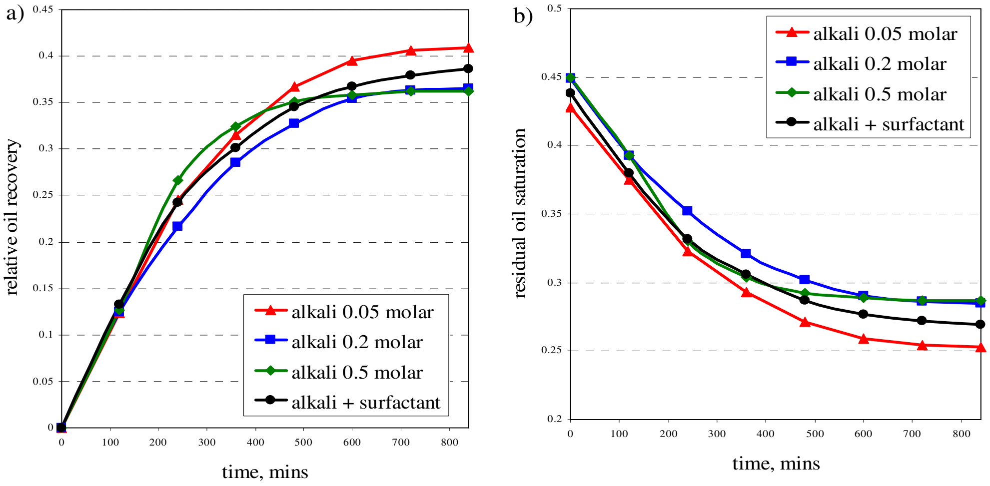


Fig. 5.12: Oil saturation of samples at different flooding time flooded intermittently: a) relative oil recovery and b) residual oil recovery.

The relative oil recovery observed from figure 5.12a can be ordered from the highest to the lowest as: alkali 0.05 molar, alkali (0.2molar)-surfactant, alkali 0.2 molar, and alkali 0.5 molar. As mention in several wettability literatures, the wettability reversal preferentially occurs at alkali concentration lower than 1.0 % w/w which is equivalent to 0.25 molar for sodium hydroxide (Arihara *et al.,* 1999). The intermittent flow allows alkali molecules to reverse the surface charge to negative; consequently, adsorbed molecules are released by the repulsion of the same charge and this results in a more favorable condition (less strong oil-wet) Alkali concentration of 0.05 molar shows the best performance in intermittent flow; yields the relative oil recovery of 41% and only 20% of OOIP is left in the sample. This means strongly oil-wet rock can be maximally extracted up to 80% of OOIP by this combination. At the higher alkali concentration than 1% w/w, the IFT reduction is predominant, resulting in a remarkable early oil production. This IFT reduction can be seen from the use of alkali concentration of 0.5 molar. Oil is early produced in the first period, reaching a relative oil recovery of 0.365 and only a bit of additional oil is produced after. The use of alkali concentration at 0.2 molar eventually yields the relative oil recovery as same as 0.5 molar. The combination of alkali and surfactant gives better result compared with the used of solely alkali solution (at the same alkali solution). Surfactant is more potential in IFT reduction and in the presence of alkali, surfactant can work effectively without the loss by surface adsorption.

5.3.3 Comparison between Continuous and Intermittent Flows

The comparisons between continuous and intermittent flow are shown in figure 5.13a and b.

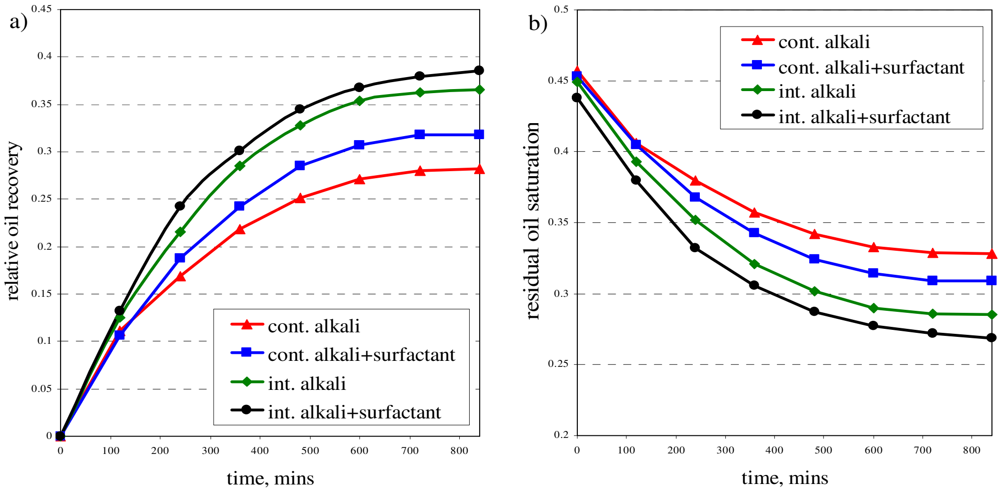


Fig. 5.13: Comparison of oil saturation of samples obtained from continuous and intermittent flows: a) relative oil recovery and b) residual oil recovery.

Intermittent flow renders relatively higher the oil recovery for every case. The increments of relative oil recovery by intermittent flow compared with continuous flow are about 10% and 7% for the use of solely alkali and alkali-surfactant respectively.

At the end of chemical flooding by centrifugal, each sample is re-measured for the Amott-Harvey wettability index. Table 5.4 summarizes the wettability index to water, wettability index to oil, wettability index, and the ultimate relative oil recovery from every case. The relationship between wettability index and ultimate relative oil recovery is consecutively plotted in figure 5.14.

Table 5.4: Wettability index and ultimate relative oil recovery from every flooding.

Flood method	δ_w	δ_o	δ	**recovery**
Continuous surfactant	0.010	0.640	-0.630	0.265
Continuous alkali	0.030	0.550	-0.520	0.282
Continuous alkali+surfactant	0.073	0.450	-0.377	0.318
Intermittent alkali 0.5M	0.155	0.381	-0.226	0.362
Intermittent alkali 0.2M	0.145	0.362	-0.217	0.365
Intermittent alkali+surfactant	0.140	0.240	-0.100	0.386
Intermittent alkali 0.05M	0.134	0.045	+0.089	0.409

From figure 5.14, the wettability index of every case is primarily affected from the wettability to oil. The wettability to water is relatively small especially in the low relative oil recovery zone (continuous floods). As described before, alkali reverses the oil-wet surface by changing the surface charge to negative. Hence, adsorbed molecules are released by charge repulsion, resulting in a less preference to oil. However, alkali does not change the preference of surface to water and this result in an ultimate wettability of a neutral-wet condition.

In the case of optimal relative oil recovery, the wettability of rock is reversed from -0.940 to +0.089 which is the neutral-wet. However, Jadhunandan and Morrow (1994) concluded that wettability ranges from neutral-wet to moderate water-wet condition, yields an optimal oil recovery (better than strongly water-wet condition) because the snapped-off as blobs of oil is absent.

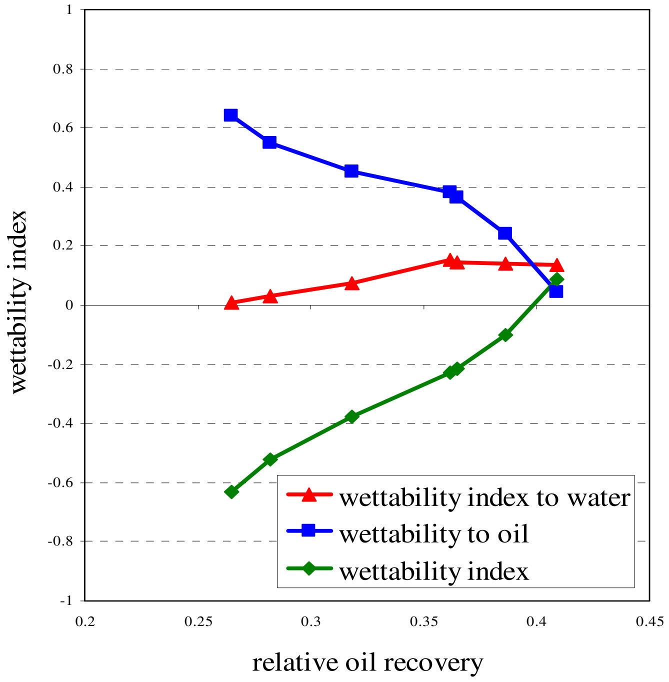


Fig. 5.14: Relationship between ultimate relative oil recovery and wettability index.

5.3.4 Summary

The preliminary wettability reversal test demonstrates that the alkali flooding combined with intermittent flow yields better oil recovery result than flooding combined with continuous flow. The improvement of oil recovery is caused by the wettability reversal from oil-wet to neutral-wet condition which is a more favorable condition for displacement process by aqueous phase. However, alkali substance changes the wettability by reducing the preferential to oil, whereas the preferential to water is not significantly changed.

5.4 Core Flooding

5.4.1 Continuous Waterflood and Brine Flood

Three samples saturated with 2.0 AN of oleic acid in soltrol170 are flooded with three flooding solutions: distilled water, brine, and soften brine. Figure 5.15 demonstrates the results from these three floods by the plots between oil recovery and the water-oil ratio (WOR). These plots are also called the waterflood performance curves.

The floods by distilled water and normal brine show the breakthrough recovery of 0.45, while the use of soften brine yields higher breakthrough recovery of 0.49. The higher in breakthrough recovery indicates the higher flooding efficiency. The flood by soften brine renders high efficiency because the presence of sodium ions and carbonate ions promotes the IFT reduction during the continuous flow. WOR from the use of normal brine increases faster than that of using distilled water and soften brine. The presence of divalent ions in normal brine, which normally are calcium and magnesium (Ca^{2+} and Mg^{2+}), suppress the IFT reduction by causing the insolubility of in-situ surfactant. Moreover, these divalent ions also increase the IFT value, yielding the less favorable condition for continuous flood (Donaldson, 1989).

Other six samples are saturated in soltrol170 with different oleic acid concentration. Three samples are saturated with 0.5 AN and other three samples are saturated with 5.0 AN of oleic acid in soltrol170. Each three samples are flooded by distilled water, normal brine, and soften brine. Figure 5.16a, b, and c show the results by the use of distilled water, normal brine, and soften brine as flooding fluid, respectively.

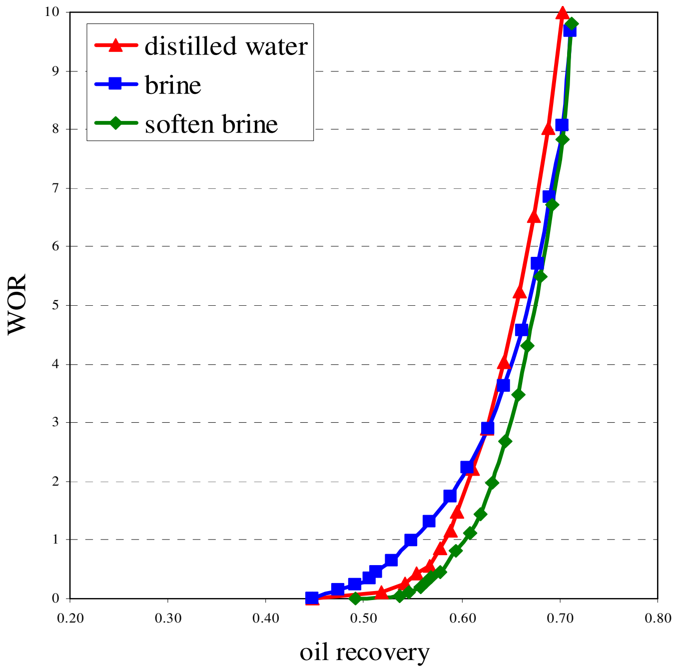


Fig. 5.15: Waterflood performance curve from samples saturated with 2.0 AN of oleic acid in soltrol170.

The use of distilled water (figure 5.16a) shows a moderate difference among three acid concentrations. Early breakthrough appears in the case of flooding in sample saturated with 5.0 AN with the corresponding oil recovery of 0.32. The breakthrough oil recovery increases as acid concentration decreases (0.45 and 0.54 for Acid number of 0.2 and 0.05 respectively). However, the increment of WOR in the first period is not clearly seen.

