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Author: Farzaneh Nikzad Amoli (signature author)
Instructor: Professor Tor Austad Supervisor: Dr. Seyed Farzad Shariatpanahi	
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Farzaneh Nikzad Amoli

Abstract

Water injection for both pressure maintenance and oil displacement is the most important secondary recovery method in sandstones. It has also been implemented with success in a few carbonate reservoirs, but because the most carbonate reservoirs worldwide is characterized as neutral to preferential oil-wet, normal water flooding is usually not successful as an EOR technique.

It has been proved that seawater can be used as an EOR fluid for hot, fractured carbonate oil reservoirs since it is able to modify the wetting conditions and to enhance the oil recovery. The potential determining ions in sea water Ca^{2+} , Mg^{2+} , and SO_4^{2-} played a crucial role in altering the wettability from oil-wet to more water-wet condition because of their reactivity towards the carbonate surface.

In this project, the potential of low salinity brine to enhance the oil recovery has been studied. Four flooding tests were conducted both on limestone cores containing anhydrite and chalk core containing no sulfate.

It is observed that low salinity brine had only effect on rock contains anhydrite. The dissolution of anhydrite, CaSO_4 , which is the source for SO_4^{2-} , is depending on salinity/composition of brine and the temperature. The dissolution of anhydrite normally increases as the temperature decreases.

Lowering the salinity of injection brine, increases the reactivity of the surface active ions SO_4^{2-} and Ca^{2+} .

Table of content

1	Introduction	6
2	Project objective	8
3	Theory and fundamentals	9
3.1	Petroleum reservoir	9
3.2	Carbonates	9
3.2.1	Carbonates minerals	10
3.2.2	Carbonates rocks	10
3.2.2.1	Limestone	11
3.2.2.2	Dolomite	12
3.2.2.3	Chalk	13
3.3	Oil recovery	14
3.3.1	Primary recovery	14
3.3.2	Secondary Recovery	15
3.3.3	Tertiary Recovery	15
3.4	Recovery Rate	16
3.5	Recovery of residual oil	16
3.6	Improvement oil recovery	20
3.7	EOR Definition	21
3.8	EOR Methodes	22
3.8.1	Thermal enhanced oil recovery methods	23
3.8.1.1	Cyclic steam stimulation (CSS)	23
3.8.1.2	Steam flooding	24
3.8.1.3	Steam assisted gravity drainage (SAGD)	24
3.8.1.4	Conduction heating in situ combustion	25
3.8.2	Miscible flooding	25
3.8.3	Chemical flooding	26
3.8.4	Mobility control process	27
3.8.5	Other methods	27
3.9	Force displacement	28
3.9.1	Gravitational force	28
3.9.2	Viscous force	28
3.9.3	Capillary force	29
3.9.4	Inertial force	29
3.10	Wettability	30
3.11	Wettability measurements	33
3.11.1	Contact angle	33
3.11.2	Amott test	35
3.11.3	USBM Wettability	37
3.11.4	Imbibition rates	39
3.11.5	New wettability test for carbonate	39
3.12	Wettability alternation	41
3.12.1	Effect of mineral surface on wettability	41
3.12.2	Effect of potential ions on surface of charge	42
3.12.3	Effect of temperature on wettability	43
3.12.4	Effect of acid number on wettability	44
3.12.5	Effect of PH on wettability	44
4	Experimental	46
4.1	Material	46
4.1.1	Porous media	46
4.1.1.1	Limestone core	46



4.1.1.2	Chalk core	47
4.1.2	Crude oils.....	47
4.1.3	Brines.....	48
4.2	Experimental methods	49
4.2.1	Core cleaning	49
4.2.1.1	Limestone core cleaning.....	49
4.2.1.2	Chalk core cleaning.....	50
4.2.2	Pore volume measurement	50
4.2.3	Porosity measurement	51
4.2.4	Initial water saturation	52
4.2.5	Permeability measurement.....	52
4.2.6	Oil saturation and aging.....	53
4.2.7	Force displacement.....	53
4.2.8	Ion chromatography.....	54
4.3	Presence of anhydrite	55
5	Result and discussion.....	56
5.1	Test #1 (core 5B)	56
5.2	Test #2 (core 6B)	59
5.3	Test #3.....	61
5.4	Test #4.....	61
5.5	Discussion	63
6	Conclusion.....	65
7	Symbols and abbreviation	66
8	References.....	69

1 Introduction

More than 60% of the world's oil and 40% of the world's gas reserves are held in carbonate. Improved oil recovery from fractured and low permeable carbonates is a great challenge. The average oil recovery from carbonate reservoirs is less than 30%, which is very low in comparing to sandstone. Nearly 2.0×10^{12} barrels of conventional oil and 5.0×10^{12} barrels of heavy oil will remain in reservoirs worldwide after conventional recovery methods have been exhausted. Much of this oil especially heavy oils and tar sands, which respond poorly to primary and secondary recovery methods, would be recovered by Enhanced Oil Recovery (EOR) methods.

EOR is defined as any process whereby oil is produced other than by natural reservoir pressure and using a suitable EOR method depends on many factors, economic as well as technological [1, 2].

EOR is usually applicable after secondary recovery operations, and the EOR target is ~45% OOIP.

Water injection for both pressure maintenance and oil displacement is the most important secondary recovery method in sandstones. It has also been implemented with success in a few carbonate reservoirs, but because the most carbonate reservoirs worldwide is characterized as neutral to preferential oil-wet, normal water flooding is usually not successful as an EOR technique.

One of the most efficient EOR methods with great success in carbonate reservoir is seawater injection. It has been proved that seawater is able to modify the wetting conditions of oil-wet carbonate reservoirs to more water-wet condition which cause increase in oil recovery [2-4].

It is documented that the reactivity between potential ions Ca^{2+} , Mg^{2+} and SO_4^{2-} in seawater at the carbonate surface is the main reason for removing the strongly adsorbed carboxylic material from the rock surface. The criteria for seawater to act as a wettability modifier, is that Ca^{2+} , Mg^{2+} , and SO_4^{2-} must have strong affinity toward the carbonate surface.

Temperature is playing important role on reactivity. The reactivity increases as the temperature increases, and it has been observed that Mg^{2+} is able to substitute Ca^{2+} on the carbonates surface at temperatures above 90°C. The potential ions Ca^{2+} , Mg^{2+} and SO_4^{2-} in combination at a high reservoir temperature are able to change wetting properties, and keep the carbonate rock preferentially water-wet

Regarding to Shariatpanahi et. al. the presence of anhydrate in carbonates and high temperature are another important factors which have large effect on the initial wetting condition. By increasing the

temperature, the solubility of $\text{CaSO}_4(\text{s})$ decreases and the adsorption of SO_4^{2-} onto the carbonate rock increases which makes an increase in recovery [4, 5].

The brine with low concentration of NaCl is able to increase the reactivity of the surface active ions SO_4^{2-} and Ca^{2+} .

2 Project objective

Evaluating the potential of low-salinity water to enhance the oil recovery from reservoir limestone is the main objective of this project.

Since, the presence of anhydrate in reservoir is one of the important factors, which can affect the initial wetting condition of the reservoir towards more water wetness, we decided to evaluate the effect of low salinity brine on both limestone core containing anhydrite and chalk core containing no anhydrite.

Furthermore, the effect of temperature on dissolution of anhydrite has been evaluated in this study.

Totally four flooding tests were conducted on three limestone cores and one chalk core, to evaluate the low salinity effect due to presence of anhydrite and different temperature.

3 Theory and fundamentals

3.1 Petroleum reservoir

A petroleum reservoir, or oil and gas reservoir, is a subsurface pool of hydrocarbons contained in porous or fractured rock formations[6]. The largest hydrocarbon reserves are located in Siberia and Middle East where the most of them are Carbonate field. Ghawar field in Saudi Arabia, Burgan in Kuwait and Ferdows in Iran are good examples of world largest carbonate field.

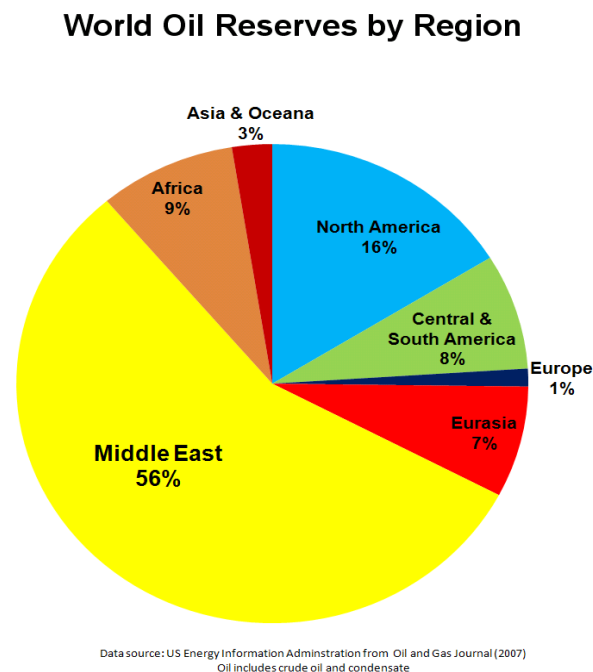


Figure 3.1 World oil reserves in different location

3.2 Carbonates

The carbonates are among the most widely distributed minerals in the Earth's crust. More than 50% of the petroleum reservoirs are trapped in carbonate rock. In geology and mineralogy, the term "carbonate" can refer both to carbonate minerals and carbonate rock (which is made of chiefly carbonate minerals), and both are dominated by the carbonate ion, CO_3^{2-} . Carbonate minerals are extremely varied and ubiquitous in chemically precipitated sedimentary rock,

3.2.1 Carbonates minerals

Those minerals containing the carbonate ion CO_3^{2-} as the basic structural and compositional units are called carbonate minerals. The carbonates tend to be soft, soluble in hydrochloric. Many carbonates minerals have a crystal structure, which reflects the trigonal symmetry of the carbonate ion. As it is showed in Fig. 3.2, it is composed of a carbon atom centrally located in an equilateral triangle of oxygen atoms. This anion group usually occurs in combination with calcium, sodium, uranium, iron, aluminum, manganese, barium, zinc, copper, lead, or the rare-earth elements[7].

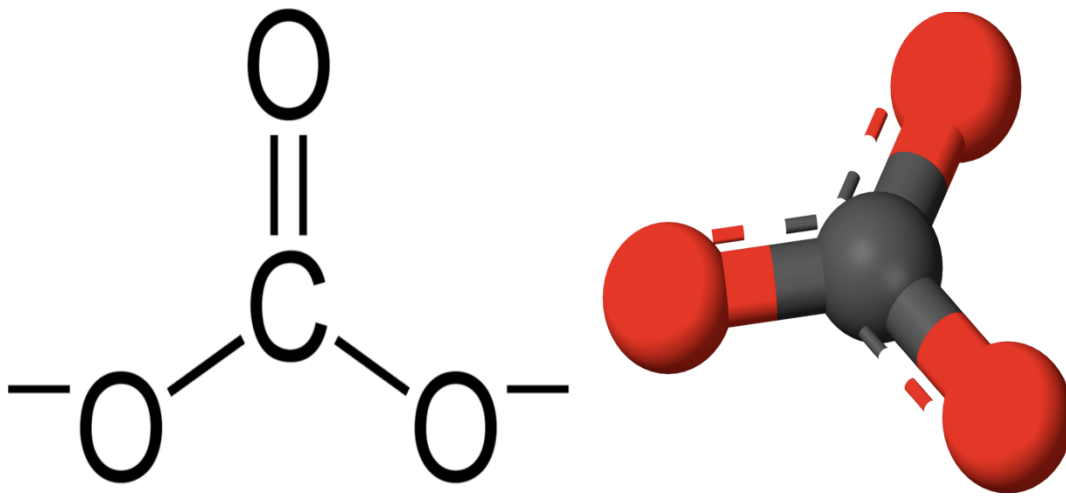


Figure 3.2 Carbonate mineral

3.2.2 Carbonates rocks

The carbonate rocks make up 10 to 15% of sedimentary rocks. They largely consist of three types of rocks. Limestone, which are composed mostly of calcite (CaCO_3) or high Mg calcite $[(\text{Ca},\text{Mg})\text{CO}_3]$, Dolostone, which are composed mostly of dolomite $[\text{CaMg}(\text{CO}_3)_2]$ and Chalk which is special case of carbonate rocks.

Carbonate rocks are of varied origins. These origins are: detrital formed of debris, constructed of the reef type and chemical formed by the precipitation of bicarbonate, and originating in marine muds.

The carbonates minerals in general are soluble in slightly acidic waters and for this reason they often have high porosity and permeability which make them ideal reservoirs for

petroleum[7]. It is documented more than 50% of the world hydrocarbon resource are trapped in carbonates, which usually show an oil recovery less than 30% due to the wettability and the fractured nature of these reservoirs.

3.2.2.1 Limestone

Limestone is a sedimentary rock, which contains at least 50% calcium carbonate in the form of calcite by weight. All limestone's contain at least a few percent other materials and particles such as quartz, feldspar, clay minerals, pyrite, siderite and other minerals. It can also contain large nodules of chert, pyrite or siderite[8].

Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation. Most of the limestones are composed of grains, which formed from skeletal fragments of marine organisms such as coral or foraminifera. There is also some limestone which are formed completely by the chemical precipitation of calcite or aragonite, i.e. travertine and they do not consist of any grain.

It is initially composed primarily of the mineral, calcite and aragonite (CaCO_3). Usually some magnesium is present and it will be called a low Mg calcite or low Mg aragonite. Magnesium containing brine (e.g., sea water) percolating through limestone will result in some of the calcium being replaced by magnesium and the resulting rock is called dolostone and the resulting mineral is called dolomite [$\text{CaMg}(\text{CO}_3)_2$] when it has equal amounts of calcium and magnesium. Fig. 3.3 shows a SEM picture of a limestone section[2, 9].

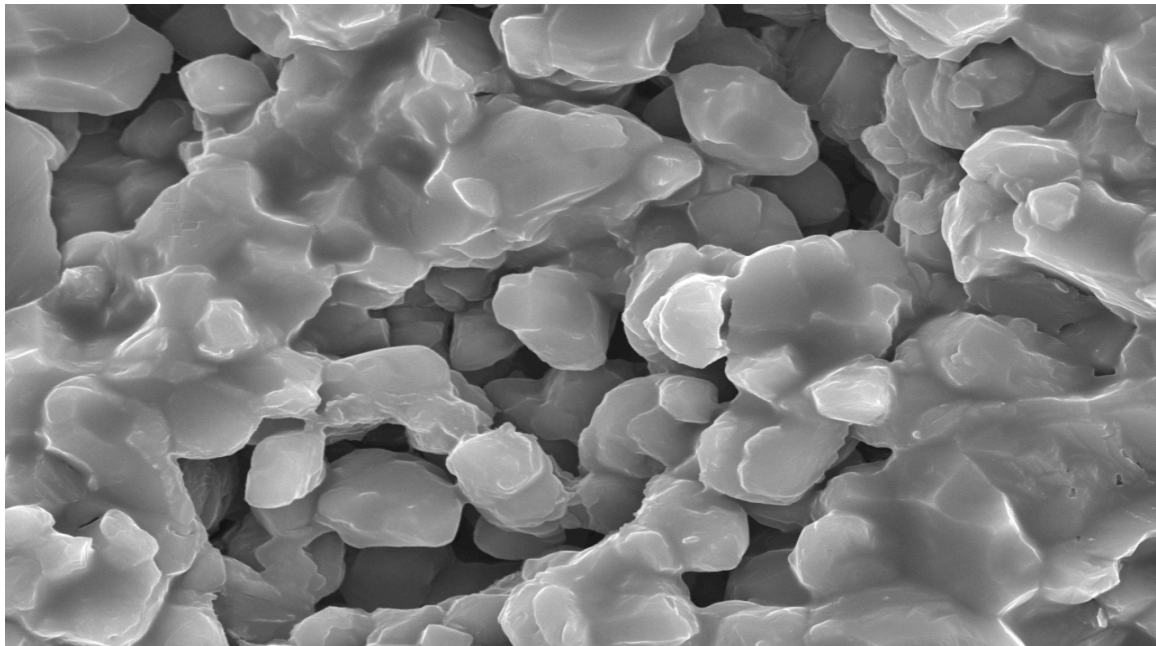
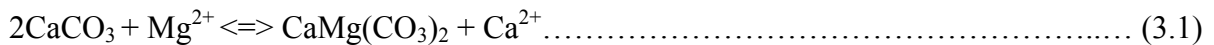


Figure 3.3 SEM image of a limestone section

3.2.2.2 Dolomite

Dolomite is a sedimentary carbonate rock that contains a high percentage of the mineral dolomite. Dolomite forms as a secondary mineral and as a result of reaction between different forms of CaCO₃ and Mg²⁺, Eq.3.1 [2].