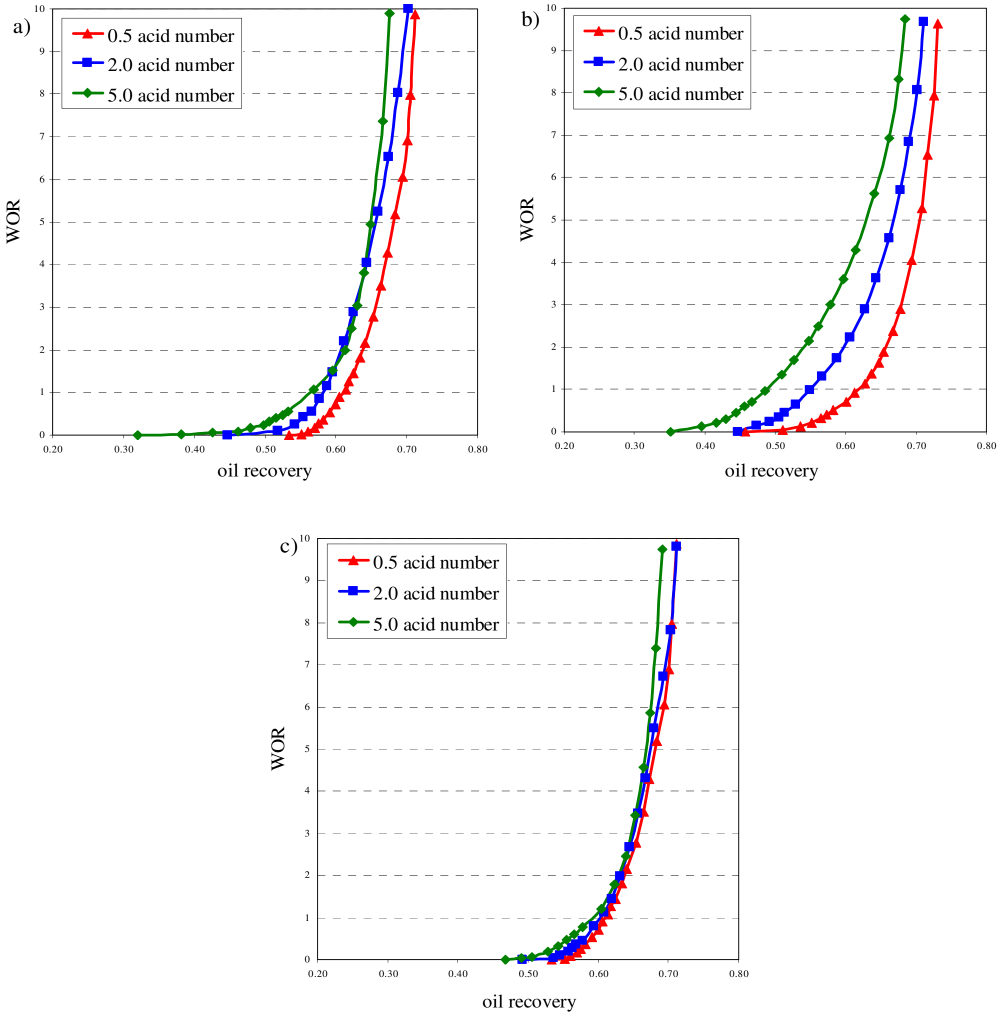


Fig. 5.16: Flood results by the use of: a) distilled water, b) brine, and c) soften brine.

The use of normal brine (figure 5.16b) clearly shows that the acid concentration in oil phase strongly affects the flooding behavior. Early breakthrough and high increment of WOR appear when the acid concentration is high. The breakthrough oil recovery of 0.35 is obtained when the AN is 5.0. This is caused by the interaction of divalent ions, acid, and rock minerals. Flooding efficiency by the use of normal brine is more sensitive in a presence of acid in oil phase. The use of soften brine (figure 5.16c) does not show a remarkable difference among the different of acid concentration. The lines almost fully overlap each other and breakthrough oil recoveries occur almost at the same point. A slight increment of WOR can be observed when the acid concentration increases.

5.4.1.1 Summary

The results in this section show that injected fluids in waterflood process strongly affect the flooding behavior. The presence of divalent ions causes the increment of WOR in the first period of waterflood. The increment of WOR directly varies with the acid concentration which strongly determines the rock wettability. Secondary recovery by the use of soften brine remarkably gives an optimal flooding behavior. The improvement by soften brine is caused by sodium ions in a divalent-ion-free environment. This condition reduces IFT and favors the flooding behavior (Jennings *et al.*, 1974). However, brine which is abundant in nature is generally chosen as an injected fluid. As WOR increases (more amount of PV of brine is injected into the sample), negative behaviors are mitigated. Therefore, normal brine can be chosen as an injected fluid for secondary recovery since EOR is normally operated after the injection of many PV of brine. Soften brine however, is recommended as a pre-slug for chemical injection and used as a solvent for chemicals to prevent the incompatibility between reservoir fluid and injected fluid.

5.4.2 The Effect of Alkali Concentration

Figure 5.17a and b demonstrate the results from alkali flooding by means of different flows: continuous and intermittent. Sodium hydroxide is used as alkali substance in this section. In the continuous flow (figure 5.17a), flooding efficiency increases as alkali concentration is raised. The curves slightly deviate from the base line (normal brine flood line, represented by black dash line) above the WOR of 3.5 which is the breakthrough of alkali slug. The IFT values decreases as alkali concentration increases. The increment of oil recovery by alkali substance in continuous flow is dominated by the reduction of IFT; as alkali concentration is raised, IFT decreases and oil recovery increases.

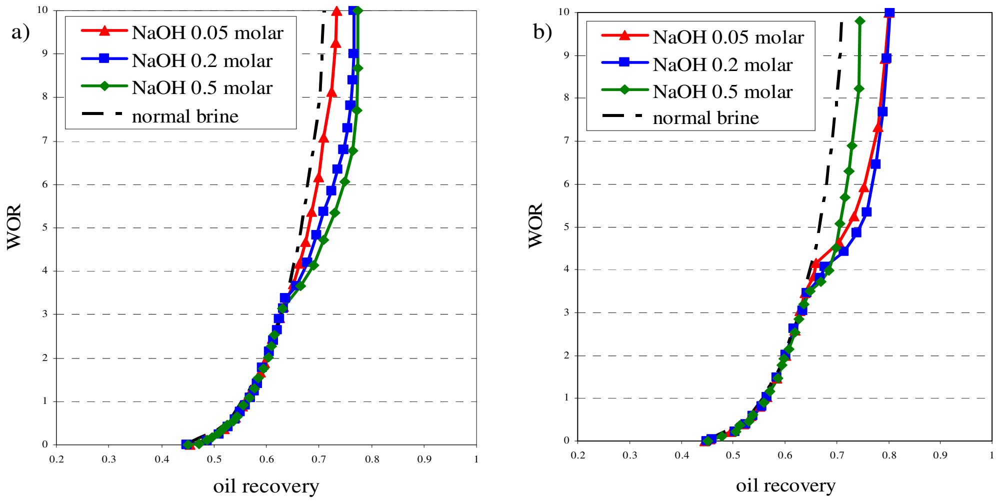


Fig. 5.17: Flooding performance by the use of sodium hydroxide in two different flows: a) continuous and b) intermittent.

On the other hand, flooding efficiency curves outstandingly deviate from base line when intermittent flow is applied with sodium hydroxide flooding (figure 5.17b). The oil recovery however does not vary with the alkali concentration as same as the continuous flow; the improvement of oil recovery increases from alkali concentration of 0.05 to 0.2 molar but the lowest oil recovery is obtained in the use of 0.5 molar alkali concentration. This low oil recovery in the use high alkali concentration is caused by the pore plugging from the in-situ sodium oleate. High alkali concentration renders high quantity of sodium oleate which is the product from in-situ saponification. Sodium oleate can be dissolved in aqueous phase when its concentration is low. At higher alkali concentration, sodium oleate is correspondingly produced and becomes insoluble. This insoluble soap then precipitates on rock surface during the aging time, plugging the pores and hence, part of oil can not be produced. However, in the use of low alkali concentration, insoluble soap is also formed but it does not precipitate on the rock surface, as seen from the insoluble colloids in the extracted effluent. These colloidal formations disappear from the effluent only in the alkali-intermittent flood using alkali concentration of 0.5 molar; this confirms the precipitation of insoluble soap. The alkali concentration remaining in effluent is obviously reduced in the intermittent flow case. However, the consumption of alkali is described in section 5.5. Table 5.5 shows several properties of the effluent from different alkali flood flow.

Table 5.5: The properties of effluent collected after the breakthrough of sodium hydroxide slug.

Sample	**color**	**colloid**	**alkali conc. (molar)**
Continuous flow			
NaOH 0.05 molar	yellow	slightly	0.024
NaOH 0.2 molar	yellow	slightly	0.095
NaOH 0.5 molar	yellow	slightly	0.285
Intermittent flow			
NaOH 0.05 molar	yellow	dense	0.001
NaOH 0.2 molar	yellow	dense	0.011
NaOH 0.5 molar	colorless	absent	0.073

5.4.2.1 Comparison between Continuous and Intermittent Flows

The comparison between sodium hydroxide flood combined with continuous and intermittent flows is shown in figure 5.18.

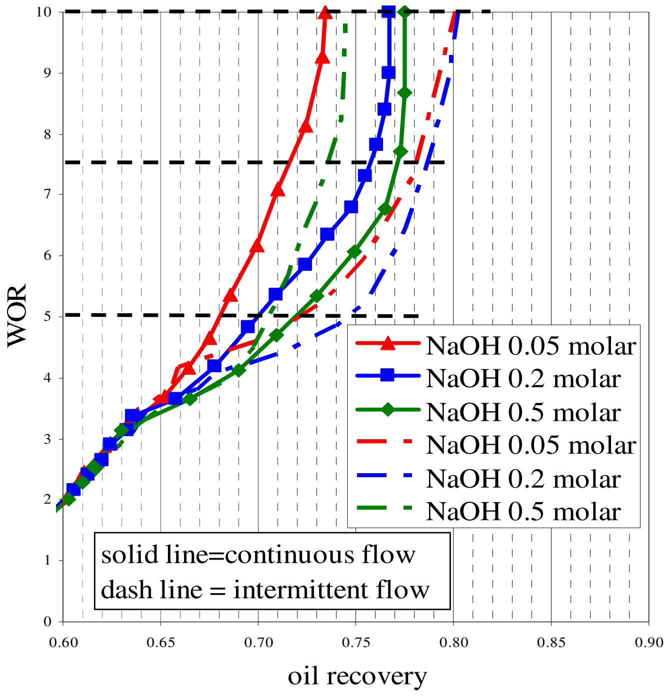


Fig. 5.18: Oil recovery at different water-oil ratio obtained from continuous- and intermittent-sodium hydroxide floods.

Solid lines represent the results from continuous flow, whereas dash lines are flood results combined with intermittent flow. Oil recovery at different WOR is emphasized in this comparison. WOR of 5.0, 7.5 and 10.0 represent the early-flood stage, middle-flood stage, and final-flood stage, respectively.

At the early-flood stage, intermittent flow by alkali concentrations of 0.05 and 0.2 molar render higher oil recovery compared with 0.5 molar alkali concentration (0.720 and 0.745 for alkali concentration of 0.05 and 0.2 molar respectively). During the aging period, low alkali concentration (lower than 1.0% w/w which is equivalent to 0.25 molar) dominates the wettability reversal from strongly-oil wet to the lesser oil-wet condition (Arihara *et al.,* 1999). This allows the injected aqueous phase to imbibe oil in micro pores. The imbibed oil is then accumulated in high permeability channels, moves upward by the gravity segregation, and remains at the top of sample during the aging period. The mobile oil bank is suddenly produced when chasing water is injected after the aging period. However, the oil recovery from the use of 0.2 molar alkali concentration is higher than that of 0.05 molar. During the aging period, part of alkali is depleted by the alkali consumption (responsible by rock and fluid interactions). The use of 0.2 molar alkali concentration provides an exceed number of alkali ions above the expected-alkali consumption quantity, where as in the case of using 0.05 molar alkali concentration, a majority of alkali ions is consumed and lesser ions are responsible for wettability reversal mechanism. The drawback of the use of high alkali concentration (0.5 molar) combined with intermittent flow can be seen from the early-flood stage. Low oil production is observed, this is caused by pore plugging, consecutively causes the reduction of permeability and the reduction of oil productivity. Higher pressure is also required to maintain the flow from partially-reduced permeability and this is considered as a major drawback.

At the middle-flood stage, oil recovery by the use of 0.05 and 0.2 molar alkali concentrations combined with intermittent flow continues to increase but with smaller gradient compared with the early-flood stage. The use of 0.5 molar alkali concentrations also continues to improve the oil production but oil recovery is relatively low compared with the use of lower alkali concentrations. At the final-flood stage, the use of 0.05 and 0.2 molar alkali concentration reaches the ultimate oil recovery of 0.80 and both concentrations still show the tendency of oil recovery improvement. On the other hand, the use of 0.5 molar alkali concentrations shows no-oil recovery at the WOR of 9.0 and none of the increment trend is observed.