Dolomite does not form on the surface of the earth and it is one of the few sedimentary rocks that undergo a significant mineralogical change after it is deposited. They are originally deposited as calcite/aragonite rich limestone, but during a process call diagenesis the calcite and/or aragonite is altered to dolomite. The process is not metamorphism, but something just short of that. Magnesium rich ground waters that have a significant amount of salinity are probably crucial and warm, tropical near ocean environments are probably the best source of dolomite formation[10].

In seawater, concentration of magnesium is much more higher than calcium ($\text{Mg}^{2+}/\text{Ca}^{2+} \approx 5$), and we would expect magnesium carbonates to be the predominant minerals formed, except

for the hydration effect. However, the sulfate ion (SO_4^{2+}) is very efficient at preventing dolomitisation. Thus, dolomitisation can easily take place, when there are few sulfate ions. Mixing with fresh water will lower the sulfate concentration without necessarily changing the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio[2].

“The significance of dolomitisation is that the process creates secondary porosity because calcite or aragonite dissolves and the precipitated dolomite does not fill the entire volume which has been dissolved away”[11].

3.2.2.3 Chalk

Chalk is a porous sedimentary rock, which comprises of a sequence of mainly soft, white very fine-grained extremely pure limestone's that composed of the mineral calcite. Chalk is resistant to weathering and slumping compared to the clays with which it is usually associated, thus forming tall steep cliffs where chalk ridges meet the sea. These rocks are special case of carbonates which consist mainly of the remains of skeletal bits of planktonic green algae, associated with varying proportions of larger microscopic fragments of bivalves, foraminifera and ostracods[12].

Due to the soft nature of the biogenic sediment, the reservoirs are usually naturally fractured. The permeability of the matrix block is low, about 2mD, and the porosity can be very high, nearly 50%. Because chalk is porous it can hold a large volume of ground water, providing a natural reservoir that releases water slowly through dry seasons.

The presence or absence of an organic coating on the chalk particles has consequences for wetting behavior[2, 12].

3.3 Oil recovery

Oil recovery is a process, which makes the oil to be produced. The amount of the oil that is recoverable is determined by a number of factors including the permeability of the rocks, the strength of natural drives and the viscosity of the oil.

The oil recovery classified in three main steps: Primary recovery, Secondary recovery and Tertiary recovery.

Figure 3.4 shows the production rate due to different recovery stages through the time.

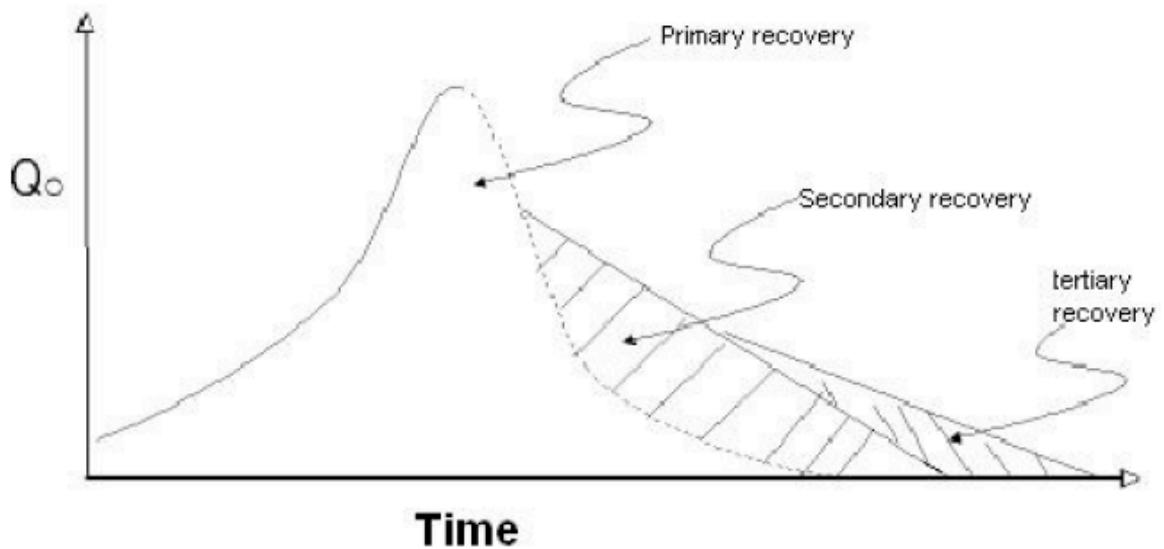


Figure 3.4 Recovery stages of a hydrocarbon reservoir through time

3.3.1 Primary recovery

The initial production or primary production is the first oil out, the “easy” oil, which is the result of the natural mechanisms in the reservoir.

Once a well has been drilled and completed in a hydrocarbon-bearing zone, the natural pressures at that depth will cause the oil to flow through the rock or sand formation toward the lower pressure wellbore.

Pressure difference inside the reservoir rock, displacing oil by natural water, expansion of the natural gas at the top of the reservoir, gravity drainage and many other natural mechanism which make the reservoir fluid flows out of the reservoir rock and into a wellbore, count as primary recovery.

Primary recovery is the least expensive method of extraction and typically recovery factor during this stage is 5-15% or original oil in place (OOIP)[6, 13].

3.3.2 Secondary Recovery

During the time, pressure inside the reservoir will decrease, as it won't be sufficient to force the oil to the surface. Thus, the secondary recovery method will be applied to adjust the reservoir pressure. To increase the reservoir pressure and reduce the overall density of fluid inside the wellbore, an external energy can be supplied into the reservoir.

Water flooding is the most common technique that utilizes injector wells to introduce large volumes of water under pressure into the hydrocarbon-bearing zone. As the water flows through the formation toward the producing wellbore, it sweeps some of the oil it encounters along with it. Upon reaching the surface, the oil is separated out for sale and the water is re-injected[13].

In addition, natural gas reinjection and gas lift or using some pumps, such as beam pump and electrical submersible pump (ESPs), are another secondary methods to bring the oil to the surface[1, 6, 13].

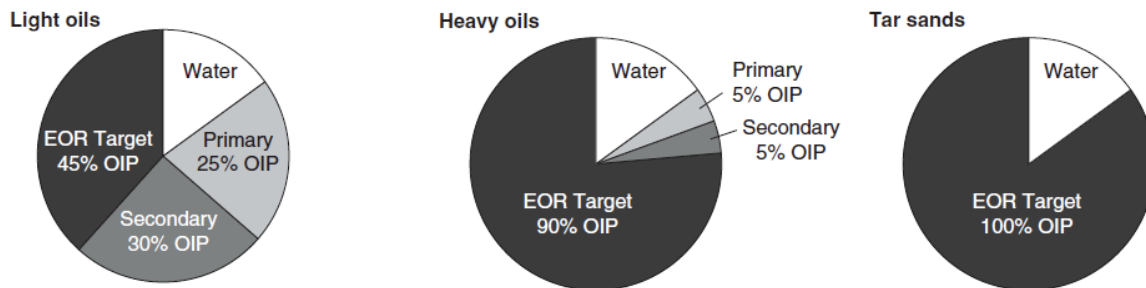
On average, the recovery factor after primary and secondary oil recovery operations is between 30% to 50%[6].

3.3.3 Tertiary Recovery

Tertiary recovery or EOR begins when secondary oil recovery isn't enough to continue adequate extraction, but only when the oil can still be extracted profitably. The EOR purpose in addition to restoring the formation pressure is to improve the oil displacement or fluid flow in reservoir. Thus, the mobility of the oil increases in order to increase extraction and it also cause another 5% to 15% of the reservoir's oil to be recovered.

The optimal application of tertiary recovery depends on many factors such as: reservoir temperature, pressure, depth, net pay, permeability, residual oil and water saturations, porosity and fluid properties such as oil API gravity and viscosity[6].

Fig.3.4 shows the effect of EOR in different hydrocarbon[1].



(Assuming $S_{oi} = 85\% \text{ PV}$ and $S_w = 15\% \text{ PV}$)

Figure 3.5 EOR target for different hydrocarbon

3.4 Recovery Rate

The amount of oil that is recoverable is determined by a number of factors including the permeability of the rocks, the strength of natural drives (the gas present, pressure from adjacent water or gravity), and the viscosity of the oil. Oil flows more freely through the permeable rock such as sandstone in comparing to tight rocks such as shale.

The flow of oil is often helped by natural pressures surrounding the reservoir rocks including natural gas that may be dissolved in the oil (GOR), natural gas present above the oil, water below the oil and the strength of gravity. Oils tend to span a large range of viscosity from liquids as light as gasoline to heavy as tar. The lightest forms tend to result in higher extraction rates[1].

3.5 Recovery of residual oil

Recovery of residual oil depends on the reservoir characterization. In a water-wet reservoir, the brine exists as film around the rock grains and the oil exist as free phase in pore space. During waterflooding, the oil saturation will be decreased and the remained oil will be exists partly as a continuous phase in some pore channels but as discontinuous droplets in other channels. At ending stage of waterflood, the oil will be reduced to residual oil saturation, S_{or} , while it exists primarily as a discontinuous phase of droplets or globules that have been isolated and trapped by the displacing brine. The mobilization of the residual oil saturation in

a water-wet system requires that the discontinuous droplets be connected to form a continuous flow channel that leads to a producing well.

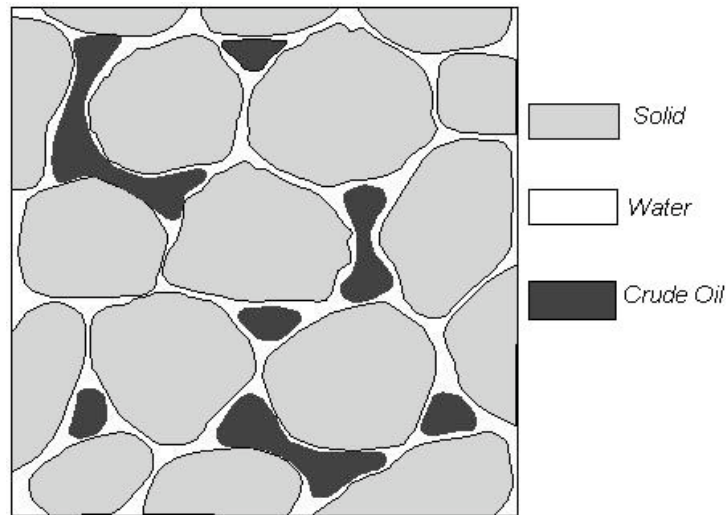


Figure 3.6 Water-wet reservoir[2]

The recovery of residual oil in an oil-wet system is different than the water-wet system. At beginning of waterflooding, the brine forms continuous flow paths through the center portions of some of the pore channels. The brine enters more and more of the pore channels as the waterflood progress. At residual oil saturation, the brine has entered a sufficient number of pore channels to shut off the oil flow. The residual oil exists as a film around the sand grains. In the smaller flow channels, the film may occupy the entire void space[14].

In an oil-wet porous medium, the film of oil around the sand grains must be displaced to large pore channels and be connected in a continuous phase before it can be mobilized. The mobilization of oil is governed by the viscous forces (pressure gradients) and the interfacial tension forces that exist in the sand grain-oil-water system[2].

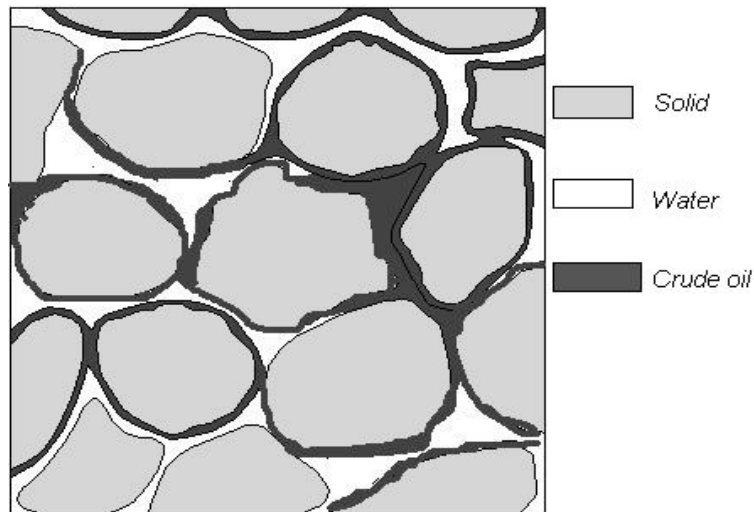


Figure 3.7 Oil-wet reservoir[2]

It has been observed that, two major factors which influence the mobilization of residual oil are:

- **Capillary Number (N_c)**, which is defined as $N_c = v\mu/\sigma$ where v is the Darcy velocity (m/s), μ is the displacing fluid viscosity (Pa.s) and σ is the interfacial tension (N/m)
- **Mobility Ratio (M)**, which is defined as $M = \lambda_{ing} / \lambda_{ed}$ where λ_{ing} is the mobility of the displacing fluid (e.g. water), and λ_{ed} is the mobility of the displaced fluid (oil).
 $\lambda = k/\mu$, where k is the effective permeability, (m^2) and μ is the viscosity (Pa.s) of the fluid concerned

One of the practical ways of increasing the Capillary Number is by reducing interfacial tension, which can be done by using a suitable surfactant or by the application of heat. Figure 3.8 shows, an approximation of the effect of Capillary Number on residual oil saturation[1].

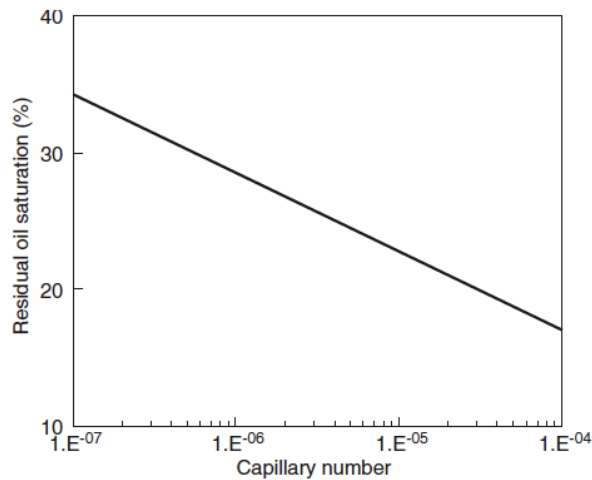


Figure 3.8 Effect of Capillary number on residual oil saturation

“Capillary number at the end of a waterflood is $\sim 10^{-7}$. A 50% reduction in residual oil saturation requires that the Capillary Number be increased by 3 orders of magnitude”[1].

Mobility ratio influences the microscopic (pore level) and macroscopic (areal and vertical sweep) displacement efficiencies. The mobility ratio is unfavourable when it has a value of $M > 1$ which indicates that the displacing fluid flows more readily than the displaced fluid (oil), and it can cause channeling of the displacing fluid, and as a result, bypassing of some of the residual oil. Under such conditions, and in the absence of viscous instabilities, more displacing fluid is needed to obtain a given residual oil saturation. The effect of mobility ratio on displaceable oil is shown in Figure 3.9. The three curves represent 1, 2 and 3 pore volumes of total fluid injected, respectively. Displacement efficiency is increased when $M = 1$, and is denoted a “favourable” mobility ratio[1].

Figure 3.10 shows the effect of mobility ratio due to oil displacement by water injection.