The use of all alkali concentration combined with continuous flow shows drastically incremental trend of oil production in the early- to middle-flood stage and the rate of oil production obviously decreases in the final-flood stage. However, the oil recovery is relatively low compared with the results obtained from the combination of alkali flooding and intermittent flow. Only the use of 0.5 molar alkali concentration yields the opposite result. Oil recovery from each flooding stage is showed in table 5.6.

Table 5.6: Oil recovery from sodium hydroxide flooding at different water-oil ratio.

Sample	**WOR 5.0**	**WOR 7.5**	**WOR 10.0**
Continuous flow			
NaOH 0.05 molar	0.680	0.715	0.735
NaOH 0.2 molar	0.700	0.760	0.770
NaOH 0.5 molar	0.720	0.770	0.775
Intermittent flow			
NaOH 0.05 molar	0.720	0.780	0.800
NaOH 0.2 molar	0.745	0.785	0.800
NaOH 0.5 molar	0.705	0.735	0.745

5.4.2.2 Summary

Sodium hydroxide remarkably expresses the ability in oil recovery improvement when it is combined with the intermittent flow. This improvement is responsible by the wettability reversal from strongly oil-wet to a lesser oil-wet condition. Nevertheless, the use of high alkali concentration should be avoided according to the precipitation of insoluble in-situ soap which plugs the pores and causes the reduction of permeability.

5.4.3 The Effect of Alkalinity

Sodium hydroxide which is a strong base is considered as a high alkalinity substance. In the opposite, sodium hydrogen carbonate is a very weak base and it is also less strong in alkalinity. Results from alkali flooding for both continuous and intermittent flows are illustrated in figure 5.19a and b respectively.

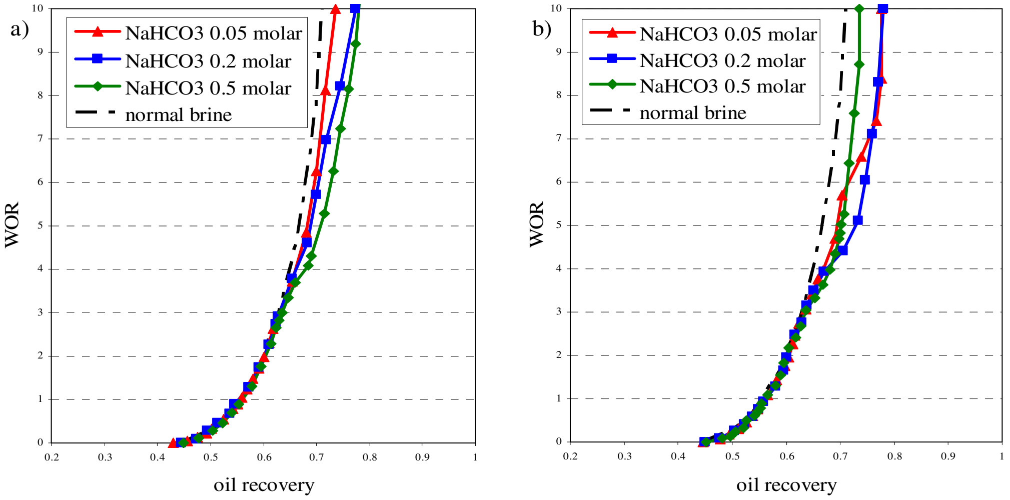


Fig. 5.19: Flooding performance by the use of sodium hydrogen carbonate in two different flows: a) continuous b) intermittent.

Similar to results from the use of sodium hydroxide, flooding performance of sodium hydrogen carbonate combined with continuous and intermittent flows expresses the same pattern. The alkali flooding combined with continuous flow yields relatively small oil increment compared with the normal brine flood. The highest alkali concentration of 0.5 molar renders the highest oil recovery, whereas the lowest alkali concentration of 0.05 molar yields the least oil recovery. The combination of alkali flooding with intermittent flow yields the highest oil recovery when the alkali concentration of 0.2 molar is used. The oil recovery is the lowest when a 0.5 molar alkali concentration is injected. Again, core plugging by the insoluble in-situ soap is the reason making a low oil recovery. The absence of colloid in effluent collected after the breakthrough of sodium hydrogen carbonate slug (shown in table 5.7) confirms that the in-situ soap is precipitated on the rock surface. The properties of the effluents from sodium hydrogen carbonate flood are similar to that of sodium hydroxide flood. The remaining alkali concentration is a bit higher compared with the use of sodium hydroxide.

Table 5.7: The properties of effluent collected after the breakthrough of sodium hydrogen carbonate slug.

Sample	**color**	**colloid**	**alkali conc. (molar)**
Continuous flow			
$NaHCO_3$ 0.05 molar	yellow	slightly	0.028
$NaHCO_3$ 0.2 molar	yellow	slightly	0.115
$NaHCO_3$ 0.5 molar	yellow	slightly	0.305
Intermittent flow			
$NaHCO_3$ 0.05 molar	yellow	dense	0.003
$NaHCO_3$ 0.2 molar	yellow	dense	0.043
$NaHCO_3$ 0.5 molar	colorless	absent	0.144

5.4.3.1 Comparison between Continuous and Intermittent Flows

The comparison between sodium hydrogen carbonate flooding combined with continuous and intermittent flows is shown in figure 5.20. At the early-flood stage, flooding combined with continuous flow shows an increasing trend of oil recovery as the alkali concentration is raised. This increment in oil recovery is responsible by the IFT reduction which is a direct function with alkali concentration. The combination of sodium hydrogen carbonate flooding with intermittent flow is slightly different. The maximal oil recovery in the early-flood stage appears at the alkali concentration of 0.2 molar, follows by 0.5 and 0.05 molar respectively. The alkali concentration of 0.2 molar exceeds the required alkali quantity consumed during the aging period. Therefore, there are alkali ions that are responsible for the wettability reversal. The use of alkali concentration of 0.5 molar generates the precipitation of in-situ soap during the aging period and the drawback can be seen from the early-flood stage. The oil recovery from the use of a 0.05 molar alkali concentration is the least in this flood stage. This is caused by consumption of the majority active alkali during aging time. Moreover, lesser amount of sodium hydrogen carbonate yields the pH value lower than the p.z.c of the carbonate surface which equals to 9 (sodium hydrogen carbonate normally yields pH value around 8-9). Therefore, the use of a 0.05 molar alkali concentration does not show a significant improvement in oil recovery during this step.

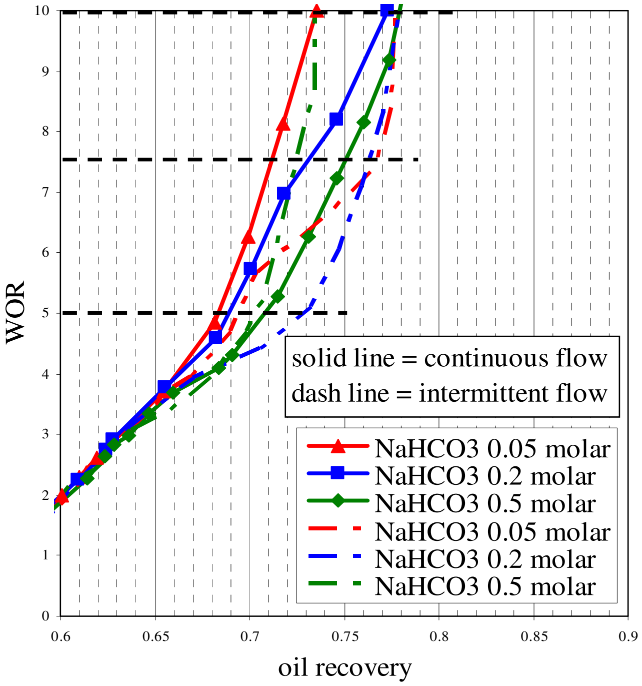


Fig. 5.20: Oil recovery at different water-oil ratio obtained from continuous- and intermittent-sodium hydrogen carbonate floods.

However, the oil recovery by the use of a 0.05 molar alkali concentrations starts to increase at the middle-flood stage. The consumed alkali partially reverse the oil-wet surface to a lesser strongly wet condition. Oil is then loosely captured on the rock surface and as a number of PV of injected water is raised, captured oil is released and produced. Alkali flood combined with continuous flow also yields the increment of oil recovery at the medium-flood stage. At the final-flood stage, the use of alkali concentration of 0.2 and 0.5 molar combined with continuous flow reach the maximal oil recovery of about 0.78 as same as other two alkali concentration (0.05 and 0.2 molar) combined with intermittent flow.

In the continuous flow cases, oil is remarkably produced in the final-flood stage. The wettability reversal function might partially occurs during the continuous flow of alkali slug and captured oil then released later when more PV of chasing water is injected. The smaller alkalinity of sodium hydrogen carbonate dominates wettability reversal function when the concentration is enough to yield pH more than 9. Therefore, the use of sodium hydrogen carbonate concentrations of 0.2 and 0.5 molars combined with continuous flow yields an increasing trend of oil recovery for the entire of flooding. The effect from IFT reduction appears in the early-to medium-flood stage, whereas the effect from wettability reversal occurs from the medium- to final-flood stage.

The combination of sodium hydrogen carbonate flood with intermittent flow shows a good result in the early-flood stage when an alkali concentration of 0.2 molar is used. The wettability reversal occurs during aging period and captured oil is released. The released oil is imbibed by injected water and then flows to the high permeability channels. After that, oil moves upward to the top of sample by the gravity segregation and is produced when chasing water is injected. The use of alkali concentrations of 0.05 and 0.5 molar obviously shows the drawbacks. Low sodium hydrogen carbonate is depleted and retards the wettability reversal mechanism, while high concentration causes core plugging and reduction in oil productivity. Table 5.8 summarizes the oil recovery by sodium hydrogen carbonate in each flood stage.

The use of sodium hydrogen carbonate which is a low alkalinity alkali substance does not show a remarkable advantage when it is combined with intermittent flow. The best result from this combination appears only when the concentration of 0.2 molar is used at the early-flood stage. At the higher WOR the flood combined with continuous flow rapidly releases the captured oil and therefore, no different gap between oil recoveries compared with the result obtained from intermittent flow. The intermittent flow is then considered a less effective than continuous flow because of more time and more chemical are consumed.

Table 5.8: Oil recovery from sodium hydrogen carbonate flooding at different water-oil ratio.

Sample	**WOR 5.0**	**WOR 7.5**	**WOR 10.0**
Continuous flow			
$NaHCO_3$ 0.05 molar	0.685	0.710	0.735
$NaHCO_3$ 0.2 molar	0.690	0.730	0.780
$NaHCO_3$ 0.5 molar	0.710	0.750	0.780
Intermittent flow			
$NaHCO_3$ 0.05 molar	0.695	0.765	0.780
$NaHCO_3$ 0.2 molar	0.730	0.765	0.780
$NaHCO_3$ 0.5 molar	0.705	0.725	0.735

5.4.3.2 Comparison between High and Low Alkalinity

The comparison between flood results by the uses of sodium hydrogen carbonate and sodium hydroxide for both continuous and intermittent flows are illustrated in figure 15.21a and b respectively.

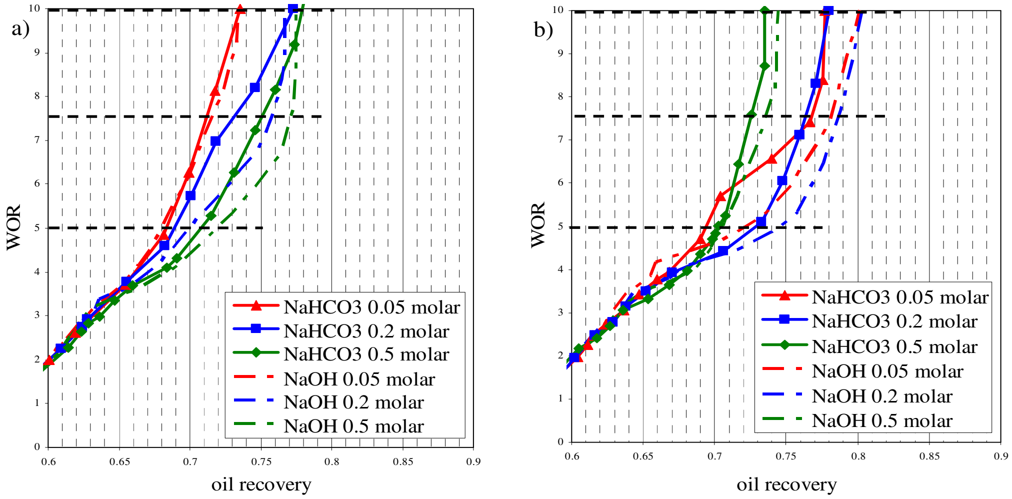


Fig. 5.21: Comparison of oil recovery at different water-oil between sodium hydrogen carbonate and sodium hydroxide floods in two different flows: a) continuous and b) intermittent.