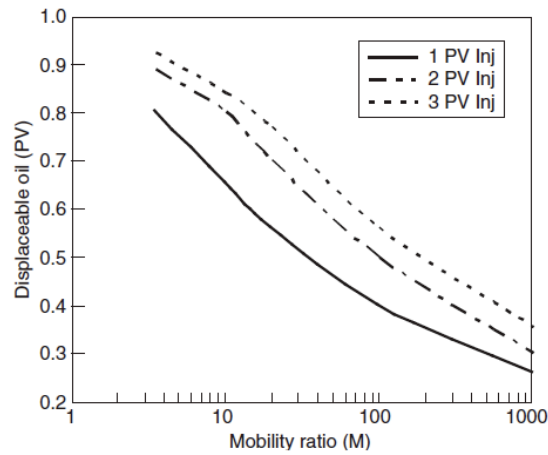


Figure 3.9 Effect of mobility ratio on displaceable oil

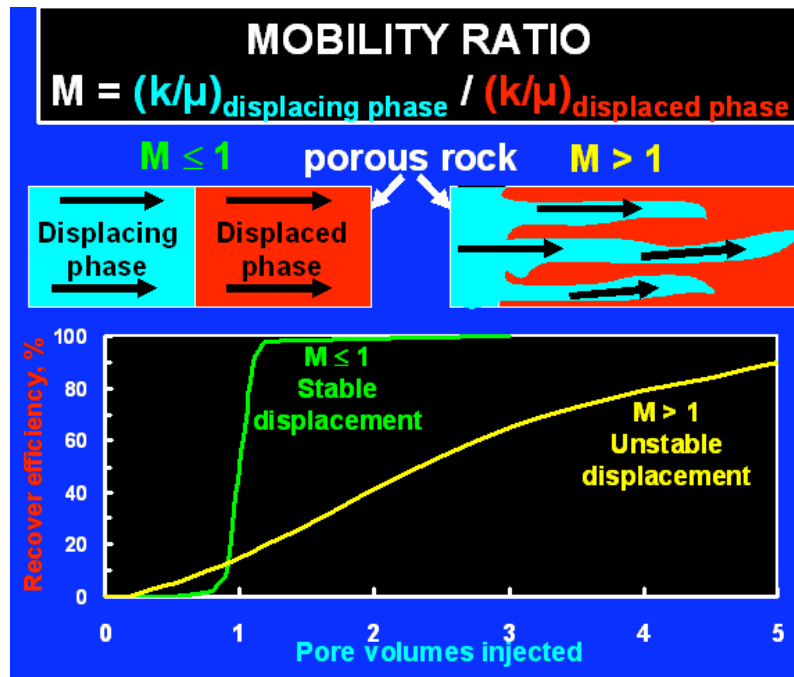


Figure 3.10 Effect of mobility ratio on oil displacement by water injection[15]

3.6 Improvement oil recovery

Improved oil recovery (IOR) is a general term that implies improving oil recovery by any means. For example, operational strategies, such as infill drilling and horizontal wells, improve vertical and areal sweep, leading to an increase in oil recovery.

Interest and investments in IOR have continued around the world, particularly in countries with aging fields. Various methods and processes have been developed and implemented in Canada and the USA because of rapidly declining oil production rates from their aging conventional oil fields and low average well productivity. In recent years, the continuous increase in oil prices has increased IOR activities to its highest level ever, both in terms of the field applications and research[16].

Figure 3.11 shows a mount of oil barrel which can/can't be recovered by IOR technologies.

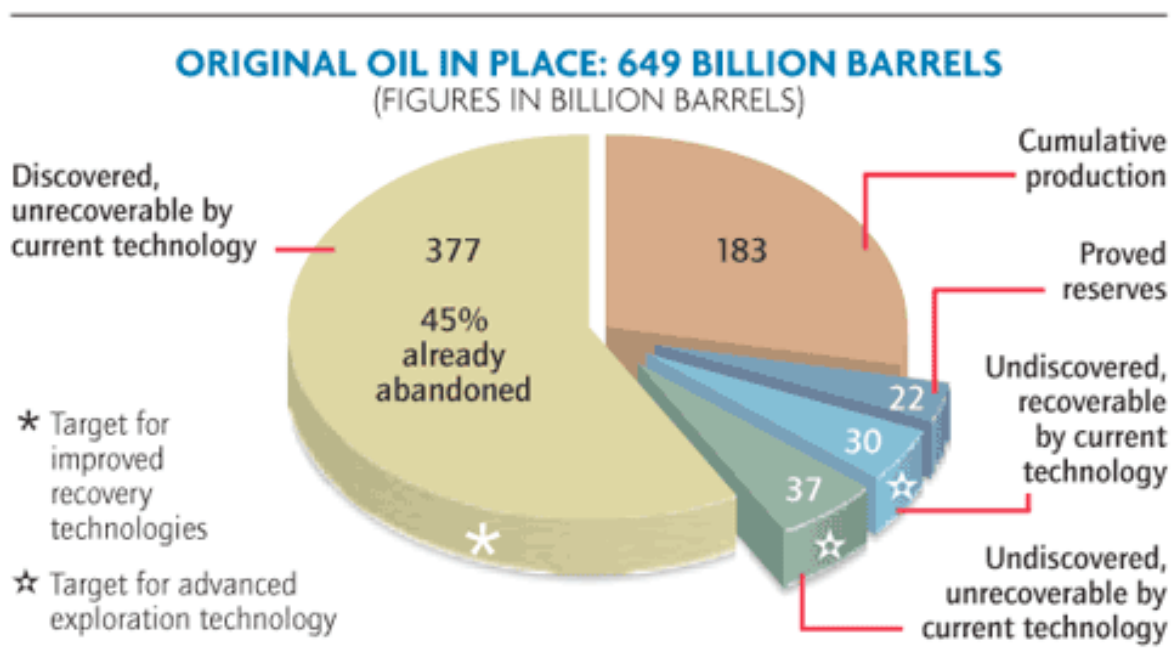


Figure 3.11 Target for IOR technologies[13]

3.7 EOR Definition

Enhanced Oil Recovery (EOR) is any process whereby oil is produced other than by natural reservoir pressure. Enhanced oil recovery, or EOR, is more specific in concept and it is a part of the general scheme of Improved Oil Recovery (IOR). It's also known as tertiary recovery. Nearly 2.0×10^{12} barrels (0.3×10^{12} m³) of conventional oil and 5.0×10^{12} barrels (0.8×10^{12} m³) of heavy oil will remain in reservoirs worldwide and much of this oil would be recovered by EOR methods.

Choosing a suitable method to enhanced oil recovery is a great challenge and the choice of the method and the expected recovery depends on many considerations, economic as well as technological. Many recovery methods have been tested, but Only a few recovery methods have been commercially successful, such as steam injection based processes in heavy oils and tar sands (if the reservoir offers favorable conditions for such applications) and miscible carbon dioxide for light oil reservoirs. Other EOR methods suffer from limitations both economics and technological[1].

Usually, the bulk of the production from heavy oils and tar sands, which respond poorly to primary and secondary, comes from EOR recovery methods. But for light oil reservoirs, EOR is usually applicable after secondary recovery operations, and the EOR target is to reach ~45% OOIP[1].

“EOR implies a reduction in oil saturation below the residual oil saturation (S_{or}). Recovery of oils retained due to capillary forces (after a waterflood in light oil reservoirs), and oils that are immobile or nearly immobile due to high viscosity (heavy oils and tar sands) can be achieved only by lowering the oil saturation below S_{or} .”

Miscible processes, chemical floods and steam-based methods are effective in reducing residual oil saturation, and are hence EOR methods.”[1].

3.8 EOR Methodes

Different EOR methods have been tested since 1950’s. When unfavorable conditions such as heavy-oil, large matrix size, high IFT, low permeability, oil-wet and poorly connected fracture network exist in an oil reservoir, additional support to enhance the oil recovery is inevitable. Water and gas can be injected in order for the trapped oil to be recovered by capillary and gravity forces, respectively. These processes may not yield significant recovery increase, as oil becomes heavier and less water wet. In this case, other EOR method can be thought to overcome the limitations[1].

These EOR method are divided into four main categories:

- Thermally enhanced oil recovery method
- Miscible flooding
- Chemical flooding
- Mobility control process

They are the most advanced among EOR methods, as far as field experience and technology are concerned.

3.8.1 Thermal enhanced oil recovery methods

Thermal methods supply heat to the reservoir, which contain heavy oil with high viscosity and low mobility. The major mechanisms of this method are vaporize some of the oil and make a large reduction in viscosity, mobility ratio and provide a displacement mechanism. Other mechanisms, such as rock and fluid expansion, compaction, steam distillation and visbreaking may also be present. Thermal methods have been highly successful in Canada, USA, Venezuela, Indonesia and other countries. There is three different methods, which can be, identify as thermal recovery method[1]:

- Cyclic steam stimulation (CSS)
- Steam flooding
- Steam assisted gravity drainage (SAGD)
- Conduction heating in situ combustion

3.8.1.1 Cyclic steam stimulation (CSS)

CSS is a “single well” process, which a well is injected with steam and then subsequently put back on production. CSS consists of three stages, as shown in Figure 3.12.

At initial stage a slug of steam is introduced into the reservoir and is continued for about a month, which is called steam injection. Then, at the second stage, or soak the well will be shut in for a few days for heat distribution, denoted by soak. Finally, during the last stage, the thinned oil is produced through the same well and the Oil rate will be increased quickly to a high rate, and stays at that level for a short time, and declines over several months. The cycle is repeated as long as oil production is profitable[1, 17].

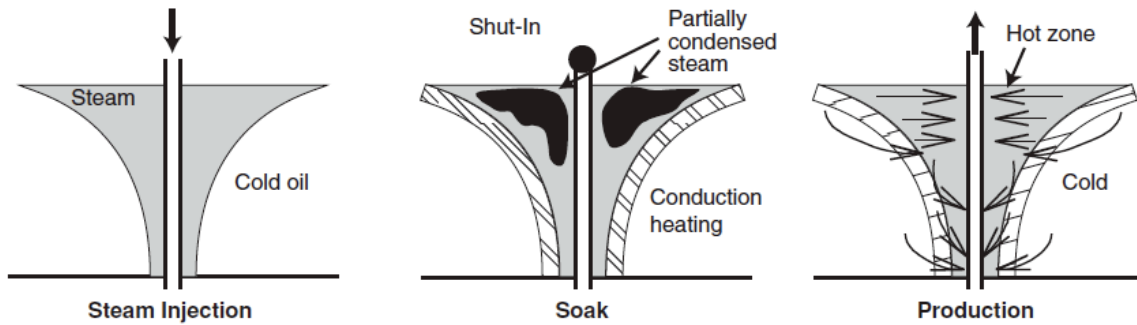


Figure 3.12 Cyclic steam stimulation method[1]

3.8.1.2 Steam flooding

Steam flooding is sometimes known as a steam drive which is similar to water flooding. In this method, steam is injected continuously, and it forms a steam zone, which advances slowly. Oil will be mobilized due to viscosity reduction, which cause a higher production rate[1, 3].

3.8.1.3 Steam assisted gravity drainage (SAGD)

SAGD is an advanced form of steam simulation. In this method a pair of parallel horizontal well are drilled. One of these well is drilled into the reservoir and the other one is a few meters above the other. The upper wellbore is used to inject the low pressure steam and to heat the oil, Fig. 3.13. *“This will be continued until the high reduction in viscosity mobilizes the bitumen, which drains down by gravity and is captured by the producer placed near the bottom of the reservoir. Continuous injection of steam causes the steam chamber to expand and spread laterally in the reservoir. High vertical permeability is crucial for the success of SAGD. The process performs better with bitumen and oils with low mobility, which is essential for the formation of a steam chamber, and not steam channels”* [1].

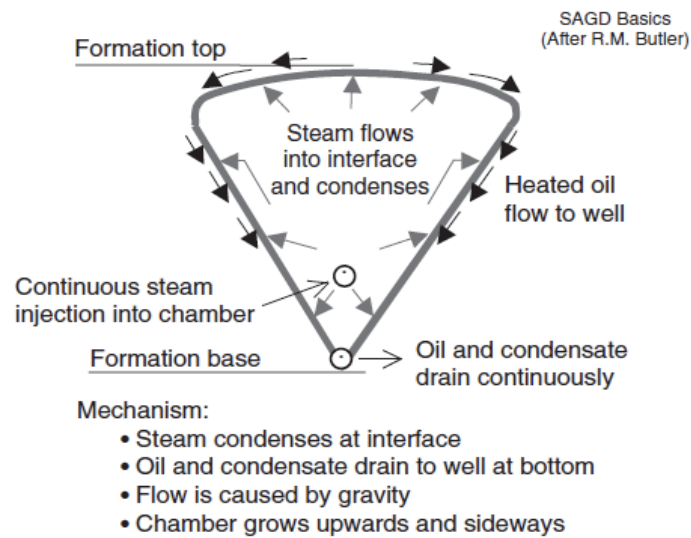


Figure 3.13 Steam assisted gravity drainage

3.8.1.4 Conduction heating in situ combustion

This method is also known as fire flooding in which thermal energy is released in the reservoir by oxygen combines with the fuel (crude oil fractions). In this method oil in reservoir is ignited and fire sustained by air injection and high reduction in oil viscosity occurs near the combustion zone. In situ combustion has been tested in many places, however, very few. The main variations of in situ combustion are Forward combustion, Reverse combustion and High pressure air injection.

In situ combustion has been tested in many places, however, very few projects have been economical and none has advanced to commercial scale[1].

3.8.2 Miscible flooding

“Miscible displacement processes are defined as processes where the effectiveness of the displacement results primarily from miscibility between the oil in place and the injected fluid”[2]. Fig. 3.14 shows a schematic of miscible flooding[18]. Displacement fluids, such as hydrocarbon solvents, CO₂, flue gas and nitrogen are considered. Miscibility plays a role in surfactant flooding processes, but is not the primary recovery mechanism for these processes

and also in other processes that are basically immiscible, such as polymer-augmented waterflooding.

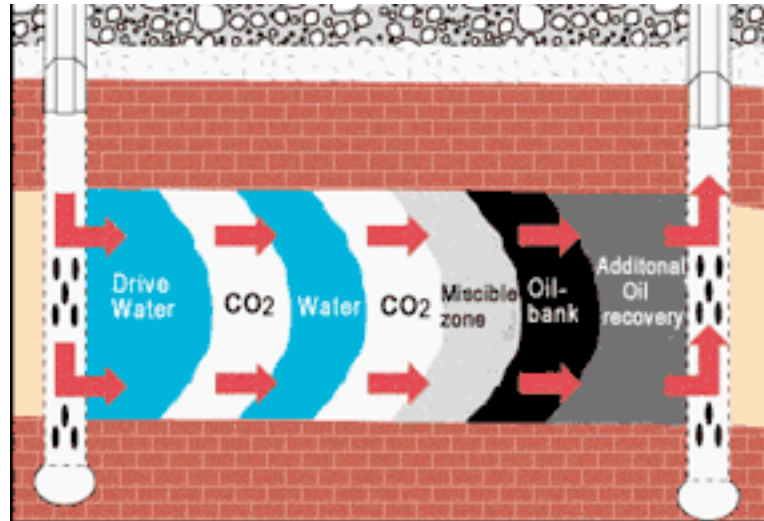


Figure 3.14 Schematic of miscible flooding

3.8.3 Chemical flooding

Chemical flooding is an important process for EOR, where various chemicals, usually as dilute solutions such as alkaline or caustic solutions into reservoirs have been injected to the reservoir. Chemical methods utilize a chemical formulation as the displacing fluid, which promotes a decrease in mobility ratio and/or an increase in the capillary number.

The major chemical flood processes are:

- Polymer flooding
- Surfactant flooding
- Alkaline flooding
- Micellar flooding
- ASP (alkali-surfactant-polymer)

3.8.4 Mobility control process

“Mobility control is a generic term describing any process where an attempt is made to alter the relative rates at which injected and displaced fluids move through the reservoir” [2] . This method is used to improve the volumetric sweep efficiency of a displacement process. In some cases, there is also an improvement in efficiency of microscopic displacement at a specified volume of fluid injected. Mobility control is usually discussed in terms of the mobility ratio, M , and a displacement process is considered to have mobility control if $M \leq 1.0$. The volumetric sweep efficiency increased as M is reduced, and it is sometimes advantageous to operate at a mobility ratio considerably less than unity, especially in reservoirs with substantial variation in the vertical or areal permeability[2].

3.8.5 Other methods

A few other methods, including combination methods such as Surfactant-Steam, Steam-Foam, and Micellar-ASP, were also tested for EOR. Notable among them are Microbial method and Foam flooding.

3.9 Force displacement

There are several forces that affect flow of different fluid in the reservoir. Among these forces gravity, capillary and viscous forces have the most effect.

3.9.1 Gravitational force

The gravitational force is caused by the differences in density between two or more fluids. In a situation where there is high density difference between fluid phase, i.e. oil-gas systems, the gravitational force has large effect on production rate. It is well known that the fluid with the lowest density will have a tendency to flow upwards in the present of a more dense fluid[2, 19]. The gravity force can be expressed by equation 3.2 [2].

$$\Delta P_g = \Delta \rho \cdot g \cdot H \dots\dots\dots (3.2)$$

ΔP_g : Pressure difference between oil and water due to gravity

$\Delta \rho$: Density difference between oil and water

g : Acceleration due to gravity

H : Height of liquid column

3.9.2 Viscous force

The viscous force is defined as the intermolecular interaction within the fluid itself and relative to the bounding conditions such as the pore channel wall or other fluids. This force causes a velocity profile to develop across the flow channel and is the reason for the viscous pressure drop in the reservoir[19]. Poiseuille’s law given in equation 3.3 gives the pressure drop for laminar flow through a single tube.

$$\Delta P = (-8\mu L v / r^2 g_c) \dots\dots\dots (3.3)$$

Δp : pressure across the capillary tube

μ : viscosity of flowing fluid

L: capillary-tube length

v: average velocity in the capillary tube

r: capillary-tube radius

g_c : conversion factor

3.9.3 Capillary force

The capillary force (P_c) is a pressure difference under dynamical flow conditions between the interface of two phases. In a petroleum reservoir the capillary force is defined as the result of the combined effect of the surface and interfacial tensions of the rock and fluids, the pore size and geometry, and the wetting characteristics of the system[20]. Capillary force has a large effect on wettability and the spreading of the wetting phase in particular[19].

In the pores of a porous medium, the displacement of one fluid by another in is either aided or opposed by the surface forces of capillary pressure. *“As a consequence, in order to maintain a porous medium partially saturated with nonwetting fluid and while the medium is also exposed to wetting fluid, it is necessary to maintain the pressure of the nonwetting fluid at a value greater than that in the wetting fluid”*[19].

3.9.4 Inertial force

The inertial force is associated with the redirection of fluid flow in the porous media. In flow through porous media the relation between an observed pressure drop and velocity is generally a nonlinear one and this nonlinearity is expected due to the inertia forces which must occur in flow through a medium which imposes frequent changes in flow direction. [19, 21].

3.10 Wettability

In general, wettability is defined as *"the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. It refers to the interaction between fluid and solid phases"*[22].

The concept of wettability in petroleum reservoir engineering appears to have been borrowed from the field of surface science. In the studies concerning surface phenomena this wettability term has been used interchangeably with spreadability. *"If a liquid spreads spontaneously on a given solid surface, it is said to be wetting the solid. On the other hand, if the liquid beads up into droplets on a solid surface instead of spreading, then it is said to be nonwetting"*. The wetting state of a solid surface in presence of a liquid phase is illustrated in Fig. 3.15[2, 23].

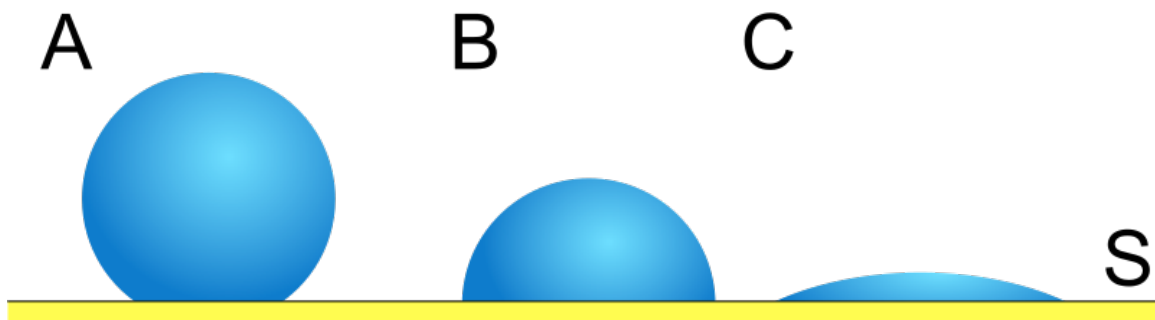


Figure 3.15 Wetting condition of the Solid surfaces (S), A: Non-wetting phase, B: intermediate wetting and C: Wetting phase

In a rock/oil/brine system, wettability describes the relative preference of a rock to be covered by a certain phase and the location of a phase within the pore structure determines the wettability of the system.

The wettability of the rock/fluid system has an important influence on controlling the location, flow, and distribution of fluids in a reservoir and oil production. In general, one of the fluids in a porous medium of uniform wettability that contains at least two immiscible fluids will be the wetting fluid. When the system is in equilibrium, the wetting fluid will completely occupy the smallest pores and be in contact with a majority of the rock surface (assuming, of course, that the saturation of the wetting fluid is sufficiently high). The non-

wetting fluid will occupy the centers of the larger pores and form globules that extend over several pore[24].

The rock is characterized to be water-wet if the rock has (much) more affinity for water than for oil. In that case, a major part of the rock surface in the pores will be covered with a water layer and the water exists more or less as a continuous film through pores and open channels. An illustration is shown in Figure 3.16. [25, 26]. *“In such a system is also typical for a result of a process referred to as snap-off of oil. This is a system where water is pushing oil through pore throats and droplets of oil are released from the main oil globule by a snap-off. This process leaves trapped oil drops in pores similar to what is shown in the figure above”*[26].

In oil wet system the oil is the phase contacting the rock surface and is located in small pores, while the brine is located in the centre of the large pores. The oil will remain as a thin film on the rock surface and in the smallest pore channels during waterflooding and water will flow through the largest pore channels. At high water saturations, the brine is continuous throughout the pore network[24, 27].

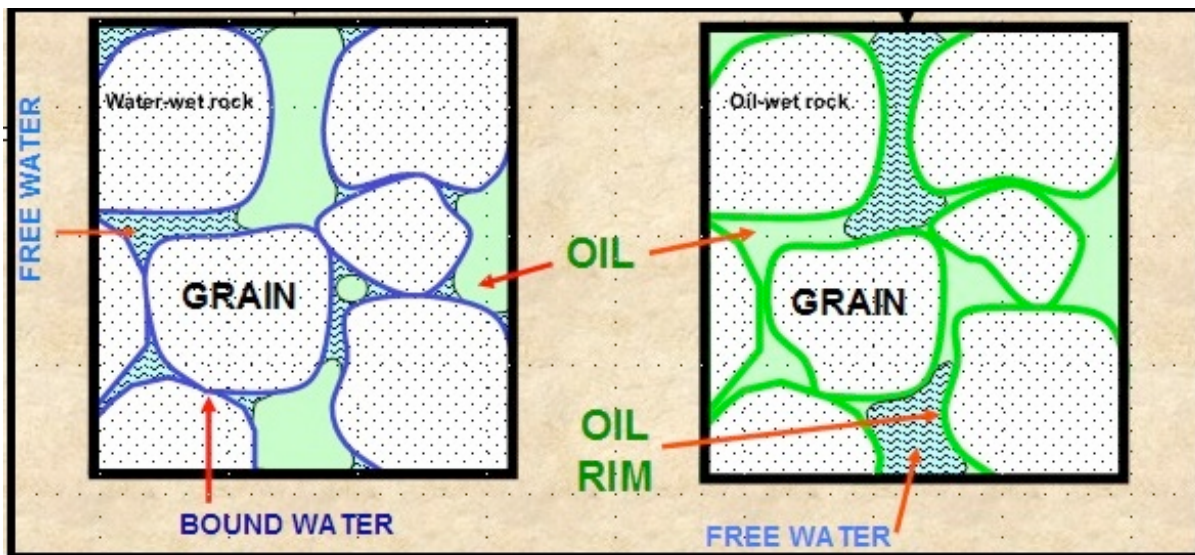


Figure 3.16 Water-wet reservoir and Oil-wet reservoir

When the rock has no strong preference for either oil or water, the system is said to be of neutral (or intermediate) wettability. Besides strong and neutral wettability, a third type is fractional wettability, where different areas of the core have different wetting preferences.

All important parameters for flow of both oil and water in porous media such as capillary pressure, relative permeabilities, fluid distribution, and flow directions are dictated by wettability. Therefore wettability of the formation is extremely important when producing oil from subterranean formations[2].

Systems with crude oil have varying degrees of wettability. Fig. 3.17 illustrates the remaining oil saturation in a core as a function of the wetting index and pore volumes of water throughput[28].

The wettability index is vary between -1.0 for oil-wet and +1.0 for water-wet conditions.

In the water-wet system the oil is trapped by the snap-off mechanism. Thus, the oil production stops immediately after water breakthrough. But this process is different in an oil-wet system where the remaining oil is in the smaller pores make a small contribution to the relative permeability for a given saturation.

In this case, the oil production tails out over many pore volumes of throughput the oil relative permeability is very small but nonzero[28].

When the system is intermediate in wetting index, snap-off is inhibited and the oil is less likely to be in the smaller pores and thus less oil remains after waterflooding[2].

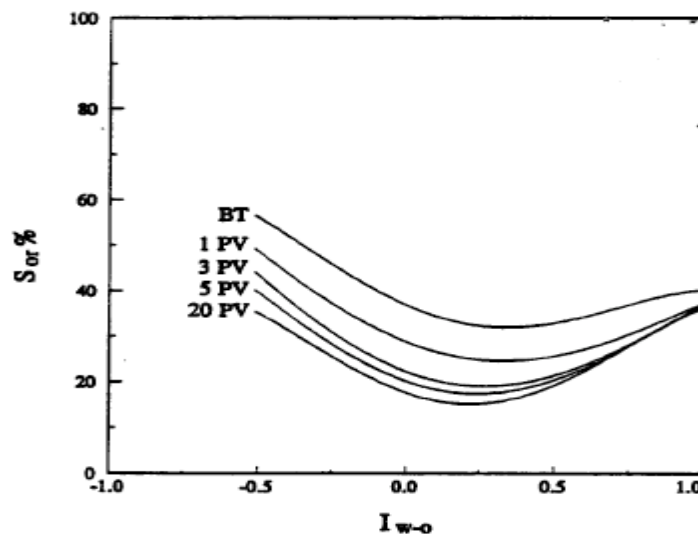


Figure 3.17 Remaining oil saturation after waterflooding[28]

The wetting condition of a reservoir rock plays a very important role in selection of methods or mechanism for enhanced oil recovery. There are different methods developed to measure

the wetting condition of a solid surface. Some of these methods will be discussed in the next sections.

3.11 Wettability measurements

Wettability can be measured in the laboratory. There are many different ways for measuring the wettability of a system. Three quantitative methods are generally used:

- Contact angle measurement
- The Amott test
- The U. S. Bureau of Mines (USBM) test
- New wettability test

3.11.1 Contact angle

The contact angle (θ) is the angle at which liquid or vapor interfaces meet a solid surface. It is not limited to a liquid/vapour interface only; it is equally applicable to the interface of two liquids or two vapors. The maximum angle, which is obtained by pushing the fluid over the surface, while, the minimum is obtained by pushing the fluid back. The maximum and the minimum angles measured through the same fluid are referred to as the advancing contact angle and the receding contact angle, respectively.

The contact angle, θ is a function of the relative adhesive tension of the liquids to the solid. The angle is described by Young’s equation[29]:

$$\cos\theta = (\sigma_{s1} - \sigma_{s2}) / \sigma_{12} \dots\dots\dots(3.4)$$

σ_{s1} : Interfacial tension (IFT) between the solid and fluid 1

σ_{s2} : Interfacial tension between the solid and fluid 2

σ_{12} : Interfacial tension between the two fluids

Interfacial tension, IFT, between two fluids can be determined by using tensiometer. For ultra low IFT a spinning drop tensiometer can be used, in other cases a ring tensiometer can be used.

To measure wettability of the reservoir rock, the IFT between rock mineral, oil and water must be calculated. The reservoir rock is described as being water wet, if $\theta < 90^\circ$, whereas if $\theta > 90^\circ$ it is oil wet[30].

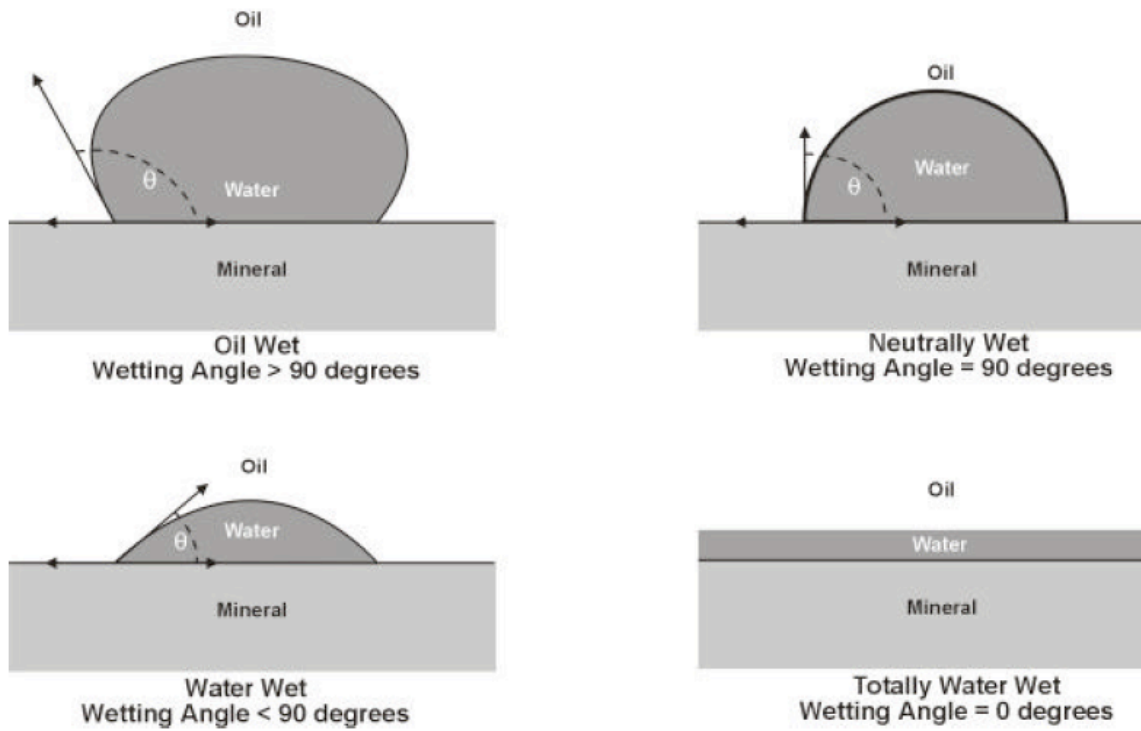


Figure 3.18 Relation wetting condition and contact Angle[30]

Contact angle	Wetting condition
0°-30°	Strongly water-wet
30°-90°	Preferentially water-wet
90°	Neutral wettability
90°-150°	Preferentially oil-wet
150°-180°	Strongly oil-wet

Table 3.1 Contact angle versus wetting condition[2]

3.11.2 Amott test

The Amott test is combination of spontaneous imbibition and forced displacement that measure the average wettability of a core. The method is based on the fact that the wetting fluid will generally imbibe spontaneously into the core and displace the non-wetting one. The ratio of spontaneous to forced imbibition is used to reduce the influence of other factors such as relative permeability, viscosity and the initial saturation of the core[24].

Usually, in the first step of the Amott test, the core is centrifuged in water and then in oil to reduce the specimen to the irreducible water saturation S_{wir} . Then the following four steps are executed:

1. Immerse the core in water, and measure the volume of oil displaced spontaneously
2. Centrifuge the core in water until the residual oil saturation S_{orw} is reached, and measure the amount of oil displaced under force
3. Immerse the core in oil, and measure the volume of water displaced spontaneously
4. Centrifuge the core in oil until S_{wir} is reached, and measure the amount of water displaced under force[24, 30].

The wettability has direct effect on capillary pressure. It is shown in Fig.19. Wettability indices may give only an (incomplete) wettability characterization of rock, but still can be useful in the design of correlations. The Amott index is based on the amount of spontaneous imbibition of a certain phase. For water, the Amott index I_w is defined as The Amott indices for water and oil can be determined by using following equation[2, 25]:

$$I_w = \frac{\Delta S_{ws}}{1 - S_{wi} - S_{or}} = \frac{\Delta S_{ws}}{\Delta S_{wt}} \dots\dots\dots(3.5)$$

$$I_o = \frac{\Delta S_{os}}{1 - S_{wi} - S_{or}} = \frac{\Delta S_{os}}{\Delta S_{ot}} \dots\dots\dots(3.6)$$

ΔS_{ws} : Increase in water saturation during spontaneous imbibition of water

ΔS_{os} : Increase in oil saturation during spontaneous imbibition of oil

ΔS_{wt} : Total increase in water saturation during spontaneous and forced displacement of oil

ΔS_{ot} : Total increase in oil saturation during spontaneous and forced imbibition of water

S_{or} : Residual oil saturation

S_{wi} : Initial water saturation

For Strongly water-wet $I_w = 1$ and $I_o = 0$, while completely oil-wet yields in $I_o = 1$ and $I_w = 0$.