The comparison of oil recovery from different alkalinity substance in continuous flow (figure 5.21a) shows that a stronger alkalinity substance yields better results. Oil recovery obtained from the use of sodium hydroxide is higher in every flood stage and every alkali concentration compared with the use of sodium hydrogen carbonate. The difference cannot be obviously seen when alkali concentration of 0.05 molar is used because the majority of both alkali is almost depleted. On the other hand, the big different gap can be seen when alkali concentration of 0.2 and 0.5 molars is used. Sodium hydroxide which is a stronger base can be totally ionized and rapidly react with oleic acid which is weak acid. Oppositely, sodium hydrogen carbonate which is a weak base can be partially ionized according to the Base Ionization Constant (K_b). The reaction between sodium hydrogen carbonate with oleic acid is then less active. A big increment of oil recovery from early- to middle-flood stage when sodium hydroxide is used also indicates that the IFT reduction is more effective compared with the use of sodium hydrogen carbonate. It can also be implied that the lower IFT values are obtained when higher alkalinity substance is used.

Similarly, sodium hydroxide also gives better results compared with sodium hydrogen carbonate when the flooding is combined with intermittent flow. Figure 15.21b demonstrates that oil recoveries after aging period with sodium hydroxide are much higher than sodium hydrogen carbonate cases. The wettability reversal of carbonate rock principally occurs when the surrounded pH is greater than 9. Sodium hydrogen carbonate normally have pH value around 8-9 in those concentration range. The depletion of sodium hydrogen carbonate therefore, reduces the pH value to under the p.z.c. zone and hence, the wettability reversal cannot be efficiently conducted.

5.4.3.3 Summary

The alkalinity of injected slug strongly affects the oil recovery by alkali flooding. Higher alkalinity dominates IFT reduction and maintains the pH above the p.z.c which is a favorable condition for wettability reversal. These reasons render higher oil recovery for both continuous and intermittent flows when sodium hydroxide is used as flooding agent.

5.4.4 The Effect of Acid Number

In the previous sections, all the samples are saturated with 2.0 AN of oleic acid in soltrol170. In this section, the effect of acid number in oil phase is investigated. The higher acid number of oil is prepared. Four samples are saturated with 5.0 AN of oleic acid in soltrol170 and aged for a week before the core flood test. Only two sodium hydroxide concentrations are chosen in this step: 0.05 and 0.2 molar, according to the predicted core plugging that will occur when alkali concentration is high (0.5 molar). Flooding results are shown in figure 5.22a and b for alkali flooding combined with continuous and intermittent flow respectively.

From figure 5.22a, an increase of alkali concentration yields higher oil recovery when flooding is combined with continuous flow. In the contrary, an increase of alkali concentration shows a reverse result in intermittent flow. The alkali concentration of 2.0 molar generates the core plug of insoluble in-situ soap as seen from the no-colloid effluent (table 5.9).

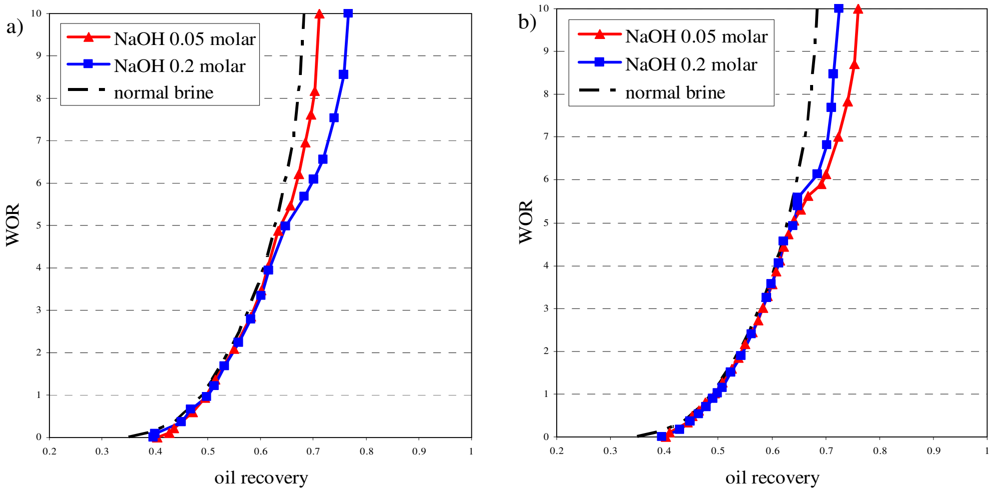


Fig. 5.22: Flooding performance by the use of sodium hydroxide in samples saturated with 5.0 acid number oleic acid in soltrol170 in two different flows: a) continuous and b) intermittent.

Table 5.9: The properties of effluent after the breakthrough of sodium hydroxide slug from flooding in samples saturated with 5.0 AN of oleic acid in soltrol170.

Sample	**color**	**colloid**	**alkali conc. (molar)**
Continuous flow			
NaOH 0.05 molar	yellow	slightly	0.018
NaOH 0.2 molar	yellow	dense	0.080
Intermittent flow			
NaOH 0.05 molar	yellow	dense	0.001
NaOH 0.2 molar	colorless	absent	0.009

5.4.4.1 Comparison between Continuous and Intermittent Flows

The comparison of oil recovery obtained from continuous and intermittent flows is shown in figure 5.23. In the early-flood stage, there is not much difference between the oil recovery obtained from continuous and intermittent flows because it is the point at which pre-flush is initially injected and thus, the enhanced oil still remains in the samples. Brine flooding in the samples containing high quantity of acid yields low efficiency because of strongly oil-wet condition and the effects from divalent ions. Therefore, the oil recovery of 0.65, which is the starting point for the pre-flush injection, is reached later compared to flooding in sample saturated with lower acid-content oil (section 5.41).

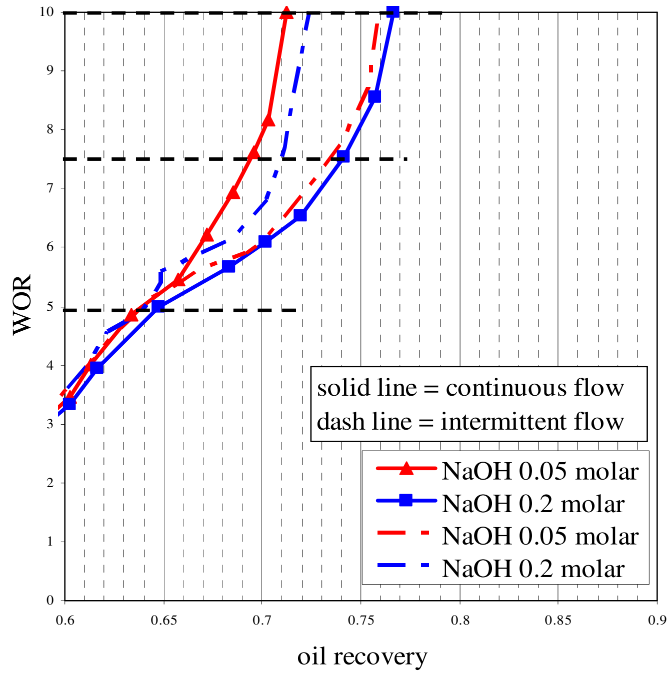


Fig. 5.23: Oil recovery at different water-oil ratio obtained from continuous- and intermittent-sodium hydroxide flooding in samples saturated with 5.0 AN of oleic acid in soltrol170.

As the chasing water is kept injected, the difference can be remarkably seen in the middle-flood stage. The oil recovery from flooding combined with continuous flow is higher when the alkali concentration of 0.2 molar is used because IFT reduction is a direct function of alkali concentration. The wettability reversal is predominant when intermittent flow is combined. The oil improvement from intermittent flow can be seen when a 0.05 molar alkali concentration is used. However, the core plugging affects the reduction of oil recovery and can be seen in this stage for the combination of 0.2 molar alkali concentration and intermittent flow. From the middle- to the final-flood stage, the oil recovery from every case keeps increasing but the ultimate oil recovery is relative high for 0.2 molar alkali concentration combined with continuous flow and 0.05 molar alkali concentration combined with intermittent flow. Oil recovery from every flood at each stage is shown in table 5.10.

Table 5.10: Oil recovery from sodium hydroxide flooding in samples saturated with 5.0 acid number of oleic acid in soltrol170 at different water-oil ratio.

Sample	**WOR 5.0**	**WOR 7.5**	**WOR 10.0**
Continuous flow			
NaOH 0.05 molar	0.640	0.695	0.710
NaOH 0.2 molar	0.645	0.740	0.765
Intermittent flow			
NaOH 0.05 molar	0.640	0.730	0.760
NaOH 0.2 molar	0.640	0.710	0.720

5.4.4.2 Comparison between High and Low Acid Concentration

The effect of acid concentration is shown in figure 5.24, comparing the current data with those obtained by the used of samples saturated in 2.0 AN. (data from section 5.4.2). The comparison is shown for both continuous and intermittent flows.

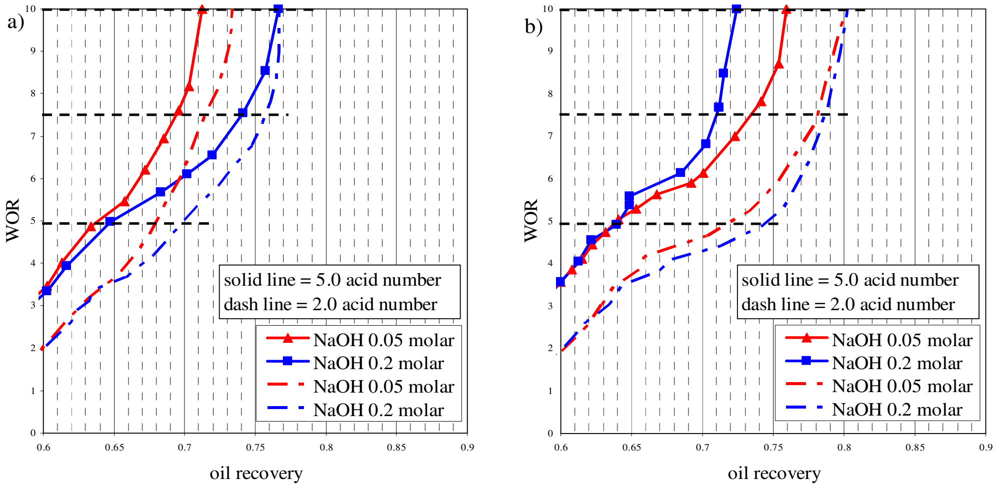


Fig. 5.24: Comparison of oil recovery at different water-oil ratio between flooding in samples saturated with 5.0 and 2.0 AN oil in two different flows: a) continuous and b) intermittent.

According to the pre-flush pre-set at 0.65, the alkali flooding in sample saturated with a 5.0 AN needs more amount of brine to produce oil until compared with alkali flooding in a 2.0 AN. The pre-flush is then injected at WOR of 5.0 instead of 3.0 as in the cases where samples are saturated with 2.0 AN oil. In the floods combined with continuous flow (figure 5.24a), the different gap can be seen from the early- to medium-flood stage. The oil recovery from flooding in 5.0 AN samples rapidly increases because high acid concentration facilitates the reduction of IFT. The saponification at the interface of fluids depends directly on both alkali and acid concentrations. The use of 2.0 molar alkali concentration flooded in samples saturated with 5.0 AN oil eventually reaches the oil recovery of 0.765 as same as flooding in sample saturated with 2.0 AN oil even the alkali slug is later injected. In the floods combined with intermittent flow, oil recovery is relatively low for the higher acid concentration. The precipitation of soap does not occurred for both 0.05 and 0.2 molar alkali concentrations when sample is saturated in 2.0 AN oil. In the opposite, the precipitation of soap occurs when 0.2 molar of alkali concentration is aged in samples saturated with 5.0 AN oil.

5.4.4.3 Summary

Acid concentration accelerates the saponification reaction at the interface of fluids as same as the concentration of alkali. The advantages are predominantly observed in continuous flow. Higher acid concentration yields lower IFT value and this helps to entrain oil in the fluid flow. The drawback occurs in the intermittent flow because the soap precipitation is sensitive to both acid and alkali concentration. However, very low alkali concentration (0.05 molar) is recommended for intermittent flow; yielding relatively high ultimate oil recovery of 0.76 compared with flooding combined with continuous flow (0.71).