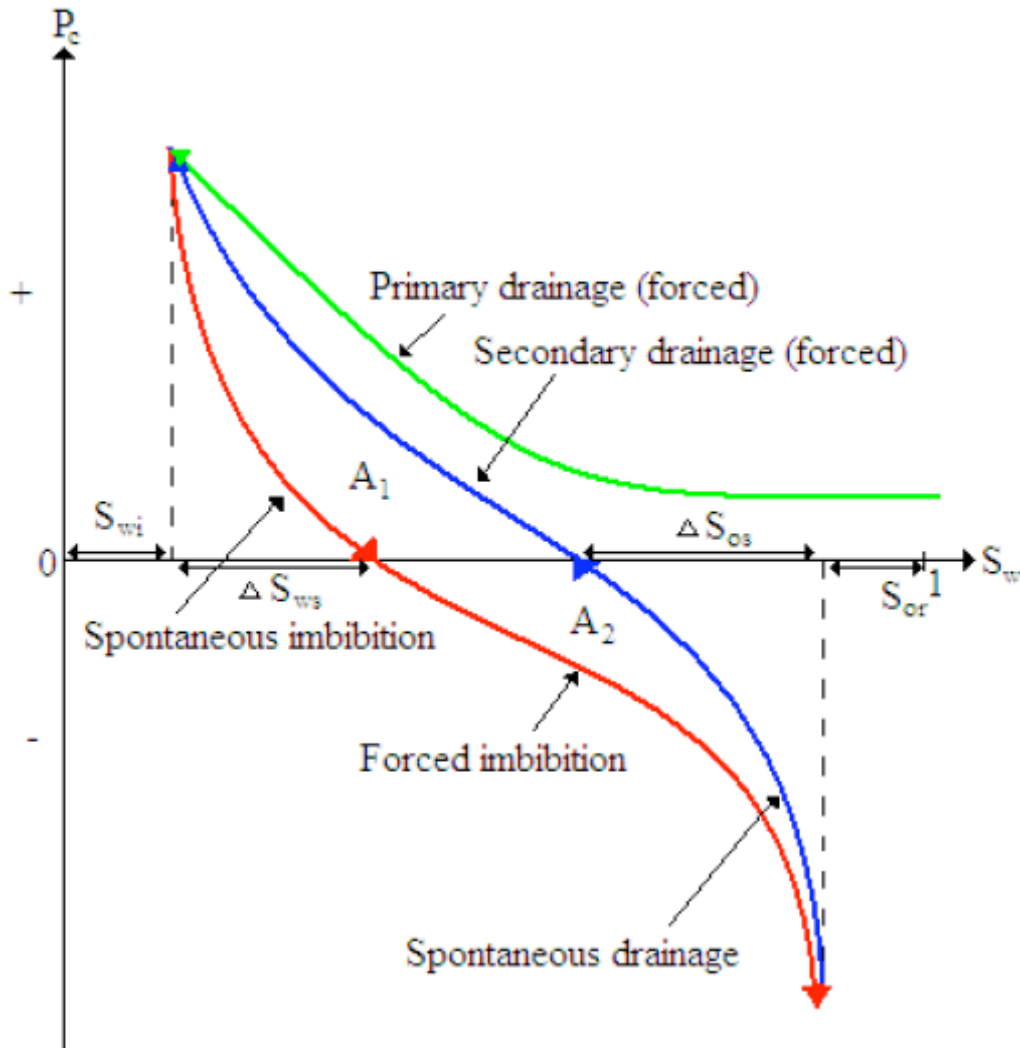


Figure 3.19 Capillary pressure diagram used to characterize wettability

By using same method that has been described above, the Amott-Harvey wettability index can be also calculated. The index compares the imbibition potential of water and oil, and varies from +1 for strongly water-wet core to -1 for strongly oil-wet core. Amott-Harvey index may be calculated directly from equation 3.6[2, 30];

$$IAH = I_w - I_o = \frac{\Delta S_{ws} - \Delta S_{os}}{1 - S_{wi} - S_{or}} \dots\dots\dots (3.6)$$

3.11.3 USBM Wettability

The USBM test is developed by Donaldson et al. to measure the average wettability of the core. A major advantage it has over the Amott wettability test is its sensitivity near neutral wettability. On other hand the test is relatively rapid, requiring a few days to test four to eight plugs. But on of the disadvantage of this test is that the USBM wettability index can only be measured on plug-size samples because the samples must be spun in a centrifuge[31]. The USBM test compares the work necessary for one fluid to displace the other. Because of the favorable free-energy change, the work required for the wetting fluid to displace the non-wetting fluid from the core is less than the work required for the opposite displacement. It has been shown that the required work is proportional to the area under the capillary pressure curve. In other words, when a core is water-wet, the area under the brine-drive capillary pressure curve (when the water displaces the oil) is smaller than the area under the capillary pressure curve for the reverse displacement. In fact, if the water-wetting is strong enough, most of the water will spontaneously imbibe into the core, and the area under the brine-drive curve will be very small[2, 24].

The USBM method uses the ratio of areas under the two capillary pressure curves to calculate a wettability index according to equation 3.7.

$$W = \log\left(\frac{A_1}{A_2}\right) \dots\dots\dots (3.7)$$

- A₁ : Area under the secondary water-drainage curve, shown in Fig. 3.19
- A₂ : Area under the imbibition curve falling bellow the zero-*P_c* axis, shown in Figure 3.19

When W is greater than zero, the core is water-wet, and for oil-wet core the W is less than zero. A wettability index near zero means that the core is neutrally wet. The larger the absolute value of W, the greater the wetting preference[30].

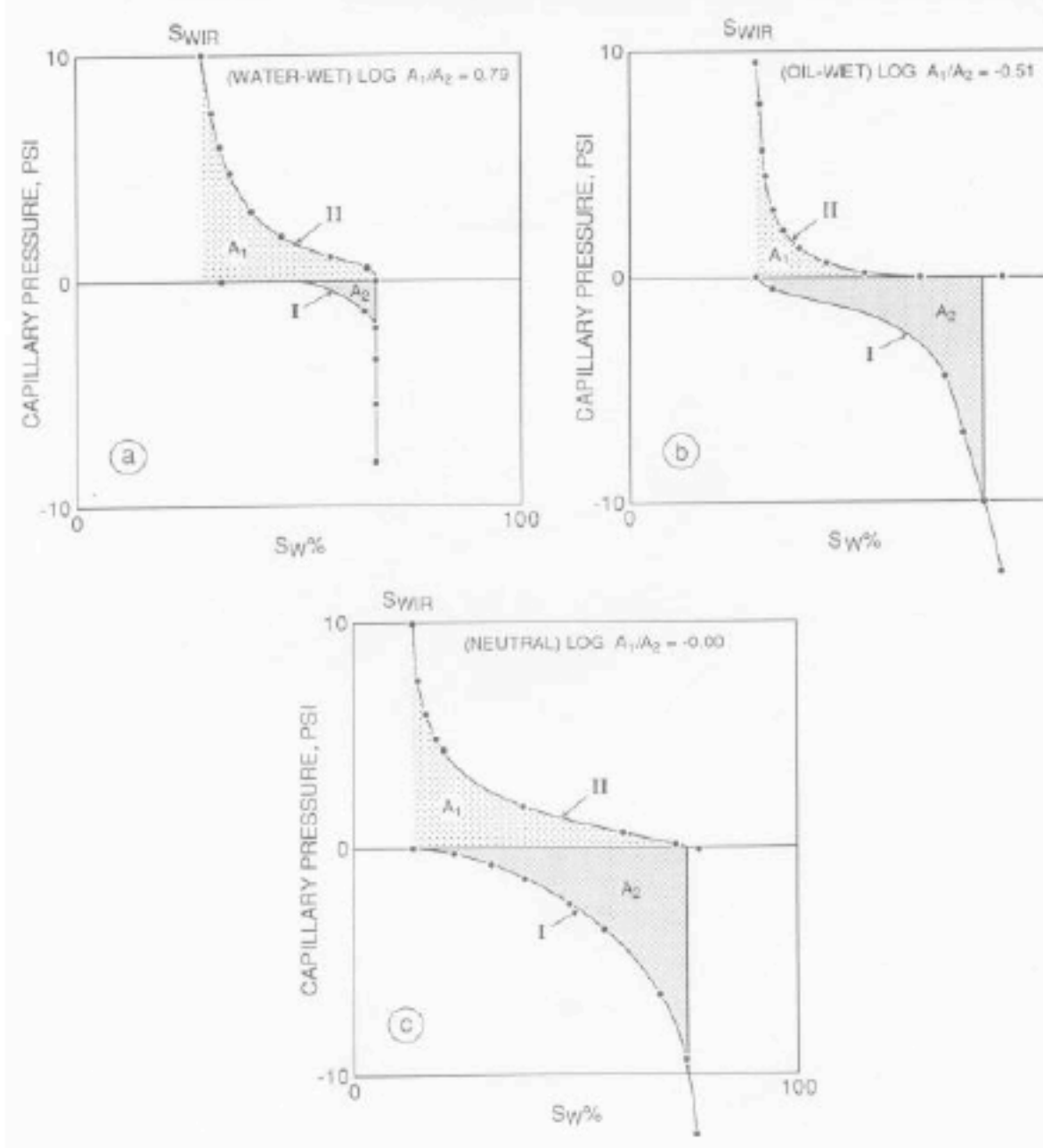


Figure 3.20 USBM wettability test Capillary pressure curve a)water wet b)oil wet 3)neutrally wet sample[30]

	Oil Wet	Neutral Wet	Water Wet
Amott wettability index water ratio	0	0	>0
Amott wettability index oil ratio	>0	0	0
Amott-Harvey wettability index	-1.0 to -0.3	-0.3 to 0.3	0.3 to 1.0
USBM wettability index	about -1	about 0	about 1
Minimum contact angle	105° to 120°	60° to 75°	0°
Maximum contact angle	180°	105° to 120°	60° to 75°

Table 3.2 Comparison of the Amott and USBM Wettability Methods[30]

3.11.4 Imbibition rates

Imbibition method is the most common wettability measurement. The major advantages of this method are, giving a quick but rough idea of the wettability without requiring any complicated equipment and also providing a useful support to the Amott indices or USBM wettability number.

In an imbibition test, a core at S_{wir} is first submerged in brine and the rate and amount of oil displaced by brine imbibition are measured. Measuring the volume of imbibed brine can recognize the wettability of the core. The core is water-wet, if large volumes of brine are rapidly imbibed and the core is weakly water-wet if lower rates and smaller volumes imbibed.

If no water is imbibed, the non water-wet core are then driven to S_{or} and submerged in oil to measure the rate and volume of water displaced by oil imbibition. Thus, if the core imbibes the oil, the core is defined as oil-wet reservoir, and is neutrally-wet if neither oil nor water is imbibed. On other hand the cores, which have either fractional or mixed wettability imbibe both water and oil. One problem with the imbibition method is depending on relative permeability, viscosity, IFT, pore structure, and the initial saturation of the core that, in addition to wettability, imbibition rates.

Frequently, this dependence on other variables is reduced by comparison of the measured imbibition rate with a reference rate measured when the core is strongly water-wet[2].

The main difference between the Amott test and the imbibition rates are that, Amott test depends mainly on the saturation at which imbibition capillary pressure falls to zero, while Spontaneous imbibition rate depends on the magnitude of the imbibition capillary pressure. Measurements of imbibition rates are of special value as a sensitive measure of wetting in the range where Amott index is or close to unity[2, 30].

3.11.5 New wettability test for carbonate

Skule Strand at University of Stavanger has published a new chromatographic technique to determine the water-wet surface fraction of carbonate. The test is based on chromatographic separation of two water-soluble components, i.e. a tracer, SCN^- , and a potential determining ion SO_4^{2-} at the water-wet sites of the carbonate surface.

Chromatographic separation will only take place at the water-wet sites at the pore surface, and the fraction of the surface area covered by water is assumed to represent the new wetting index parameter.[2, 4, 32]

In this test the brine containing equal molar concentration of sulfate SO_4^{2-} and tracer SCN^- will be used to flood the core. The core is flooded with at least 2 pore volumes. By using a fraction collector some small fractions (1ml) of the effluent will be collected and the exact volume and PV of each fraction could then be calculated by using the weight and the density of the fluid. Each fraction will be analyzed in ion chromatograph for relative concentrations of sulfate and thiocyanate, and plotted against pore volume injected. The delay in the sulfate concentration compared to the thiocyanate concentration in the effluent is proportionate to the pore surface accessible to “adsorption”. The area between the effluent curves for SCN^- and SO_4^{2-} is proportional to the area contacted by water during the flooding process. The ratio between this area and the corresponding area obtained by using a completely water-wet condition as a reference system. This ratio is defined as wetting index which has a rang between 0 and 1, representing completely oil-wet and water-wet conditions, respectively[2, 4, 32].

$$WI_{New} = \frac{A_{Wett}}{A_{Heptane}} \dots\dots\dots(3.8)$$

A_{wett} : The area between sulfate and thiocyanate curves for a core aged with oil

$A_{Heptane}$: Reference area for the saturated core by heptanes that assumed to be strongly waterwet.

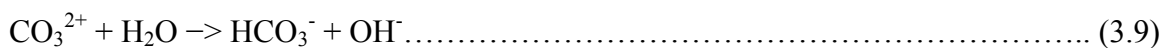
The area between the two curves is calculated by subtraction of the area under each of the curves which were determined by the trapeze method[2, 4].

3.12 Wettability alternation

Several studies have been done on wettability alteration of oil-wet carbonates by surfactant flooding. Normally, wetting condition of carbonates is dictated by many parameters such as: pH of the equilibrium brine, temperature of the reservoir, brine salinity, crude oil properties (e.g. acid/base number), and composition of the equilibrium brine (e.g. potential determining ions). These parameters, of course, are not independent of each other but in previous studies by Austad et al. and Strand et al. on chalk cores, the potential ions in seawater and temperature observed as the key factors leading to wettability alteration towards more water-wetness and removing the strongly adsorbed carboxylic material from the rock surface.[2, 4, 5, 33]. They also have proved that, adsorption of SO_4^{2-} and co-adsorption of Ca^{2+} increases at higher temperature. The criteria for seawater to act as a wettability modifier are that Ca^{2+} , Mg^{2+} , and SO_4^{2-} must have strong affinity toward the carbonate surface. The reactivity increases as the temperature increases, and it has been observed that Mg^{2+} is able to substitute Ca^{2+} on the chalk surface at temperatures above 90°C. Recently, it has been observed that a reservoir limestone rock reacts chemically in the same way as chalk toward the potential determining ions, although the reactivity was lower than for chalk.

3.12.1 Effect of mineral surface on wettability

The type of mineral surface in a reservoir is important in determining the wettability. Carbonate reservoirs are typically known as oil-wet reservoir, which composed largely of calcite (CaCO_3) minerals. Carbonates tend to adsorb simple organic acids because of its positively charged, weakly basic surface. Equation 3.9 shows the reaction on the carbonates surface which makes it weakly basic [2].



The calcite surface will preferentially adsorb components of the opposite polarity (acidity) by an acid/base reaction as shown in Fig. 3.21.

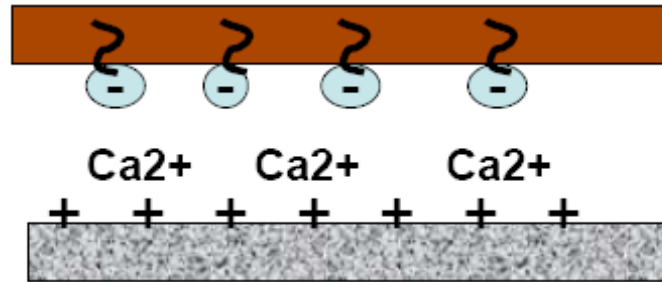


Figure 3.21 Adsorption of carboxylic acids on positive charged calcite surface[2]

The acidic compounds that adsorbed on carbonates surface include naphthenic acid and a number of carboxylic acids (RCOOH), including caprylic (octanoic, palmitic, hexadecanoic), stearic (octadecanoic), and oleic (cis-9-octadecanoic) acids. This acid-base interaction between the solid and oil is a strong polar interaction[2].

3.12.2 Effect of potential ions on surface of charge

Previous studies showed that seawater acted as a wettability modifying fluid towards weakly water-wet carbonate, and improved oil recovery especially at high temperature. Ca^{2+} , SO_4^{2-} and Mg^{2+} are potential determining ions towards the carbonate surface, which have impact on the surface charge (zeta potential)[3]. Among the divalent ions present in seawater, Mg^{2+} has the highest concentration, and the relative concentration of SO_4^{2-} is twice the concentration of Ca^{2+} , while in formation brine the concentration of Ca^{2+} is much more higher than concentration of SO_4^{2-} .

In a dynamic equilibrium, the adsorption of two potential determining ions of opposite charge Ca^{2+} and SO_4^{2-} onto the carbonate surface is depending on their relative concentration. Thus, adsorption of SO_4^{2-} onto a positively charged carbonate surface decreases the positive charge density, which increases adsorption of Ca^{2+} due to less electrostatic repulsion [3]. Ca^{2+} can then reacts with adsorbed carboxylic groups bond to the carbonate surface and release some of the organic carboxylic materials. Mg^{2+} in seawater can substitute Ca^{2+} at the surface of carbonate at high temperature. Illustration below shows the schematic reaction between the potential ions and calcite surface.

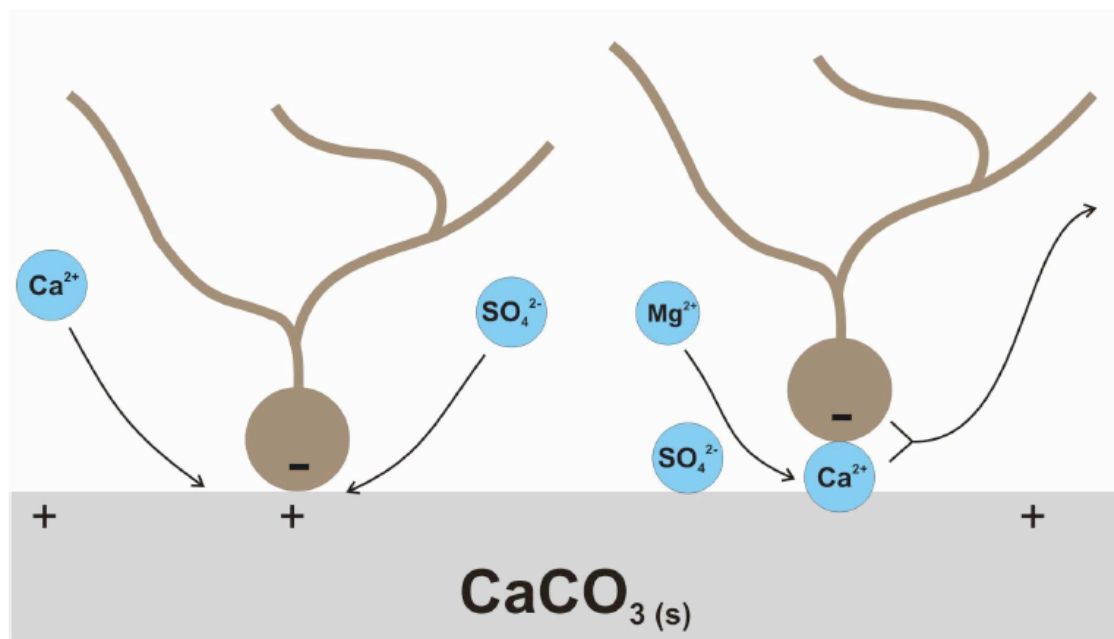


Figure 3.22 Schematic reaction between potential ions and calcite surface[2]

The ionic interaction between Mg^{2+} and SO_4^{2-} in solution can also increase the concentration of Mg^{2+} close to the limestone surface because of the excess of SO_4^{2-} due to adsorption[4]. The ionic interaction between Mg^{2+} and SO_4^{2-} is only happening at high temperature. It is therefore reasonable to believe that Ca^{2+} , Mg^{2+} and SO_4^{2-} , are involved in the chemical mechanism for wettability alteration[3, 4].

In seawater, the relative interaction between Ca^{2+} and Mg^{2+} towards limestone is dictated by the presence of SO_4^{2-} . Ca^{2+} appeared to adsorb more strongly than Mg^{2+} due to the ion-pair formation between Mg^{2+} and SO_4^{2-} and the strong adsorption of SO_4^{2-} onto the rock. Decreasing in concentration of Mg^{2+} in effluent when temperature increases, indicates that Mg^{2+} can substitute Ca^{2+} at the limestone at high temperature[4].

3.12.3 Effect of temperature on wettability

The temperature appeared to be a very important parameter for the wettability modification, and increased oil recovery by spontaneous imbibition was observed as the temperature increased. As the temperature increases the water-wetting nature of carbonate reservoir increases too. It has been proved that temperature and acid number are not independent wetting parameter, because the carboxylic group, $-\text{COOH}$, decomposes as the temperature

increases. During the decomposition process, the CaCO_3 acts as catalyst and the AN will decrease as the temperature of the reservoir increases[4]. The affinity of sulfate towards the carbonate surface increases as the temperature increases.

The fact that the wettability modification using Mg^{2+} and SO_4^{2-} is only active at high temperatures strongly supports the suggested mechanism. In seawater, the relative interaction between Ca^{2+} and Mg^{2+} towards limestone is dictated by the presence of SO_4^{2-} . Ca^{2+} appeared to adsorb more strongly than Mg^{2+} due to the ion-pair formation between Mg^{2+} and SO_4^{2-} and the strong adsorption of SO_4^{2-} onto the rock. Decreasing in concentration of Mg^{2+} in effluent when temperature increases, indicates that Mg^{2+} can substitute Ca^{2+} at the limestone at high temperature[4].

3.12.4 Effect of acid number on wettability

The amount of carboxylic acid group in a chemical compound such as fatty acid or mixture compounds measured as acid number (AN). As it has been discussed in previous section the AN and temperature have influence on the wettability of carbonate. The higher acid number refers to more oil-wet rock or in another way the water wetness decreases as the AN increases. Decarboxylation of crude oil will take place while temperature increases. Due to content of carboxylic acid in the crude oil, the charge of the oil-water interface is usually negative, while Ca^{2+} content in the brine makes water-rock interface positive charged.

Catalytic effect of CaCO_3 causes decarboxylation process in carbonate reservoir and it has also been proved that presence of calcium carbonate will degrade fatty acids to alkane. The formation of carbonate reservoir has same effect as catalyser. Thus, the AN will have significant change even the decarboxylation process by catalyst effect of CaCO_3 is very slow[4].

3.12.5 Effect of PH on wettability

The pH in carbonate reservoir becomes quite constant due to the buffer capacity of calcium carbonate from formation. It is usually in the range of 7-8 and great changes in it are not

expected provided that the system (oil/brine/carbonate) is in chemical equilibrium. It is therefore expected that wettability alterations due to changes in pH are only temporary.

Usually, the calcite surface is positively charged below a pH-value of about 9.5, and the charge of the oil-water film is negative because of dissociation of surface active carboxylic acids present in the crude oil. The water-film between the rock and the oil then becomes instable, and oil will contact the surface. The carboxylic group, which is usually present in large molecules (resins and asphaltenes) adsorbs chemically strongly onto the carbonate surface by displacement of water [4].

4 Experimental

Evaluating the potential of low-salinity water to enhance the oil recovery from reservoir limestone is the main objective of this project. To reach the goal, four core flooding tests were conducted at reservoir temperature with initial formation water between 7%-10%.

In this chapter, the different material and methods, which were used during this study, will be described.

4.1 Material

Four reservoir cores, three crude oils and five different brines were the basic materials, which were used in this project.

4.1.1 Porous media

In this study we have used three reservoir limestone cores and as a reference carbonate rock, we have used one outcrop chalk core.

4.1.1.1 Limestone core

The limestone cores, were taken from different section of a well. All the core plugs had a diameter of 3.80cm and lengths of 8.1 except core 6B, which has a length of 8.4cm.

The permeability of the cores were low, about 0.3-1mD. The porosity of the cores was between 17% to 18%, which was measured in laboratory. Table 4.1 summarized the limestone cores data.

Core ID	Length <i>cm</i>	Diameter <i>cm</i>	Porosity Φ %	Permeability K_a , <i>mD</i>
5B	8.1	3.8	18	1.2
6B	8.4	3.8	17	1.1
9B	8.1	3.8	17	0.8

Table 4.1 Limestone core data

4.1.1.2 Chalk core

The chalk core was drilled from a Stevns Klint (SK) outcrop chalk block. The core had a high porosity about 45% and low permeability about 4.2 mD.

Table 4.2 shows the chalk core data.

Core ID	Length <i>cm</i>	Diameter <i>cm</i>	Porosity Φ %	Permeability K_a , <i>mD</i>
F1	8.0	3.8	45	4.2

Table 4.2 Chalk core data

4.1.2 Crude oils

Three different crude oils were used in the experiments. All of the oils were examined macroscopically and no wax or other deposits were observed. To remove water and solids from the oils, they were centrifuged and filtered through a 5 μ m Millipore.

The Acid numbers are measured by a modified version of ASTM D664. The base numbers are determined by a modified version of ASTM D2896. Both methods were developed by Fan and Buckley (2006). Density and viscosity of the crude oil were measured at 20°C by Anton Parr DMA 4500 Density Meter and Physica Parr UDS 200 Spectrometer, respectively. Table 4.3 shows the chemical and physical properties of crude oils.

Oil ID	AN mgKOH/gOil	BN mgKOH/gOil	Density g/cm^3 @20 C	Viscosity cP @20 C
Oil A	0.08	0.34	0.824	4.3
Oil C	0.34	0.45	0.821	4.2
Oil B	0.70	0.42	0.818	3.8

Table 4.3 Chemical and physical properties of crude oils

In addition, Kerosene, toluene and n-heptane were used in core cleaning procedure.

4.1.3 Brines

Totally five different brines were used in this project as initial and displacement fluid. The Brines were made from deionized water (DIW) and the available reagent-grade salts in laboratory. The brines were diluted through a 0.22 μ m Millipore filter prior to uses. The terminology and the specification of those brines are as follows:

- Formation water (FW) was used as initial formation water in both chalk and limestone cores. FW contains Ca^{2+} , Mg^{2+} , but doesn't contain SO_4^{2-}
- 100 times diluted FW by distilled water, was used as a low-salinity formation water.
- Seawater (SW) was used to evaluate the surface reactivity of the core's surface.
- 10 times diluted SW was used as low-salinity seawater

Furthermore, seawater with half amount of tracer (SW1/2T) was used as reference fluid in ion chromatograph and. The composition of the brines is listed in table 4.4.

Ions	HCO_3^-	Cl^-	SO_4^{2-}	SCN^-	Mg_2^+	Ca_2^+	Na^+	K^+	TDS [g/L]	IS (mol/L)
FW[mol/l]	0.003	3.643	0.000	0.000	0.076	0.437	2.620	0.000	208.94	4.158
SW[mol/l]	0.002	0.525	0.024	0.000	0.045	0.013	0.450	0.010	33.39	0.657

Table 4.4 Composition of brines

4.2 Experimental methods

4.2.1 Core cleaning

Before conducting any experiment the core were cleaned for easily participated salt and any crude oil.

The core was placed inside a core sleeve and then was mounted inside the Hassler core holder and outlet and inlet lines were attached to the core ends.

A confining pressure of 20 bars from a nitrogen tank was applied on the core, to make sure that it is only core exposed to injecting cleaning fluid and to avoid fluid bypassing.

A Gilson 307 HPCL piston pump was used to inject the cleaning fluids and the Batch test with Ba^{2+} on the effluent from limestone cores was continued until the core was free from sulfate. Then the core was dried in a heating chamber at initial constant weight.



Figure 4.1 Core cleaning setup

4.2.1.1 Limestone core cleaning

The reservoir limestone cores were pre-flooded and stored in kerosene prior to delivery.

To maintain the initial wetting condition, the cores were pre-flooded with kerosene.

In the mildly cleaning of limestone core, the kerosene was used to remove oil from the core, and then toluene was used to displace the kerosene in the core.

The n-heptane was injected in order to remove the toluene and kerosene from the core and finally the DIW was used to displace the n-heptane and to remove the salt.

The injection volume of DIW was kept as low as possible to minimize the dissolution of limestone rock. The Batch test was done on the effluent until the core was free from sulfate. Then, the core was dried at 90°C to the constant weight.

4.2.1.2 Chalk core cleaning

Previous studies in outcrop SK chalk without anhydrite present showed that about 4 PVs of DIW must be injected to remove sulfate from the core material[5]. Thus, the outcrop chalk core was flooded with 5 pore volumes (PV) of DIW to remove initial soluble salts, which could affect the wetting properties significantly. Then, the core was dried at 90°C to the constant weight.

4.2.2 Pore volume measurement

The dried core was weighted and the dimensions of the core were measured.

The core was placed in a container and evacuated as shown in Fig.4.2 and then saturated with 10 times diluted formation water. The pore volume was calculated by weight difference between dry and saturated core divided by density of brine (Eq. 4.1):

$$V_p = (W_{wet} - W_{dry})/\rho_{fluid} \dots\dots\dots(4.1)$$



Figure 4.2 Evacuating and saturating the core with formation brine[2]

4.2.3 Porosity measurement

The porosity was calculated from Eq. 4.2:

$$\Phi = V_p / V_b \dots\dots\dots (4.2)$$

Where Φ indicates the porosity. This number can be multiplied by 100 to get the porosity in percent. V_p is the pore volume and V_b is the bulk volume. Table 4.5 shows porosity in percent for different cores.

Core ID	5B	6B	9B	F1
Porosity Φ	18%	17%	17%	45%

Table 4.5 Porosity of different core in percent

4.2.4 Initial water saturation

Initial water saturation was established by using the desiccator technique. This method is based on evaporation and adsorption of water, which was performed by using drying agent (silica gel)[5].

The dry core sample was vacuumed and saturated with degassed 10 times diluted FW. Because of the low permeability of cores, the core was left immersed in the brine for at least 12 hours. The porosity and pore volume were determined from the change in weight, as it has been discussed in section 4.2.2 and 4.2.3.

The saturated core was placed in desiccator with silica gel. The weight reduction was monitored during the time and when the desired weight was reached, the core was placed in a sealed container and equilibrated for 3 days in order to obtain uniform water saturation inside the core.

Core ID	5B	6B	9B	F1
Initial water saturation (S_{wi})	7%	8%	7%	10%

Table 4.6 Initial water saturation in different core

4.2.5 Permeability measurement

A 100% water saturated core was placed into the sleeve and mounted into a Hassler core holder. A confining pressure of 20 bars was applied on the core.

The core was flooded with a specific rate until stable condition while the pressure drop over the core was monitored. A back-pressure of 10bar was applied on the core during the flooding.

The effluent volume versus time was recorded in order to calculate permeability. The Darcy equation could be used to calculate core's permeability.

4.2.6 Oil saturation and aging

The amount of carboxylic material present in the crude oil is the most important wetting parameter for carbonates. In this project the potential of three oils with different AN and BN to impose wetting on carbonates was evaluated.

The initial water saturated core was placed in a Hassler core holder and a confining pressure of 20 bars from a nitrogen tank was applied on the core. The core was flooded with rate of 0.2ml/min at 50°C.

After core flooding, the core was removed from core holder and wrapped with Teflon tape to avoid unrepresentative adsorption of polar components on the surface during aging. The core was placed in a closed stainless-steel aging cell, immersed in the actual oil and it aged for 2weeks at 90°C.

Core ID	5B	6B	9B	F1
AN of oil used mgKOH/g	0.73	0.73	0.08	0.34

Table 4.7 The AN of different crude oils which were used in different test

4.2.7 Force displacement

The oil saturated and aged core was placed in a rubber sleeve and mounted in the core holder with a confining pressure of 20bar.

HPCL piston pump was used as a driving force for flooding of the core. It pumped distilled water from a water reservoir into two piston cells to displace the different injection brines.

A manifold valve on top of piston, made it easy to switch the flow of two different brines into the core. The brine was flowing directly from the piston cell to the Hassler core holder containing the core.

Using a valve system on the outlet of the Hassler core holder controlled the outlet flow from the core holder. Fig.4.3 is schematic illustration of flooding setup.