The acid concentration in oil phase is the fluid property that cannot be easily changed. The alkali concentration which is variable is then more emphasized. However, these results provide an awareness for the use of alkali injection in a very concentrated-acid oil reservoir especially with the combination of intermittent flow.

5.4.5 The Effect of the Presence of Initial Water Saturation

Samples are initially saturated with normal brine and flooded by soltrol170 (2.0 AN). The water saturation after oil breakthrough is around 0.5 for every sample. After breakthrough, no additional brine is produced. Therefore, initial water saturation for the samples in the experiment is set at 0.5. According to the wettability measurement, the sample firstly saturated with aqueous phase is less oil-wet. The wettability condition obtained from section 5.2.2 appears at neutral- to moderately water-wet. All the samples are aged for a week before the core flooding test in order to allow acid in oil to create the wettability equilibrium with carbonate surface. Figure 5.25a and b illustrate the results from alkali flooding in samples with the presence of initial water saturation of 0.5 combined with continuous and intermittent flows respectively. The black dash line represents the normal brine flood which is used as the reference line.

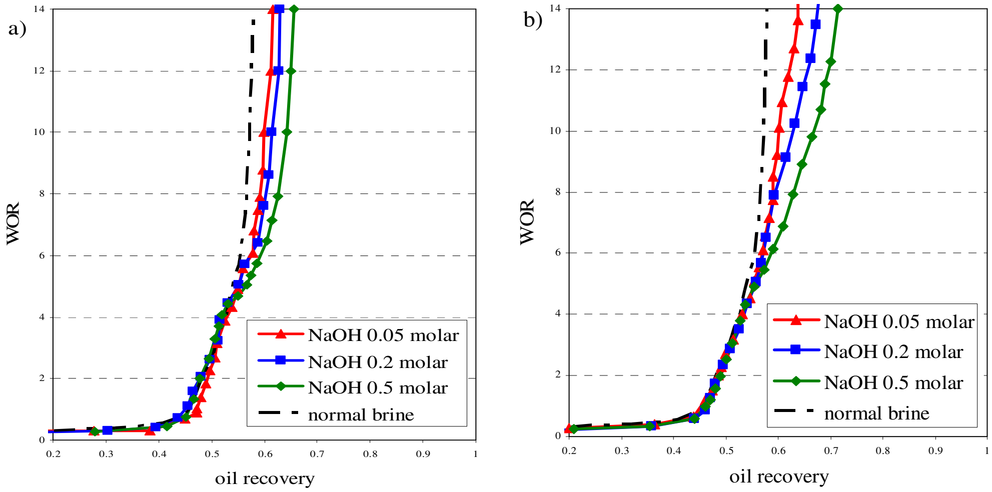


Fig. 5.25: Flooding performance by the use of sodium hydroxide
in samples with the presence of 0.5 initial water satiation
in two different flows: a) continuous and b) intermittent.

From figure 5.25a and b, all curves do not start from the WOR of zero because after samples are aged for a week, acid in oil bines the bond with carbonate surface via brine film. Hence, part of oil reaches the carbonate surface, creating the oil wettability equilibrium and water film is ruptured and released as water droplets. These water drops are then produced when the samples are flooded. Water breakthrough appears around the oil recovery of 0.45 which is similar to the case where the initial water saturation is absent. However, the shape of curves in this experiment is slightly different from the cases where the initial water saturation is absent. The line becomes straighter after the water breakthrough with the small amount of additional produced oil. This represents a less strongly oil-wet condition (Craig, 1993). Pre-flush of soften brine is injected at 3.0 WOR and the breakthrough of alkali slug appears at WOR of 5.0. The breakthrough of alkali slug appears at later

WOR compared with the non-initial water saturation cases because the smaller proportion of oil in place yields the higher increment of WOR. The WOR is therefore extended to the value of 14 in these experiments.

From figure 5.25a, the flooding performance curves from continuous flow start deviating from the base line after the breakthrough of alkali slug. The use of sodium hydroxide at 0.5 molar renders maximally the IFT value and therefore, the emulsification and entrainment of oil are more efficient. At the higher WOR, oil recovery increases slowly and the lines become almost perpendicular, meaning that no more oil is being produced. At the end of the flood process, the highest ultimate oil recovery is obtained by the use of 0.5 alkali concentration; appears at 0.655. In the intermittent flow (figure 5.25b), there is not an outstanding oil increment after aging period as found in cases where initial water saturation is absent. In the presence of initial water saturation, the rock is neutral to moderately water-wet. Most producible oil can be flooded by normal brine during secondary recovery. The rest of oil is captured in the inaccessible zone. However, this captured oil, which is difficult to be produced, is released at the higher WOR. Flooding efficiency increases as the alkali concentration is raised. From table 5.11, none of precipitation of insoluble soap occurs during the flood process. After the normal brine flood, the residual oil is reduced to 0.25. Therefore, the quantity of acid to create the saponification is correspondingly small and moreover, higher water saturation allows the in-situ soap to be soluble in aqueous solution.

Table 5.11: The properties of effluent collected after the breakthrough of sodium hydroxide slug from flooding in samples with the presence of initial water saturation of 0.5.

Sample	**color**	**colloid**	**alkali conc. (molar)**
Continuous flow			
NaOH 0.05 molar	yellow	slightly	0.026
NaOH 0.2 molar	yellow	slightly	0.118
NaOH 0.5 molar	yellow	slightly	0.320
Intermittent flow			
NaOH 0.05 molar	yellow	slightly	0.001
NaOH 0.2 molar	yellow	slightly	0.015
NaOH 0.5 molar	yellow	slightly	0.092

5.4.5.1 Comparison between Continuous and Intermittent Flows

The comparison between continuous and intermittent flows is shown in figure 5.26. However, the flood stage in this section is modified. The WOR of 6.0, 10.0, and 14.0 represent the early-, middle-, and final- flood stage, respectively.

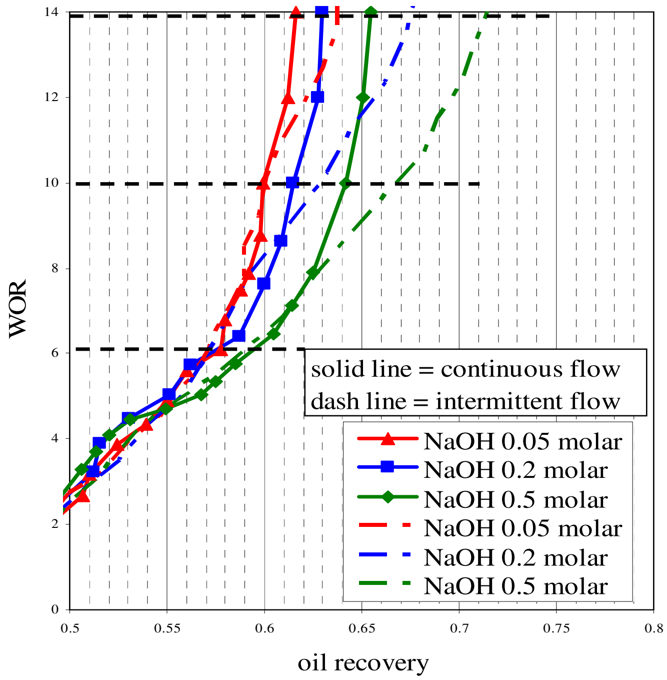


Fig. 5.26: Oil recovery at different water-oil ratio obtained from continuous- and intermittent-sodium hydroxide flooding in samples with the presence of 0.5 initial water saturation.

At the early-flood stage, oil recovery for both continuous and intermittent flows ranges between 0.57-0.59. In this stage, the higher alkali concentration shows the better result. No big difference between the results obtained from continuous and intermittent flows can be observed in this stage. In the medium-flood stage, intermittent flow rapidly increases the oil recovery especially in the higher alkali concentration (0.5 molar). When the alkali concentration of 0.05 is used, a major part of alkali is depleted and only a few ions can precede the wettability reversal mechanism. At the final-flood stage, the intermittent flow keeps producing oil and the oil recovery obtained is relatively high compared with the use of same concentration combined with continuous flow. The oil recovery from both continuous and intermittent flows at each flood stage is shown in table 5.12.

Table 5.12: Oil recovery from sodium hydroxide flooding at different water-oil ratio, flooded with samples with the presence initial water saturation of 0.5.

Sample	**WOR 6.0**	**WOR 10.0**	**WOR 14.0**
Continuous flow			
NaOH 0.05 molar	0.575	0.600	0.615
NaOH 0.2 molar	0.580	0.615	0.630
NaOH 0.5 molar	0.595	0.640	0.655
Intermittent flow			
NaOH 0.05 molar	0.575	0.600	0.640
NaOH 0.2 molar	0.575	0.630	0.675
NaOH 0.5 molar	0.590	0.670	0.715

5.4.5.2 Summary

In the presence of initial water saturation, the wettability is less oil-wet and a major part of oil can be produced by normal brine injection. The rest of oil which is captured in inaccessible zone can be further produce by the alkali flooding combined with intermittent flow. High concentration of alkali has less effect on the precipitation of insoluble in-situ soap because the ratio of water in place to oil is very high and as a consequence, soap can remain soluble in aqueous phase. The increment of oil recovery by the intermittent flow cannot be obviously seen immediately after the breakthrough of alkali slug. But the oil is kept continuing being produced from the inaccessible zone as a more PV of chasing water is injected.

5.4.6 Advanced Combination with Surfactant and Polymer

Alkali flooding is modified by the addition of surfactant and polymer substances. The concentration of alkali and surfactant are fixed at the optimal concentration obtained from IFT measurement (0.2 molar and 0.05 %w/w for alkali and surfactant respectively). Sodium hydroxide and dodecylbenzenesulfonate are used as alkali and surfactant substances respectively. Polyacrylamide is prepared at the concentration of 1.0 ppt (this optimal concentration advised by Wanchao *et al.* (1995)). The results from advanced flooding are illustrated in figure 5.27.

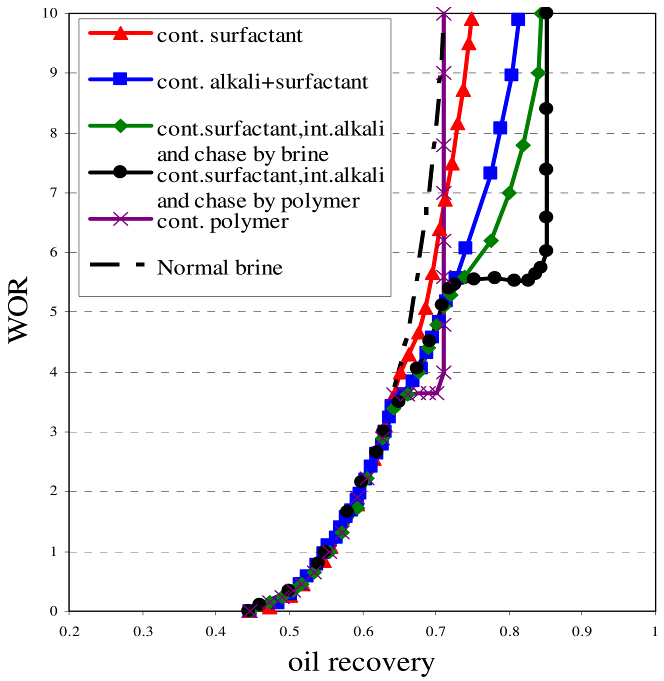


Fig. 5.27: Flooding performance in several advanced flooding: combination of alkali-surfactant-polymer.

From figure 5.27, three flooding cases are combined with continuous flow, whereas the rests are combined with intermittent flow (excluded the reference line). Surfactant flooding at the optimal concentration combined with continuous flow (red solid line) does not yield a remarkable oil improvement. The combination of alkali and surfactant flowing continuously shows much better oil improvement compared with flooding solely surfactant substance. Basically, the use of low surfactant concentration has a major drawback. Dodecylbenzenesulfonate or petroleum sulfonate is an anionic surfactant. A major part of surfactant in an injected slug is rapidly adsorbed onto the positive charged carbonate surface. Therefore, the oil recovery improvement is low according to the surfactant depletion. As retention time has risen, the surfactant is more depleted. It is therefore recommended that surfactant should not be aged or flooded intermittently (since it does not have the wettability reversal function). The combination of alkali and surfactant (blue solid line) shows better result because alkali reduces the adsorption rate of surfactant onto the rock surface by reversing the surface charge of carbonate surface to negative (Seethepalli *et al.* (2004)). Thus, free surfactant molecules can reduce the IFT effectively. The polymer flooding combined with continuous flow (purple solid line) shows an obvious advantage. The movable oil is effectively swept, the oil bank is suddenly produced and there is no more oil production after. Polymer reduces the mobility ratio of an injected fluid and the use of polymer in homogeneous reservoirs remarkably shows the advantage. Very few PV of displacing phase is required to obtain the ultimate oil recovery.