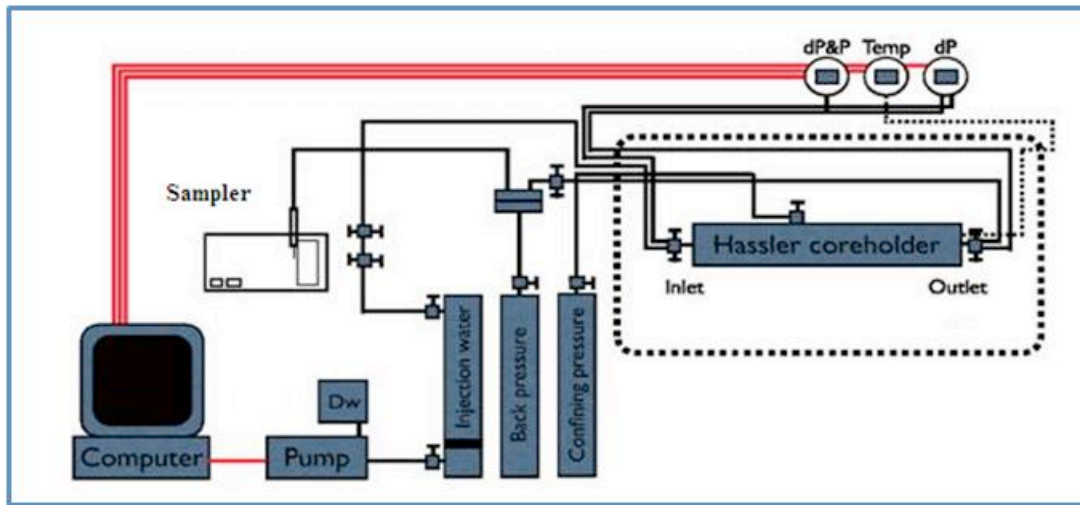


Figure 4.3 Schematic illustration of flooding setup[4]

A back pressure was applied on the core, to avoid oil boiling. The injection brine was injected with rate 0.01ml/min \approx 0.6 PV/day. The core holder was placed in an oven which supplied high temperature during the test.

The produced fluid was collected in a buret, and oil recovery was measured as a percentage of OOIP versus injected pore volumes (PVs). During the tests some samples of produced brine were collected to be analyzed for sulfate, calcium and magnesium in ion-chromatograph.

4.2.8 Ion chromatography

“Ion-chromatography (or ion exchange chromatography) is a process that allows the separation of ions and polar molecules based on their charge and it measures the concentration of ions in a solvent with very high accuracy”[4].

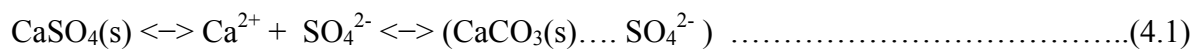
The effluent samples collected from the core flooding test were diluted and then filtered in order to prevent particles to enter the columns inside the ion chromatograph, because of the sensitivity of the columns. Particles may easily block the tubing and cause an over pressure.

By placing effluent samples in Dionex ion chromatograph and running the test, the concentrations of anions (sulfate and thiocyanate) and cations (Ca^{2+} and Mg^{2+}) were calculated based on external standard.

4.3 Presence of anhydrite

As it has been reported by Shariatpanahi et. al. the presence of anhydrate in carbonates could affect the initial wetting condition[5].The potential ions Ca^{2+} , Mg^{2+} and SO_4^{2-} in combination with high reservoir temperature are able to change wetting properties, and keep the carbonate rock preferentially water-wet.

This is illustrated in the following chemical equilibrium[5]:



It is observed that the dissolution of anhydrite normally decreases as the temperature increases.

In the next section we will evaluate the effect of low salinity injection brine on the reactivity of the surface active ions SO_4^{2-} and Ca^{2+} .

5 Result and discussion

As discussed in section 3.12, the potential determining ions present in seawater, Ca^{2+} and SO_4^{2-} , can modify the wettability during water injection.

In the formation brine, the concentration of Ca^{2+} is usually very high compared to Mg^{2+} , and the concentration of SO_4^{2-} is negligible. But in seawater, Mg^{2+} has the highest concentration, about twice the concentration of SO_4^{2-} , and about four times the concentration of Ca^{2+} . It has been verified that adsorption of SO_4^{2-} and co-adsorption of Ca^{2+} increased as the temperature increased, and the oil recovery increased as the injection fluid was switched from FW to SW[5].

It has been stated that improved oil recovery with diluted seawater in a spontaneous imbibition process is not possible in carbonates, because the concentration of the active ions decreases, and will affect the chemical mechanism for wettability modification[34].

Furthermore, it has been reported that viscous flooding with low salinity brine improved the oil recovery.

In this work, we are testing the low salinity effects on low permeable limestone cores containing traces of sulfate/anhydrite.

During the core cleaning of the three reservoir limestone cores, some traces of sulfate were observed in effluent. These three limestone cores were used as core containing sulfate/anhydrite and one chalk core containing no sulfate was used as reference core.

5.1 Test #1 (core 5B)

Core 5B with $S_{wi}=7\%$ was saturated and aged with a crude oil with $AN=0.7$.

The core flooding in this test was performed at 110°C , first with FW and then with diluted FW. As it has been discussed earlier, the FW doesn't content any sulfate, thus it doesn't cause wettability alteration in the rock.

The result, which is presented in Fig. 5.1 shows that the flooding with FW gave an ultimate recovery about 65% of OOIP after 5PVs FW injected. Then, in order to verify low salinity

effect on the limestone core, the injection brine was switched to the 100 times diluted FW. The oil recovery increased from 65% to 69% OOIP.

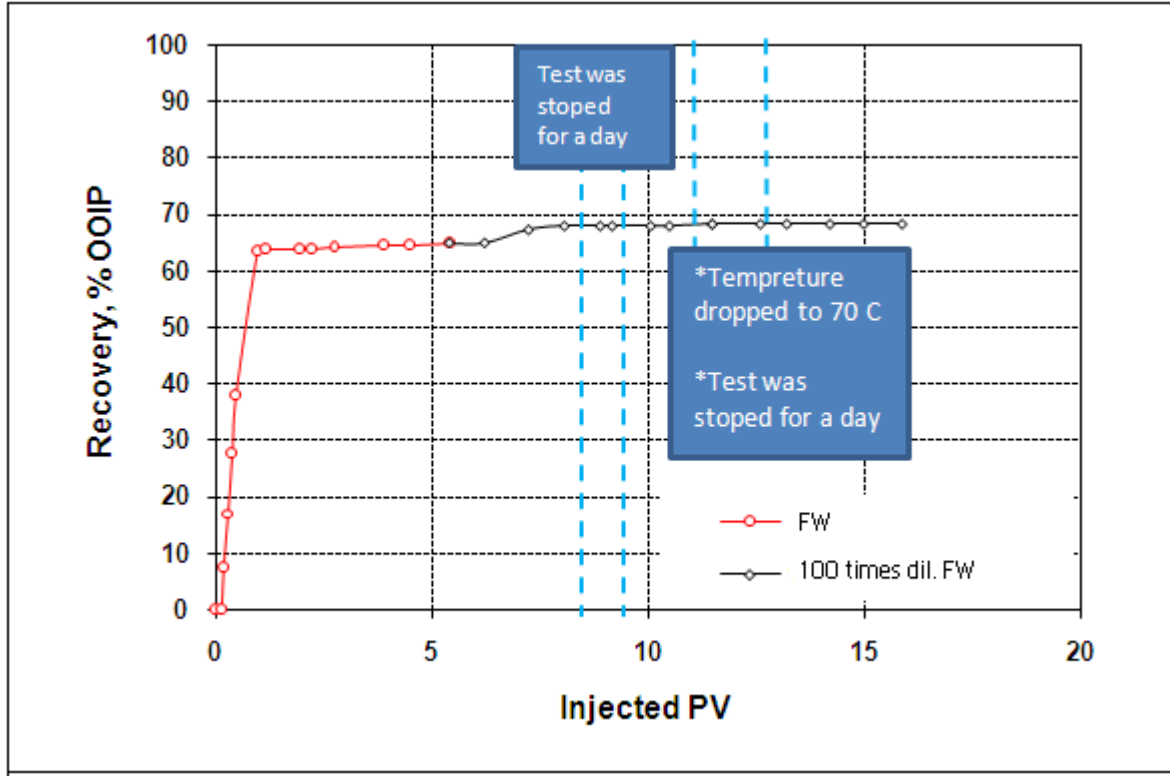


Fig. 5.1 Viscous flooding of limestone core 5B. The core was flooded first with FW and then with 100 times diluted FW with a constant rate 0.01ml/min (=0.6PV/day)

Fig. 5.2 shows the differential pressure over the core versus PV injected. A reduced pressure drop was observed during oil mobilization and the injecting diluted FW.

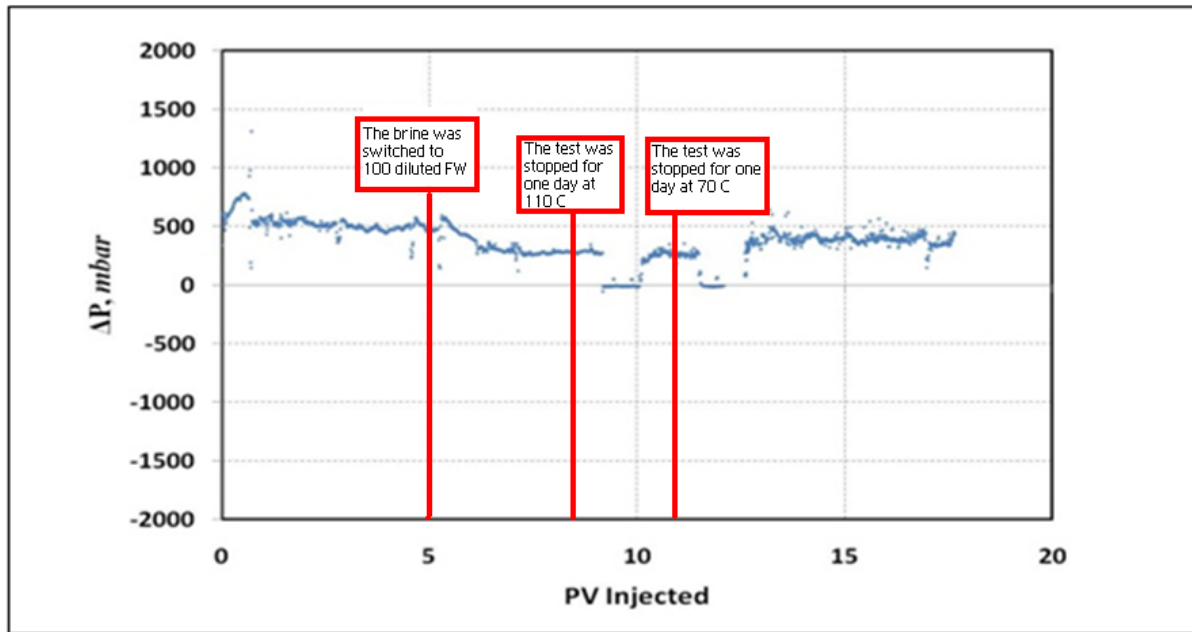


Fig. 5.2 The differential pressure over the limestone core 5B versus PV injected. ΔP decreased as the 100times diluted FW remobilized oil

Effluent brine samples were analyzed for SO_4^{2-} concentration in ion chromatograph. The results are plotted versus PVs injected, Fig.5.3.

The concentration of sulfate gradually decreased from 0.8mMole/L to 0.3mMole/L and even more to 0.1mMole/L after switching FW to diluted FW.

After reaching ultimate recovery by injecting 8PVs of brines, the flooding was stopped for one day in order to observe any change in sulfate concentration.

By restarting the test, an increase in the concentration of sulfate in the effluent was observed.

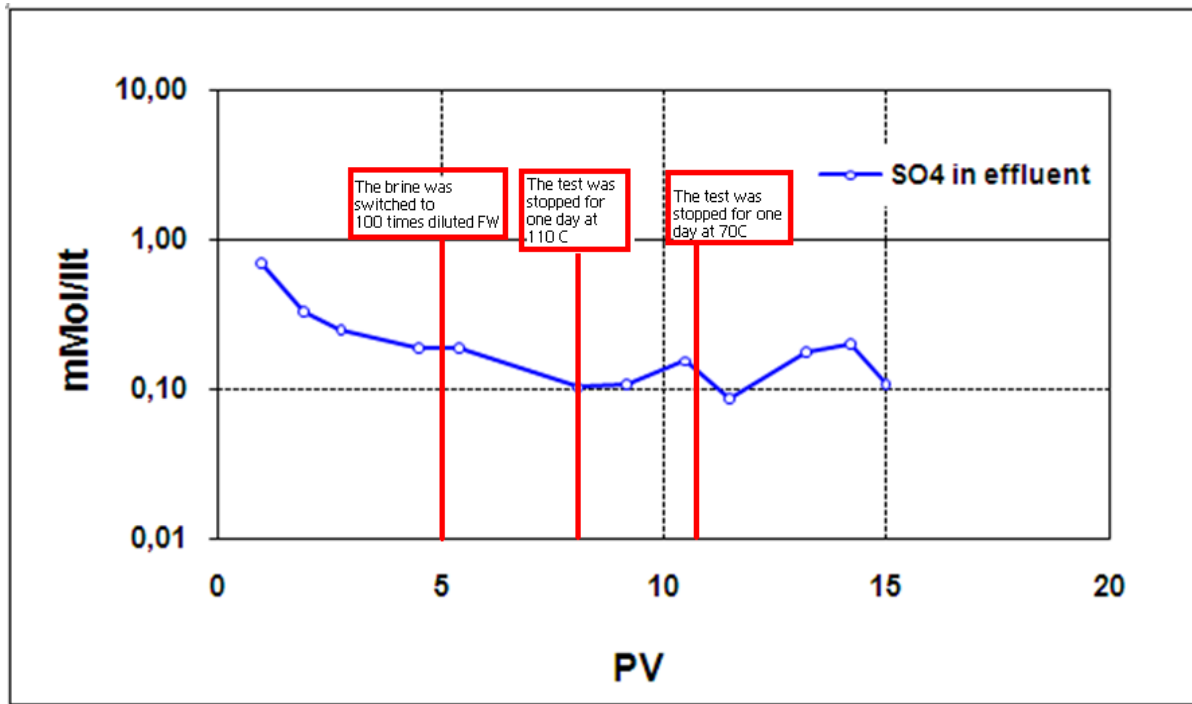


Fig. 5.3 Concentration of SO_4 in the effluent of core 5B versus PV injected. A reduction in concentration of sulfate is observed when the brine was switched from FW to 100 times diluted FW

After injecting 11PVs the injection was stopped for one more day and the temperature was reduced to 70°C. This was done to monitor any changes in dissolution of $CaSO_4$.

By further flooding at 70°C, a jump in both ΔP and concentration of sulfate was observed, but no increased in oil recovery was observed.

The dissolution of sulfate after first shut in period (10PVs) at 110°C, is lower than the dissolution of sulfate after the second shut in period (13 PVs) at 70°C, indicating that the dissolution of $CaSO_4$ increased with decreasing temperature.

5.2 Test #2 (core 6B)

Limestone core 6B with $S_{wi}=8\%$ was saturated and aged with $AN=0.73\text{mgKOH/g}$, the same as core 5B.

Initially the core was flooded with FW at constant temperature 90°C. The ultimate recovery of 68% was reached after 6PVs injected, Fig.5.4.

Then the injection brine was switched to 100 times diluted FW. An increase in oil recovery from 68% to 72% was observed .

The ΔP decreased as the diluted FW remobilized more oil, Fig.5.5.

The test was stopped after injecting 9PV brines in total.

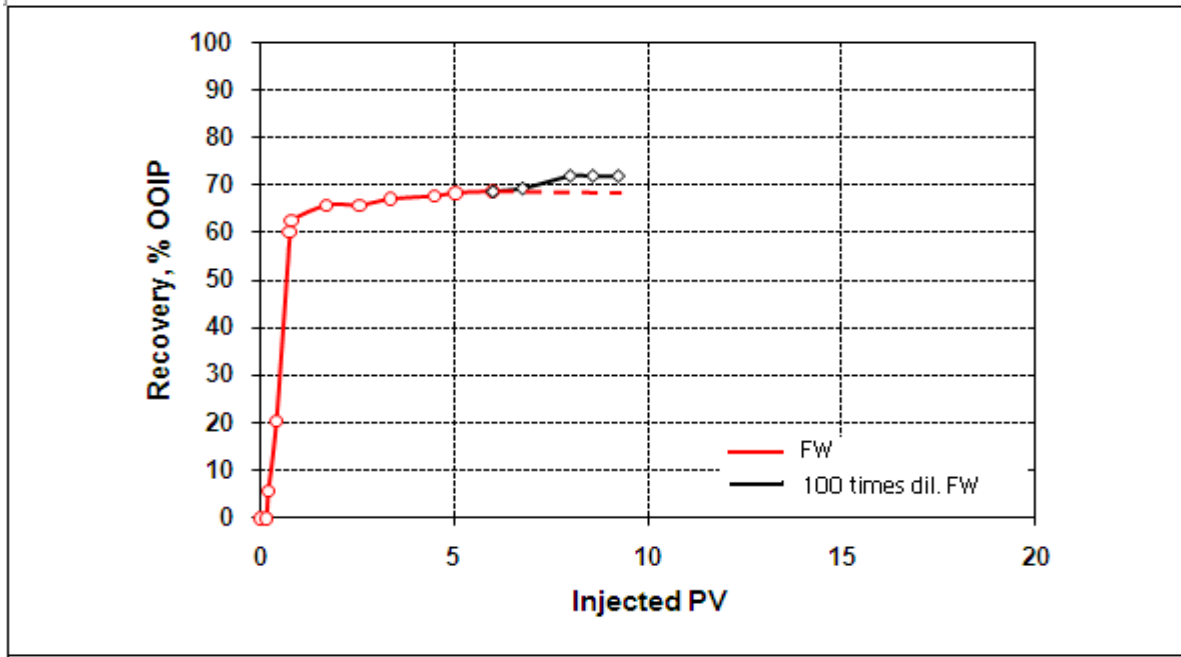


Fig. 5.4 The viscous flooding of limestone core 6B at 90°C. The core was flooded first with FW and then with 100times diluted FW with a constant rate 0.01ml/min (=0.6PV/day)

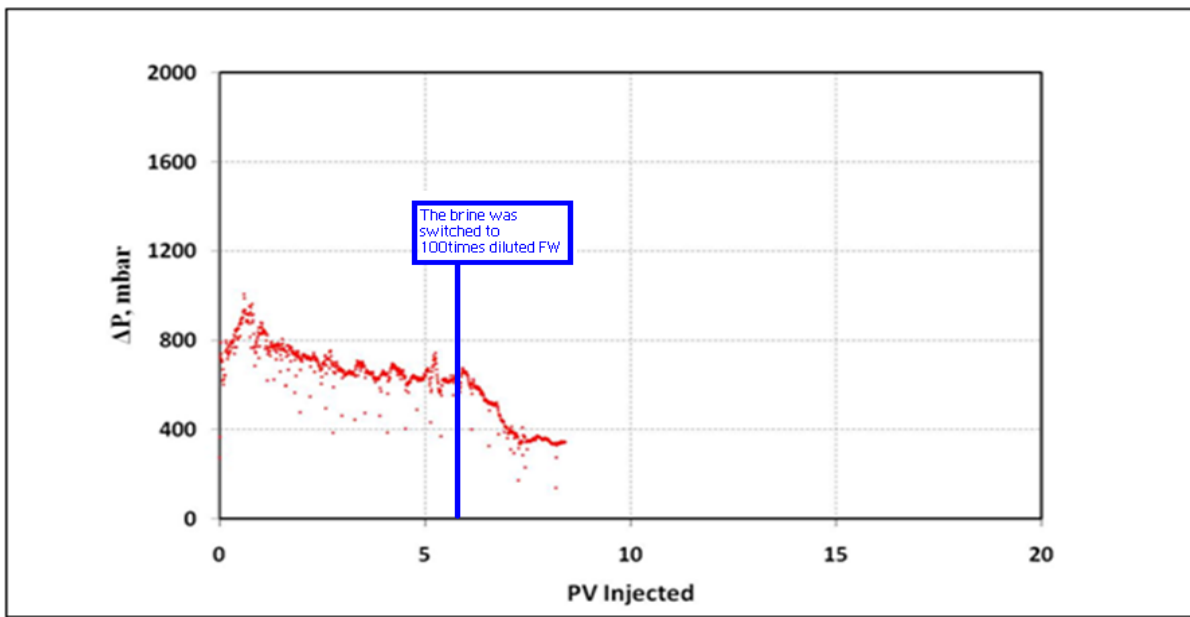


Fig. 5.5 The differential pressure over core 6B versus PV injected. The ΔP decreased as 100times diluted FW remobilized oil

5.3 Test #3 on core 9B

Limestone core 9B with $S_{wi}=7\%$, was saturated and aged with crude oil with low acid number about $AN=0.08$.

The core 9B was flooded first with SW at temperature 110°C which gave an ultimate recovery of 60% after 3PVs injected, Fig. 5.6. The flooding brine was then switched to 10 times diluted SW. An increase in recovery from 59% to 61% was observed due to low concentration of Ca^{2+} and NaCl ions in diluted seawater.

The test was stopped after injecting 10PVs of brines.

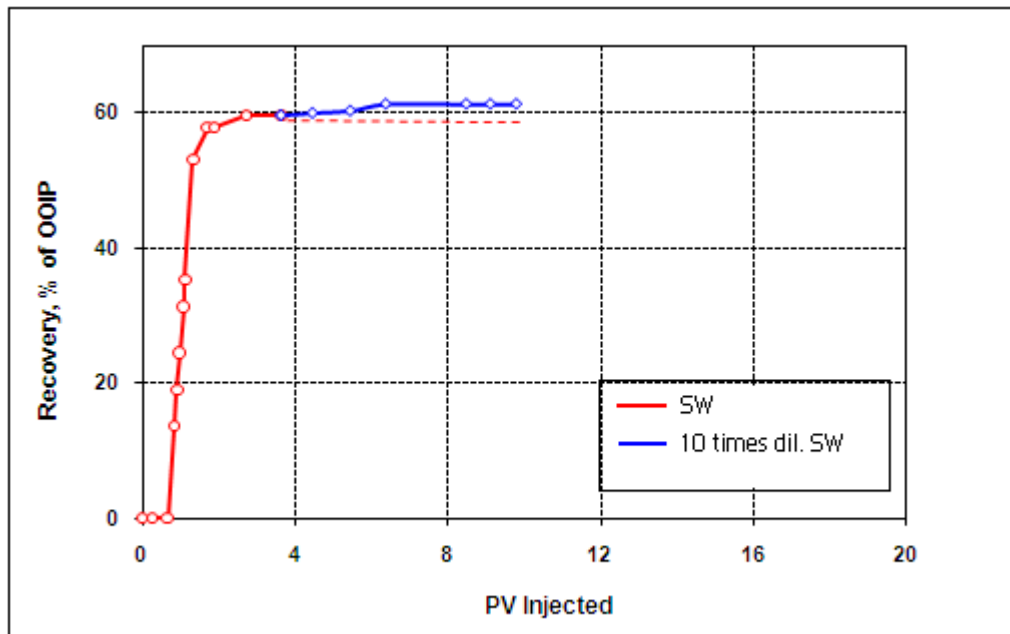


Fig. 5.6 Viscous flooding of core 9B at 110°C . The core was flooded first with SW and then with 10 times diluted SW with a constant rate $0.01\text{ml}/\text{min}$ ($=0.6\text{PV}/\text{day}$)

5.4 Test #4 on core F1

The Chalk core F1 containing no anhydrite with $S_{wi}=10\%$ was saturated and aged with crude oil with $AN=0.34\text{mgKOH}/\text{g}$.

Initially, the core was flooded with FW at temperature 110°C . the ultimate recovery was about 65% after injecting 7PVs, Fig.5.7.

Then the brine was switched to 100 times diluted FW, but no improved recovery was observed after injecting 14PVs.

By cleaning the chalk core, it was confirmed that the chalk core did not contain any anhydrite which can release sulfate ions.

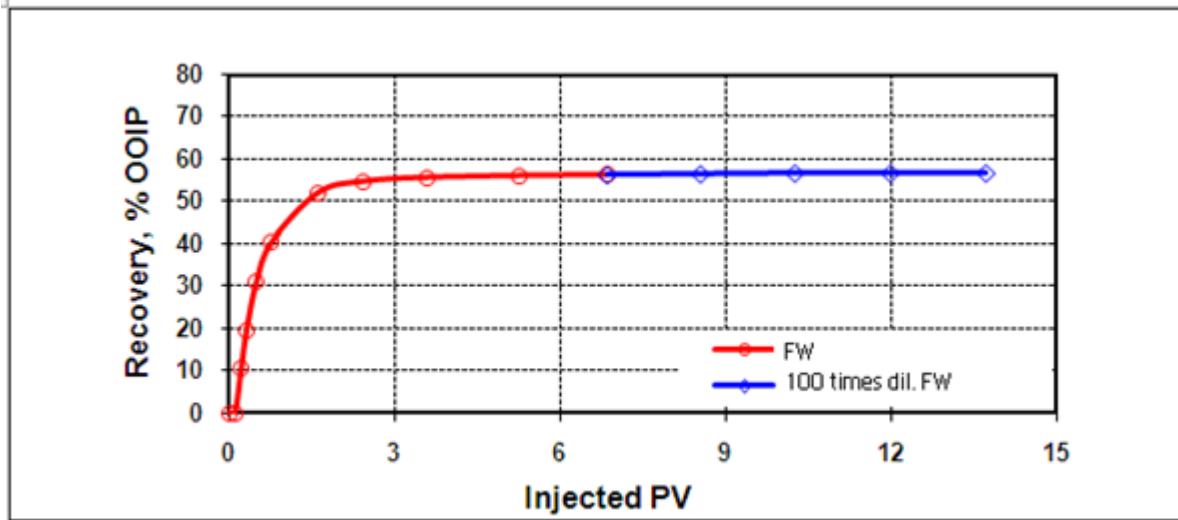
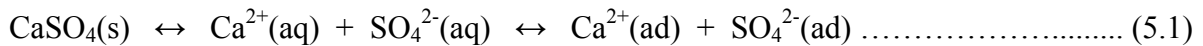


Fig. 5.7 Viscous flooding of Chalk core F1 containing no anhydrite at 110°C. The core was flooded first with FW and then 100times diluted FW

5.5 Discussion

Refer to section 4.3, presence of anhydrite in the carbonate rock has effect on oil recovery. Equation 5.1 shows chemical equilibrium for carbonate cores containing anhydrite where $\text{Ca}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ are ions dissolved in the pore water, and $\text{Ca}^{2+}(\text{ad})$ and $\text{SO}_4^{2-}(\text{ad})$ are ions adsorbed onto the carbonate surface.



As discussed earlier in this thesis, the concentration of $\text{SO}_4^{2-}(\text{aq})$ is one of the key factors determining the wetting properties.

It is stated that different parameters such as salinity and composition of initial formation brine are able to affect dissolution of CaSO_4 .

Observing traces of SO_4^{2-} during core cleaning in effluent of all limestone cores, indicate that the increased oil recovery with low salinity brine could be result of dissolution of anhydrite. Thus, in both cores 5B and 6B, the enhanced recovery about 4%, by switching the brine from FW to Diluted FW is due to low salinity and temperature effect on dissolution of anhydrate. The dissolution of anhydrite normally increases as the temperature decreases.

We observed also an increased recovery for core 9B, when switching from SW to diluted SW, even the core was saturated and aged with a crude oil with AN=0.08. The core with low acid number tends to be more water-wet and it has a lower potential of increased recovery.

Lowering the salinity of injection brine increases the reactivity of the surface's active ions SO_4^{2-} and Ca^{2+} [34]. The dissolution of anhydrite takes place in the injection front. SO_4^{2-} , which is the catalyst for wettability alteration process are always present in the injection front in a viscous flooding process.

A tertiary low salinity flooding was not to change the wetting condition of the cleaned chalk that did not contain any anhydrite. Thus, the recovery did not change.

We should note that the low salinity effect is only be observed in the carbonate rock containing a mineral that can release sulfate ions.

6 Conclusion

From the literature review and experimental results of this study, the following conclusions was observed:

- The low salinity brine, increased the recovery in carbonate, which contained anhydrite
- Sulfate ions are dissolved in the injection front when the low salinity brine invaded the rock
- The amount of non-active salt (NaCl) is very low in the diluted FW, which promotes increased reactivity of SO_4^{2-} and Ca^{2+} . Thus, diluted FW can be used as smart water to enhance the oil recovery
- Increasing the temperature will also increase the reactivity of SO_4^{2-} and Ca^{2+}
- In the cores containing anhydrite, the dissolution of CaSO_4 can increases by using diluted seawater which contains lower concentration of Ca^{2+} than seawater
- Since the dissolution of anhydrite CaSO_4 is depending on salinity ad temperature, and the dissolution decreases with increasing temperature, we presumed that it is an optimum temperature for maximum low salinity effect.

7 Symbols and abbreviation

σ	Interfacial tension, mN/m
σ_{os} ,	Interfacial tension oil-solid
σ_{ws} ,	Interfacial tension water-solid
σ_{ow}	Interfacial tension oil-water
ρ	Density, kg/m ³
$\Delta\rho$	Density difference between oil and water, kg/m ³
Δp	Pressure across the capillary tube, Pa
ΔP_g	Pressure difference between oil and water due to gravity, Pa
ΔS_{os}	Increase in oil saturation during spontaneous imbibition of oil
ΔS_{ot}	Total increase in oil saturation during spontaneous and forced imbibition of water
ΔS_{ws}	Increase in water saturation during spontaneous imbibition of water
ΔS_{wt}	Total increase in water saturation during spontaneous and forced displacement of oil
μ	Viscosity, cP
θ	Contact angle, °
φ	Porosity, fraction or %
\emptyset	Diameter, cm
A_1	Area under the secondary water-drainage curve
A_2	Area under the imbibition curve falling below the zero- P_c axis
A_{Heptane}	Reference area between the thiocyanate and sulfate curves generated by flooding a core assumed to be strongly water-wet (saturated with heptane)
A_{Wett}	Area between the thiocyanate and the sulfate curves generated by flooding a core aged in crude oil.
C	Concentration of effluent ions, mole/l
C_0	Concentration of injected ions, mole/l
C/C_0	Relative concentration of effluent ions
EOR	Enhanced oil recovery

g	Acceleration due to gravity, m/s^2
g_c	Conversion factor
H	Height of liquid column, m
IAH	Amott-Harvey index
IFT	Interfacial tension, mN/m
I_o	Amott oil index
IOIP	Initial oil in place
IOR	Improved Oil recovery
I_w	Amott water index
k	Absolute permeability. m^2 or mD
k_c	Effective permeability of non-wetting phase
k_o	Effective permeability of oil
k_{rg}	Relative permeability of gas
k_{ro}	Relative permeability of oil
k_{rw}	Relative permeability of water
k_{row}	Relative permeability to oil in an oil/water system
K_{rog}	Relative permeability to oil in an oil/gas system
k_w	Effective permeability of water
L	Capillary-tube length, m
L	Core length, cm
m	Core weight wet, gr
mD	Millie Darcy
m_o	Core weight dry, gr
N_{ca}	Capillary Number
N_w	Wettability number, USBM
OHIP	Original hydrocarbons in place
p_1	Pressure in a fluid, Pa
p_2	Pressure in a fluid, Pa
P_c	Capillary pressure, Pa
P_{cow}	Capillary pressure in a 2 phase, oil/water system, Pa
P_{cgo}	Capillary pressure in a 2 phase, oil/gas system, Pa
PV	Pore volume, cm^3
r	Radius

S_{iw}	Initial water saturation
S_g	Critical gas saturation
S_{or}	Residual oil saturation, fraction or %
SSW	Synthetic seawater
SW-U	Modification of SSW, without sulfate and thiocyanate
SW- $\frac{1}{2}$ M	Modified seawater with half the sulfate concentration and thiocyanate as tracer
S_w	Water saturation, fraction or %
S_{wc}	Saturation of wetting phase, fraction or %
S_{nc}	Saturation of non-wetting phase, fraction or %
S_{orw}	Residual oil saturation in oil water system
S_{org}	Residual oil saturation in an oil/gas system
S_p	Fluid saturation
S_{wi}	Initial water saturation, fraction or %
TDS	Total dissolved solid gr/l
V_p	Pore volume, cm ³
V_b	Bulk volume, cm ³
V	Volume cm ³
v	Average velocity in capillary tube, m/s
W	USBM wettability index
W_{New}	New wettability index
W_{wet}	Core weight wet, gr
W_{dry}	Core weight dry, gr

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