In the flood cases applied with intermittent flow, oil recovery is relatively higher compared with the continuous flow. The first case (green solid line), 0.2 PV of surfactant solution is injected and followed by 1.0 PV of alkali solution. Surfactant primarily entrains the moveable oil. Alkali slug also swept the rest of oil emulsions that are instantly released from rock surface. After that, the sample is aged for a week. The post-flush by using normal brine shows that the oil recovery gradually increases. The use of polymer solution as chasing phase (black solid line) shows an outstandingly advantage by producing high oil recovery with few PV of injected water. After the aging period, part of oil that was captured by rock surface is released. Polymer is then injected to chase this released oil. Before the breakthrough of polymer slug, released oil is produced and no more oil is produced after the polymer breakthrough.

Polymer substance is proven to have an ability to chase oil effectively. However, since water or brine is modified by polymer, the viscosity of fluid increases. This causes a higher injection pressure to maintain the productivity.

Table 5.13 demonstrated the properties of effluent collected after the breakthrough of injected chemicals from several advanced floods. The alkali concentration measurement is not performed for solely surfactant and polymer flooding cases. Color of effluent appears yellow except the cases where surfactant and alkali are used. Colloid of in-situ surfactant is found in every case (expect polymer flooding where in-situ interaction does not occur), indicating that there is no precipitation of insoluble soap.

Table 5.13: The properties of effluent collected after the breakthrough of injected chemical from advanced flooding.

Sample	**color**	**colloid**	**alkali conc. (molar)**
Continuous flow			
Surfactant	yellow	slightly	-
Alkali and Surfactant	yellow	slightly	0.105
Polymer	yellow	-	-
Intermittent flow			
Surfactant, Alkali, Brine	yellow	dense	0.013
Surfactant, Alkali, Polymer	yellow	dense	0.013

The comparison between advanced flooding with solely alkali flooding in terms of oil recovery at different flood stages is shown in figure 5.28.

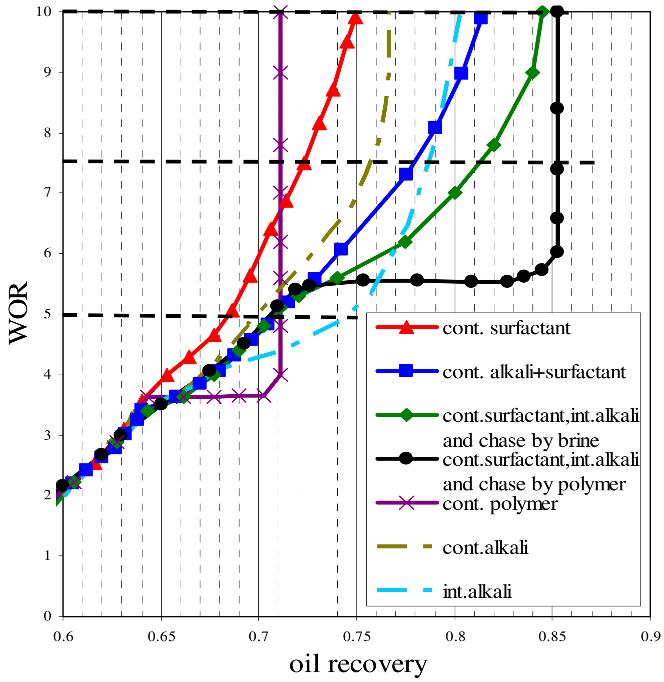


Fig. 5.28: Oil recovery at different water-oil ratio obtained from several advanced flooding (the combination with of alkali-surfactant-polymer).

At the early-flood stage, oil recovery from the solely alkali flooding combined with intermittent flow is highest because released oil moves upward by gravity segregation and suddenly produced after chasing water is injected. In the cases where alkali and surfactant are used, there is not a big amount of oil produced suddenly after chasing water (or polymer) is injected. The combination of alkali and surfactant flooding effectively sweeps oil during the slug injection by the action of IFT reduction to an ultra-low condition. However, the wettability reversal mechanism is not dominant as the case where solely alkali flooding because surfactant is firstly injected and firstly adsorbed onto rock surface. Therefore, alkali, which is flooded after, cannot reverse effectively the rock wettability to a more favorable condition.

As chasing water is kept injected, the surfactant-alkali flooding shows an obvious oil improvement at the middle-flood stage. Oil, which is captured by rock loosely, is released. Moreover, adsorbed surfactant molecules are liberated as the carbonate surface charge is reversed to negative and causes the repulsion with negavie anions. Surfactant then reactivates and entrains the released oil. The use of polymer as chasing phase after surfactant and alkali slugs yields the best oil recovery (oil recovery of 0.85). The entrained fluid is pushed upward with a planar flood front. Thus, there is no oil production after the polymer slug breakthrough. From medium to final-flood stage, flooding with the use of brine as a chasing phase keeps producing an additional amount of oil, whereas oil is no more produced in the case where polymer is used. Oil recovery at each flood stage is shown in table 5.14.

Table 5.14: Oil recovery from advanced flooding at different water-oil ratio.

Sample	**WOR 5.0**	**WOR 7.5**	**WOR 10.0**
Continuous flow			
Surfactant	0.685	0.720	0.750
Alkali and Surfactant	0.715	0.780	0.810
Polymer	0.710	0.710	0.710
Intermittent flow			
Surfactant, Alkali, Brine	0.710	0.810	0.845
Surfactant, Alkali, Polymer	0.710	0.850	0.850

5.4.6.1 Summary

The combination of alkali, surfactant and polymer flooding shows obviously high oil improvement. Surfactant is very potential in IFT reduction and thus, creates the emulsion of fluids. However, surfactant can be quickly depleted by the adsorption onto rock surface. The combination of alkali and surfactant therefore, resolves this problem. Alkali assists surfactant by reversing the surface charge of carbonate surface to negative and hence, reduces surfactant depletion rate. The alkali-surfactant combined with continuous flow yields ultimate oil recovery up to 81%. However, surfactant is not recommended to be aged in the reservoir as alkali substance because it does not have a direct function to reverse the rock wettability. In the intermittent flow cases, alkali and surfactant are separated in different slugs. Surfactant is firstly injected to sweep the moveable oil and after that, alkali slug is followed. During the surfactant slug injection, adsorbed surfactant molecules from the previous slug are liberated after the charge of rock surface is reversed to negative side. Surfactant is then reactivated to emulsify and entrains the released oil. Polymer is recommended to be flushed as a chasing phase because it reduces the mobility of an injected fluid and hence, the displaced phase (included released oil) can be readily pushed out. By the combination of alkali-surfactant-polymer flooding, the ultimate oil recovery reaches 85%; this is the highest ultimate oil recovery obtained in this research.

5.5 Alkali Consumption Test

The alkali consumption test is performed by measuring the remaining alkali in the effluent after the breakthrough of alkali slug. A few centiliters of effluents are collected and titrated with proper color indicators. The alkali consumption is expressed as percentage of alkali consumed compared to the initial alkali concentration.

5.5.1 The Effect of Alkali Concentration

Table 5.15 shows the alkali consumption from the sodium hydroxide flooding in the samples saturated with 2.0 AN oil for both continuous and intermittent flows.

Table 5.15: Alkali consumption from sodium hydroxide flooding.

Alkali Concentration	Continuous Flow	Intermittent Flow
0.05 molar	52.0%	98.0%
0.2 molar	52.5%	94.5%
0.5 molar	43.0%	85.4%

From table 5.15, the alkali consumption from flooding in continuous flow appears around 40-50 percent, whereas the alkali consumption can reach almost hundred percent when flooding is combined with intermittent flow. Alkali consumption is a direct function with time and temperature. As retention time has risen, a more quantity of alkali is consumed. However, this higher alkali consumption is believed to have a responsibility for the wettability reversal which is absent in the continuous flow.

The alkali consumption includes the reaction with acid in oil phases and the reaction with rock minerals (Donaldson, 1989). The reaction with acid in oil phases occurs quickly and this renders the IFT reduction. Few alkali quantities are consumed with the acid during the aging period. On the other hand, the reaction with rock minerals occurs relatively slow and this results in the reversal of wettability. The percentage of alkali consumption decreases as the alkali concentration increases. In low alkali concentration, the reaction rate is also low but there are plenty of available mineral site for the reaction with alkali. Therefore, most of alkali is consumed during aging period. In higher concentrations, the reaction rate increases. Available rock minerals to react with alkali decrease as time increases, causing the lower percentage of alkali consumption.

5.5.2 The Effect of Alkalinity

The alkali consumption of flooding by sodium hydrogen carbonate in both continuous and intermittent flows is shown in table 5.16.

Table 5.16: Alkali consumption from sodium hydrogen carbonate flooding.

Alkali Concentration	Continuous Flow	Intermittent Flow
0.05 molar	44.0%	94.0%
0.2 molar	42.5%	78.5%
0.5 molar	39.0%	71.2%

Alkali consumption is relatively high when the flooding is combined with intermittent flow. As same as sodium hydroxide flooding, aging time allows sodium hydrogen carbonate to react with acid in oil phase and rock minerals, causing the high alkali consumption. The alkali consumption in continuous flow is around 40 percent, whereas the alkali consumption in flooding combined with intermittent flow varies from 70 to almost hundred percent. The reason of high alkali consumption range in intermittent flow is similar to case of sodium hydroxide.

The comparison of alkali consumption of flooding combined with continuous and intermittent flow between sodium hydroxide and sodium hydrogen carbonate is shown in table 5.17.

Table 5.17: Comparison of alkali consumption between the use of sodium hydroxide and sodium hydrogen carbonate.

Alkali Concentration	**Sodium Hydroxide**	**Sodium Hydrogen Carbonate**
Continuous flow		
0.05 molar	52.0%	44.0%
0.2 molar	52.5%	42.5%
0.5 molar	43.0%	39.0%
Intermittent flow		
0.05 molar	98.0%	94.0%
0.2 molar	94.5%	78.5%
0.5 molar	85.4%	71.2%

The alkali consumptions from continuous flows show small gap of difference. The use of sodium hydroxide which is strong base results in higher consumption for every alkali concentration. Sodium hydroxide, with strong alkalinity, can react with acid in oil phase quicker because it can be totally ionized, whereas sodium hydrogen carbonate can be partially ionized and hence, the alkali consumption is lower.

The difference of alkali consumption between the use of sodium hydroxide and sodium hydrogen carbonate is obviously seen when flooding is combined with intermittent flow. The alkali consumption is higher for every alkali concentration in sodium hydroxide flooding. The difference is higher as alkali concentration is raised. Greater alkalinity consumes more alkali because the rate of reaction between alkali and rock minerals increases with alkalinity. The effect of alkalinity can be remarkably seen at high alkali concentration. Even though the alkali consumption is higher in the use of sodium hydroxide flooding, oil recovery is also higher because the wettability reversal mechanism is more preceded to the favorable wettability condition.

5.5.3 The Effect of Acid Number

The alkali consumption from sodium hydroxide flooding in samples saturated with 5.0 AN oil is shown in table 5.18.

Table 5.18: Alkali consumption from sodium hydroxide flooding in samples saturated with 5.0 AN oil.

Alkali Concentration	Continuous Flow	Intermittent Flow
0.05 molar	64.0%	98.0%
0.2 molar	60.0%	95.5%

Alkali consumption is relatively high in intermittent flow compared to continuous flow. This is caused by reaction between alkali-acid and alkali-rock minerals. However, in intermittent flow, alkali-rock mineral reaction is predominant. Alkali consumption decreases in percentage when alkali concentration is raised. This can be explained as same as two previous sections (5.5.1 and 5.5.2).

The comparison of alkali consumption in samples saturated with different acid concentration is shown in table 5.19.

Table 5.19: Comparison of alkali consumption from sodium hydroxide flooding in samples saturated with 2.0 and 5.0 AN oil.

Alkali Concentration	2.0 AN	5.0 AN
Continuous flow		
0.05 molar	52.0%	64.0%
0.2 molar	52.5%	60.0%
Intermittent flow		
0.05 molar	98.0%	98.0%
0.2 molar	94.5%	95.5%

The alkali consumption is remarkably different when alkali is flooded into samples continuously. High acid concentration accelerates the alkali consumption by the saponification reaction at the interface between oil and aqueous phases. The alkali consumption from flooding combined with intermittent reaches almost hundred percent for both acid concentrations.

5.5.4 The Effect of Presence of Initial Water Saturation

Alkali consumption from sodium hydroxide flooding in samples with the presence of initial water saturation of 0.5 is shown in table 5.20 for both continuous and intermittent flows.

Table 5.20: Alkali consumption from sodium hydroxide flooding in samples with the presence of initial water saturation of 0.5.

Alkali Concentration	**Continuous Flow**	**Intermittent Flow**
0.05 molar	48.0%	98.0%
0.2 molar	41.0%	92.5%
0.5 molar	36.0%	81.6%

The alkali consumption is relatively small in flooding combined with continuous flow compared with the results from flooding combined with intermittent flow. As described in previous sections, this is caused by the alkali consumption during the aging time. The comparison of alkali consumption from sodium hydroxide flooding in samples with and without initial water saturation is shown in table 5.21.

Table 5.21: Comparison of alkali consumption from sodium hydroxide flooding in samples with and without initial water saturation.

Alkali Concentration	$S_{wi} = 0$	$S_{wi}=0.5$
Continuous flow		
0.05 molar	52.0%	48.0%
0.2 molar	52.5%	41.0%
0.5 molar	43.0%	36.0%
Intermittent flow		
0.05 molar	98.0%	98.0%
0.2 molar	94.5%	92.5%
0.5 molar	85.4%	81.6%

The difference between alkali consumption in samples present and absent of initial water saturation is more remarkable in the flooding combined with continuous flow. Higher alkali consumption is observed when sample does not have the presence of initial water saturation. At the starting of alkali injection, residual oil in the cases where sample is absent from initial water saturation is much higher than the residual oil in samples with initial water saturation (0.35 and 0.25 for samples absent and present of initial water saturation respectively). Therefore, higher residual oil consumes more alkali, resulting in higher alkali consumption. In intermittent flow, a slight difference can be seen. The alkali consumption is smaller at higher alkali concentration in samples the presence of initial water saturation. Samples are neutral- to mildly water-wet when they are initially saturated with water. Thus, the rock consumes less alkali for the wettability reversal mechanism, resulting in less alkali consumption.

5.5.5 Advanced Combination with Surfactant and Polymer

The alkali consumption test is done only in the cases where alkali substance is present. Table 5.22 shows the data from alkali consumption test in several advanced flooding cases compared with solely alkali flooding in both continuous and intermittent flows.

Table 5.22: Comparison of alkali consumption from advanced flooding cases with solely alkali flooding.

Flooding case	Alkali Consumption
Continuous flow	
Alkali	52.5%
Alkali + Surfactant	47.5%
Intermittent flow	
Alkali	94.5%
Surfactant, Alkali, Brine	93.5%
Surfactant, Alkali, Polymer	93.5%

In continuous flow, alkali consumption is slightly less in the cases where surfactant is present. Both surfactant and alkali provide ionic ions, thus they compete each other in adsorption onto the rock surface. This results in a slight less alkali concentration in the presence of surfactant. In intermittent flow, no significance can be clearly observed; the alkali consumption almost reaches hundred percent.

5.5.6 Summary

The alkali consumption from intermittent flow appears almost hundred percent because rock consumes alkali during the aging period. The proportion of consumed alkali to the initial concentration decreases with the increment of alkali concentration. The alkali concentration, alkalinity of alkali substance, acid concentration, the presence of initial water saturation and the presence of surfactant all have a slight effect on alkali consumption. The effects of these variables can be more clearly seen in continuous flow where the retention time is much shorter and alkali consumption by liquid-liquid reaction is predominant. However, the alkali consumption is responsible for the surface charge reversal, and consecutively changes the wettability to a more favorable condition. Therefore, the consumed alkali is not considered as loss during the process.

CHAPTER 6

CONCLUSION

The combination of alkali flooding and intermittent flow has remarkably shown an improvement of oil recovery from strongly oil-wet carbonate rock sample. Naturally, oil-wet carbonate surface captures oil by the surface charge interaction; positive surface charge of carbonate rock interacts with negative charge of carboxylic acid in oil phase, causing the occupation of non-polar materials. Alkali substance has an ability to build up the high pH value in the solution by providing the hydroxide ions. This high pH value results in the reversal of charge on the carbonate surface, resulting in repulsion between carbonate surface and adsorbed materials. The unfavorable condition is hence reversed to a more favorable condition for waterflood process.

Many previous studies mostly are dedicated for wettability reversal by the use of surfactant. The mechanism of surfactant in wettability reversal is different from that of alkali substance. Surfactant emulsifies oil from the rock surface, resulting in cleaned surface, whereas alkali causes the repulsion between rock surface and adsorbed material. Alkali is then more potential in wettability reversal because it also reverses the surface charge which is the reason of attraction between rock surface and wettability-induced molecules. Moreover, alkali is relatively cheap. These are the advantages of alkali substance over surfactant.

In this chapter, the conclusions from sections in previous chapter are summarized.

1. The interfacial tension (IFT) measurement is primarily performed in order to indicate the optimal range of the concentration of injected chemical substances. From the IFT measurements, each chemical directly and indirectly affects the IFT between liquids in 2-phase system. Alkali substance (sodium hydroxide) reacts with acid in oil phase, causing an in-situ soap which drastically reduces IFT in a very low concentration range and gradually reduces IFT in alkali concentration higher than 0.2 molar. Surfactant (petroleum sulfonate) is much more potential in IFT reduction compared with alkali substance. The IFT reduction by surfactant is caused by the hydrophilic-hydrophobic link at the interface. The optimal concentration of surfactant

appears at 0.05%w/w which is also the CMC where the highest number of monomer appears in the solution. Salinity indirectly affects the IFT by supplying the cations and hence, alkali and surfactant are forced to reach the interface. The optimal salinity appears at the concentration higher than 20 ppt (or 0.2%). Salinity moreover, maintains the equilibrium of in-situ soap and surfactant at interface.

2. Wettability measurement has shown that the treatment of samples by oleic acid yields a strongly oil-wet condition. Naturally, the Lecce stone is neutral to mildly water-wet surface. The change of wettability to strongly oil-wet condition occurs by the polar interaction between the positive charges on rock surface and negative charges from carboxylic acids. The wettability reversal is directly dependant from aging time. From the sample detection by MRI technique, the reversal of wettability occurs by the diffusion of acid from outer skin to the inter core of the sample (following the direction of saturation). A period of one week is adequate to allow the carbonate rock surface reaching the wettability equilibrium.

3. The wettability reversal test by the use of alkali and surfactant demonstrates that alkali is a more potential substance in wettability reversal from strongly oil-wet to a less strong oil-wet condition which is more favorable. From this test, it is moreover found that alkali substance at very low concentration (0.05 molar) can maximally reverse oil-wet surface. When the alkali concentration is higher (0.2 and 0.5 molar) alkali molecules tend to react with acid in oil phase, causing the IFT reduction. Alkali improves oil recovery by two functions at different preferential concentrations. Wettability reversal is predominant at low concentration, whereas the IFT reduction is predominate at higher concentration. In this study, the point of vice versa between these two functions cannot be detected precisely, however; it should lay between 0.05 and 0.2 molar.

At the end of wettability reversal test, all the samples are re-measured for the wettability index. The plot between ultimate oil recovery and the wettability index shows that the change of wettability is primarily caused by the wettability index to oil. However, alkali does not change the preference of rock to water (as seen from the change of wettability index to water that is relatively small compared with wettability index to oil). Therefore, alkali reverses strongly oil-wet rock to only the neutral or mildly water-wet condition instead of strongly water-wet condition.

4. The effect of alkali concentration in core flooding is different in continuous and intermittent flows. In the continuous flow case, the oil recovery increases as the alkali concentration is raised. The increment of oil recovery by continuous flow is primarily responsible by the reduction of IFT which is a direct function of alkali concentration. In the intermittent case, sodium hydroxide 0.2 molar yields the highest oil recovery (also higher compared with the sample concentration but flooded continuously). The use of sodium hydroxide at 0.05 molar also yields an increment oil recovery but the result is not outstanding because of early depletion of alkali substance. The use of sodium hydroxide of 0.5 molar shows the drawback because high alkali concentration creates high quantity of soap during the aging time and hence this soap precipitates onto the rock surface and plugs the core. The use of sodium hydroxide at 0.2 molar is considered as an optimal alkali concentration in core flood.

5. Alkalinity of the alkali substance is also another important parameter in alkali flooding. Alkalinity directly affects the pH value of the alkali solution. The use of low alkalinity substance such as sodium hydrogen carbonate provides low pH value which is not adequate for the wettability reversal from oil-wet to a more favorable condition. The use of sodium hydrogen carbonate combined with continuous flow shows an increasing trend of oil recovery when the alkali concentration is raised. As same as the use of sodium hydroxide, sodium hydrogen carbonate shows the same result in flooding combined with intermittent flow: the best oil recovery is obtained from 0.2 molar alkali concentration, lesser oil is produced by the used of 0.05 molar alkali concentration, and soap precipitation is formed when 0.5 molar alkali concentration is used. The improvement of oil recovery by sodium hydrogen carbonate is much lower than the cases where sodium hydroxide is used. The concentration of sodium hydrogen carbonate has to be kept higher than the amount of depletion in order to keep pH value above the p.z.c. and this concentration has not to exceed the point in which the soap precipitation is formed. However, the use of sodium hydrogen carbonate is more effective in continuous flow because less time

and chemical are consumed, while the oil recovery does not show much difference compared with the combination with intermittent flow.

6. Acid quantity in oil phase, which is represented by the acid number, also affects the improvement of oil recovery by alkali flooding. Acid concentration in oil phase drives the saponification reaction at the interface as same as the alkali concentration in aqueous phase. Flooding alkali continuously to improve high acid-contained oil yields an advantage. The IFT can be reduced to very low value by the use of low alkali concentration. The application of intermittent flow with alkali flooding in high acid-contained oil is more restricted. In-situ soap precipitation can occur even at the low alkali concentration. From the experiments, 0.05 molar is the only alkali concentration that does not cause the soap precipitation during the aging period. However, the acid quantity is an unchangeable property; therefore the aim of this study is less significant than that of alkali concentration. Nevertheless, more restrictions have to be considered when oil contains high acid concentration.

7. Initial water saturation prevents the carbonate surface from the adsorption of acid in oil phase that causes the alteration of wettability to an unfavorable condition. A less strongly oil-wet surface permits brine to sweep oil effectively, thus; residual oil is low. The combination of alkali flooding and continuous flow slightly increases the oil recovery. The increment in oil recovery directly varies with alkali concentration. The combination of alkali flooding with intermittent flow is also effective. The restriction in alkali concentration is much lesser compared with the case where there initial water saturation is absent. This is caused by the small portion of oil remaining. The alkali depletion is not restricted when low alkali concentration is used and soap precipitation does not appear in the use of high alkali concentration. The alkali concentration of 0.5 molar yields the best oil recovery in this case.

8. The modification of alkali flooding by the uses of surfactant and polymer provides an outstanding improvement of oil recovery. In the continuous flow, surfactant is mixed with alkali. The cooperation of these two substances at their optimal concentration reduces IFT to an ultra-low condition. Surfactant can work effectively in the IFT reduction because alkali reverses the carbonate surface charge, therefore; the rate of depletion of surfactant is low compared with the use of solely

surfactant. In the intermittent flow, surfactant is separated from the aging slug to avoid the adsorption onto the rock during aging period. Thus, a short slug of surfactant is pre-injected in order to drain the producible oil by the IFT reduction. During the pre-injection of surfactant, part of surfactant is adsorbed on the rock surface. Alkali is injected after surfactant slug and aged. During the aging period, surface charge is reversed to negative, hence; all adsorbed compounds are released by the repulsion. Adsorbed surfactant is then re-active and continue to emulsify released oil to the entrainment. Polymer is recommended to be injected as chasing phase. Polymer reduces the mobility of an injected fluid. The movable phase in front of the flood front can be effectively swept. Oil bank can be quickly produced by the injection of only a few PV of injected fluid. However, polymer increases the viscosity of an injected fluid, therefore; higher pressure is required to maintain the flood velocity and the great loss can occur in low permeability reservoir. The best ultimate oil recovery is 0.85 obtained by injecting surfactant slug continuously, aging the alkali slug, and re-flooding by polymer solution. The ultimate oil recovery is obtained at the early-flood stage. Problem from produced water is then neglected.

9. Alkali consumption is a compelling issue for alkali flooding. High quantity of alkali is unavoidably expected from the adsorption onto rock surface during the aging period (or even in the continuous flow). Parameters explained in previous paragraphs such as alkali-acid concentration, alkalinity, initial water saturation, and additional chemical, all affect the alkali consumption. Aging time permits rock surface to adsorb alkali maximally. The alkali consumption from alkali flooding applied with intermittent almost reach a hundred percent. The consumption is less when alkali concentration is raised because less adsorption sites on rock surface are available. However, quantity of alkali consumed during the aging time is also responsible for the wettability reversal. In case that the oil-wet surface has been reversed to a more favorable condition by this consumed alkali and then oil recovery is improved, the consumption is no more considered as loss. On the other hand it is considered as a compulsory quantity that is consumed to improve the oil recovery.

10. The use of alkali flooding-intermittent flow could be applied with heterogeneous carbonate reservoir. Thief zone or non-accessible zone of the reservoir could be effectively flooded because the surface charge can be reversed by the ion

diffusion during the intermittent period. This ion diffusion would cause the charge reversal and consecutively, the spontaneous imbibition by injected fluid.

Alkali flooding was not widely used for carbonate reservoirs in the past decades because it is believed to cause the severe problems especially the depletion of alkali slug. However, with a well design of alkali slug regarding concentration, alkalinity, pH, salinity, pre-flush and post flush system etc., the alkali flooding can be carried out in the carbonate reservoir. Many limestone reservoirs have been proven that alkali flooding is compatible. Aging alkali substance in the rock formation foresees high alkali depletion but this consumption is proven that it is consumed for the wettability reversal that consequently, oil recovery is improved.

Last but not least, the combination technique of alkali flooding and intermittent flow might be a good candidate for specific reservoirs that meet all the requirements. In another word, the advantages proven by the experiments might be taken as a consideration to exploit the reservoir in the future since the drawbacks are proven to be acceptable and expected result is economical.

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APPENDIX A

A BRIEF MICROFACIES STUDY OF LECCE LIMESTONE (PIETRA LECCESE)

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The limestone sample received from Mr. Falan Srisuriyachai for carbonate microfacies study was prepared, studied, photographed, and described.

Methods

A 2-cm fragment of the limestone was immersed in two-component Araldite™ resin stained with Berlin blue for 24 hours in an exsiccator under vacuum produced by a water pump. Three thin sections were prepared by making a flat surface by electric rock saw, grinding by progressively finer grade silicium carbide powder. This surface was glued to a glass plate by Araldite resin and left to harden for 24 hours. The sample was sawed again by electric rock saw parallel to the glued face to produce a 0.5 mm thick slab, then grinded to 30 micrometer thickness by progressively finer silicium carbide powder.

Thin sections were studied by a Nikon Eclipse E600 microscope under transmitted light with 20× to 200×magnification. Photographs were made by Nikon Coolpix 955 digital camera of 3.34 megapixel resolution.

Texture, fossil content, palaeoenvironment, and porosity were studied by industry-standard methods (Flügel , 2004).

Results

Matrix: Both sparite and micrite are visible, in irregular distribution. There are sparite patches surrounded by micrite.

Components: Bioclasts only: planktonic foraminifers (Globigerina, etc.) of various size and grea preservation (pore canals in walls are clearly visible). Tests of various size, walls of various thickness. Ostracods: symmetrical double valves. Molluscs: thin bivalve shells.

Texture:

Folk: bimicrite
Dunham: packstone
Distribution of bioclasts is rather homogeneous as seen in thin sections. No particular arrangement of bioclasts of various sizes was observed.

Porosity: Mostly intragranular porosity: foraminifer tests are often empty.

Discussion

Globigerina limestone with minor amount of non-foraminifer components – and lack of organisms requiring light – indicate an open marine sedimentary environment below the photic zone. Terrestrial input was blocked by local topography. Sedimentation was rapid, allowing at part of the foraminifer tests to remain unfilled by micrite.

Sparite patches within micrite suggest mild recrystallization of micrite by growth of larger crystals on the expense of dissolution of minor ones.

32 % porosity reported by physical measurements cannot really be seen in the sample studied. Possibly SEM study can reveal the true nature of porosity of Lecce Limestone.

Reference

Flügel, E. (2004): Microfacies of Carbonate Rocks. Analysis, interpretation, and applications. Springer-Verlag, Berlin, 976 p.

Caption

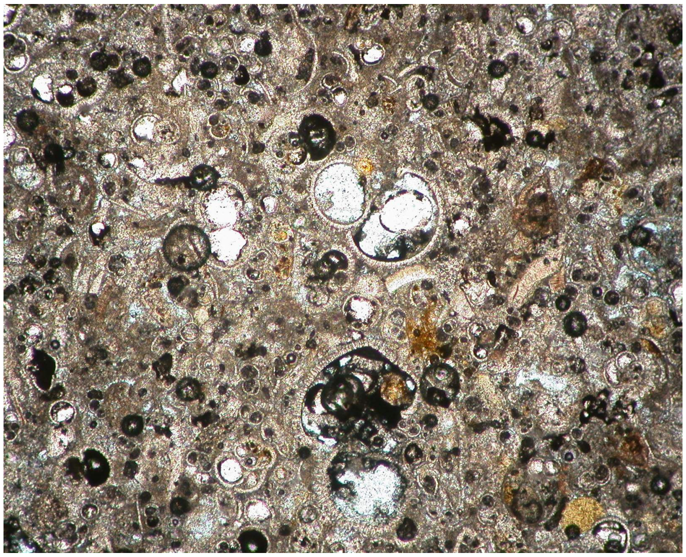

Fig. 1: Lecce limestone as seen in thin section. Planktonic foraminifers (probably *Globigerina*) of various sizes are distributed irregularly in a micritic matrix partly recrystallized to sparite (microsparite). Chambers of a few foraminifera are empty (blue tint of dyed Araldite resin visible), while others are filled by micrite or glauconite (dark material). Round dark spots with white centre are bubbles within Araldite resulting from imperfect removal of air by vacuum. Foraminifera in lower centre of picture is 500 micrometer long.

APPENDIX B

ACID NUMBER DETERMINATION BY COLOR TITRATION

(IP 139/98, ASTM D974-97)

1. Definition

Acid number is a quantity of base, expressed in milligrams of potassium hydroxide (KOH) per gram of sample, that is required to titrate with acid constituents present in 1 g of sample when titrated under prescribed condition. To determine the acid number, the portion is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base to the end-point indicated by the color change of added *p*-naphtholbenzein solution (orange in acid and green-brown in base)

2. Reagents and Material

During the analysis, use only reagents of recognized analytical grade, and only water in accordance with Grade 3 of ISO 3696.

- **Propan-2-ol**, anhydrous, maximum water content 0.9% v/v (volume fraction 0.9%).
- **Toluene**.
- **Titrate solvent**. Add 500 ml of toluene and 5 ml of water to 495 ml of propan-2-ol.
- **Hydrochloric acid**, $c(HCl) = 0.1$ molar. Mix 9 ml of concentrated HCl (35.4% w/w or mass fraction of 35.4 %) with 1 l of propan-2-ol. Standardize frequently enough to detect changes of 0.0005 mol/l, preferably by electrometric titration of approximately 8 ml (accurately measured) of the 0.1 molaralcoholic KOH solution diluted with 125 ml of carbon dioxide-free water.
- **Potassium hydroxide**, $c(KOH) = 0.1$ molar. Add 6 g of solid KOH to approximately 1 l of propan-2-ol in a 2-litre conical flask. Boil the mixture gently for

10 min to 15 min, stirring to prevent solids from forming a cake on the bottom. Add at least 2 g of barium hydroxide [$Ba(OH)_2$] and again boil gently for 5 min to 10 min. Allow to cool to room temperature and then to stand for several hours. Filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide during filtration. Store the solution in a chemical resistant dispensing bottle of contact with the cork, rubber or saponifiable stopcock lubricant and protected by a guard tube containing soda lime or nonfibrous soda silicate absorbent. Glass bottles are not recommended for storage. Standardize frequently enough to detect changes of 0.0005 mol/l, preferably against 0.1 g to 0.15 g of pure potassium acid phthalate weighted with an accuracy of 0.0002 g and dissolved in approximately 100 ml of carbon dioxide-free water, using phenolphthalein to detect the end point.

- ***p*-naphtholbenzein** indicator solution, meeting the specifications given in annexes A and B. Dissolve 1.0 g of *p*-naphtholbenzein in 100 ml of titration solvent.
- **Phenolphthalein**, indicator solution. Dissolve 0.5 g of phenolphthalein in 100 ml propan-2-ol.
- **Potassium acid phthalate**.

3. Apparatus

Ordinary laboratory apparatus and **burette**, capacity 50 ml, graduate in 0.1 ml subdivisions, or capacity 10 ml, graduated in 0.05 ml subdivisions.

4. Preparation of Used Oil Sample

As used oil may change appreciably in storage, samples should be tasted as soon as possible after removal from lubricating system; the dates of sampling and testing should be noted. Heated the laboratory sample of used oil at 60^oC in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can, or if it is a glass and more than three-quarters full, transfer the entire sample to a clear glass bottle having a capacity at least one-third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by violent agitation of portions of the sample in the original container.

After complete suspension of all sediment, filter the test sample, or convenient aliquot, through a 150 μm wire mesh filter to remove large contamination particles.

5. Determination of Acid Number

Into a 250-ml conical flask, introduce the appropriate mass of test portion in table 1. Add 100 ml of the titration solvent and 0.5 ml of the indicator solution (*p*-naphtholbenzein) and without stoppering, swirl until the test portion is completely dissolved by the solvent. Titrate immediately at a temperature below 30^{o}C. Add the potassium hydroxide solution in increments and swirl to disperse the potassium hydroxide as necessary. Shake vigorously near the end-point but avoid dissolving carbon dioxide in the solvent. Consider the end-point definite if the color change persists for 15 s or if it is reverses on addition of two drops of the hydrochloric solution. In acidic oil, the orange color changes to a green to green-brown as the end point is approached. To observe the end-point of dark-colored oil, shake the flask vigorously to produce momentarily a slight foam when the color change occurs as the last few drops of titrant are added and observe the titration under a white fluorescent lamp at bench-top level. Carry out the black titration on 100 ml of the titration solvent and 0.5 ml of the indicator solution, adding the potassium hydroxide in 0.05 ml or 0.1 ml increments. Record the quantity of potassium hydroxide solution required to reach the end-point (orange to green).

6. Calculation

Calculation the acid number, AN, in milligrams of KOH per gram of the test sample , from the equation

$$\mathrm{AN} \quad = \quad [(V_1 - V_0)\, c_{KOH} \times 56.1] \,/\, m$$

where V_1 is the volume, in milliliters, of potassium hydroxide solution required for titration of the test portion, V_0 is the volume, in milliliters, of potassium hydroxide required for titration of the black solution, c_{KOH} is the concentration, in mole per liter, of the standard volumetric potassium hydroxide solution, and *m* is the mass, in grams, of the test portion.

Table 1: Mass of test portion.

Type of oil	**AN**	**Mass (g)**	**Accuracy of weight (g)**
New of Light-colored	≤3	20	0.05
	>3 to 25	2	0.01
	>25 to 250	0.2	0.001
Used or dark-colored	≤25	2	0.01
	>25	0.2	0.001

APPENDIX C

CALCULATION OF ACID NUMBER MODIFICATION

For the oil sample proven to be acid-free, the acid number modification can be done by adding the corresponding quantity of carboxylic acid. This appendix contains the calculation of acid quantity to obtain the desirable acid number.

In order to calculate acid quantity, some parameters are required: mass of oil portion (*m*), molecular weight of carboxylic acid, and desire acid number (AN). From the calculation of acid number 's equation

$$\mathrm{AN} = [(V_1 - V_0)\, c_{KOH} \times 56.1] / m \qquad (1)$$

the equation can be rearaged as

$$V_1 - V_0 = (\mathrm{AN} \times m) / (c_{KOH} \times 56.1) \qquad (2)$$

where V_1 is the volume, in milliliters, of potassium hydroxide solution required for titration of the test portion, V_0 is the volume, in milliliters, of potassium hydroxide required for titration of the black solution, and c_{KOH} is the concentration, in mole per liter, of the standard volumetric potassium hydroxide solution.

Substiute mass of oil portion and acid number in the equation. In case that oil contains no acid, V_o is zero. Therefore the left hand side is only V_1. Calculate V_1 from (2) and substitute in the equation

$$m_{\mathrm{acid}} = [(c_{KOH}/1000) \times V_1] \times \mathrm{MW}_{\mathrm{acid}} \qquad (3)$$

where and are mass of acid and molecular weight of acid respectively.

VITAE

Falan Srisuriyachai was born on January 1, 1980 in Ubonratchathani, Thailand. He received his B.Sc. in Chemical Engineering from the faculty of Science, Chulalongkorn University in 2000. He received his Master's Degree in Petroleum Engineering from the Department of Mining and Petroleum Engineering, faculty of Engineering. Chulalongkorn University in 2004. A part of his Master's Degree is accomplished by the cooperation with the Department of Territory, Environmental and Geotechnological Engineering (DITAG), faculty of Engineering, Politecnico di Torino, Italy. He has been a doctorate student in the PhD. program of Georesource and Geotechnology at the Department of Chemical, Mining, and Environmental Engineering (DICMA), faculty of Engineering, University of Bologna since 2005.