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ABSTRACT

The success of oil recovery, by water flooding, in naturally fractured, low permeable limestone reservoirs strictly depends on imbibition of injected water into the reservoir matrix block. Prerequisite of imbibition process is the presence of positive capillary pressure inside the reservoir which is directly related to the wetting state.

In previous experimental studies on surface reactive limestone cores performed by the EOR group in University of Stavanger, two different oil recovery ratios were encountered during spontaneous imbibition tests on the same core after cleaning the core with different solvents.

After mild cleaning with kerosene & n-heptane (preserved state) around 40% of OOIP was recovered indicating that the core behaved preferentially water-wet. On the other hand, after cleaning the same core with toluene and methanol oil recovery was below 10% indicating that the core was oil-wet.

Chromatographic wettability tests were utilized to examine the wetting states inside the cores after mild cleaning with kerosene & n-heptane and after cleaning with toluene and methanol. The results of the tests have shown small changes in water-wet fraction inside the cores indicating infinite small wettability changes due to the adsorbed organic components to the rock surface.

It has been concluded that the reason behind this recovery difference is due to successive toluene and methanol injection which removes the water in smaller pores. Polar components dissolved in toluene could adsorb on the initially water-wet smaller pores, change the capillary pressure and affect oil recovery.

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1) INTRODUCTION

I would like to begin my thesis by emphasizing the importance of oil, alias black gold, to mankind with the words of George Clemenceau, prime minister of France (1917-1920) during the last quarter of the First World War [7], "one drop of oil is worth one drop of blood of our soldiers".[38, 42]

The figure below shows how oil demand has been increased since the First World War in parallel with the discoveries until mid sixties.
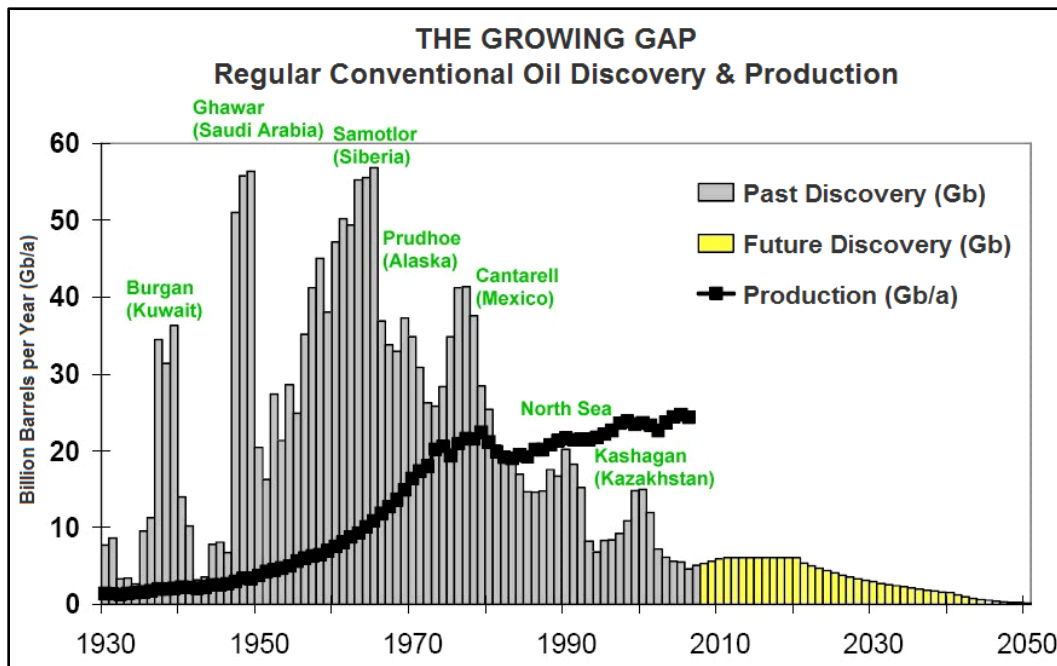
Figure 1. Demand & supply of oil from 1930 till today.[17]

After sixties, even though the demand has kept increasing, the number of discoveries has been decreasing since then and specialists are pessimistic about the future discovery of new giant fields. This means that in order to supply the oil demand, current reservoirs must be exploited more efficiently by implementing appropriate methods.

1.1 Oil Recovery Steps

Oil recovery from a reservoir can be divided into three steps which are primary recovery, secondary recovery and tertiary recovery.

1.1.1 Primary Recovery

In primary recovery, reservoir energy is utilized to displace oil through the production wells. The sources of energy in reservoir are solution gas drive, gas cap drive, natural water drive, fluid and rock expansion and gravity drainage.[36]

1.1.2 Secondary Recovery

In secondary recovery, water or gas is injected to enhance oil production by improving the energy of the reservoir. Water flooding is the most common secondary recovery method in oil industry.[36]

1.1.3 Tertiary Recovery

In tertiary recovery, physical and/or chemical properties of the reservoir fluids are altered to sweep as much oil as possible remaining after primary and secondary production by injecting some type of fluids into the reservoir.

In oil industry the term tertiary recovery generally refers to enhanced oil recovery (EOR).
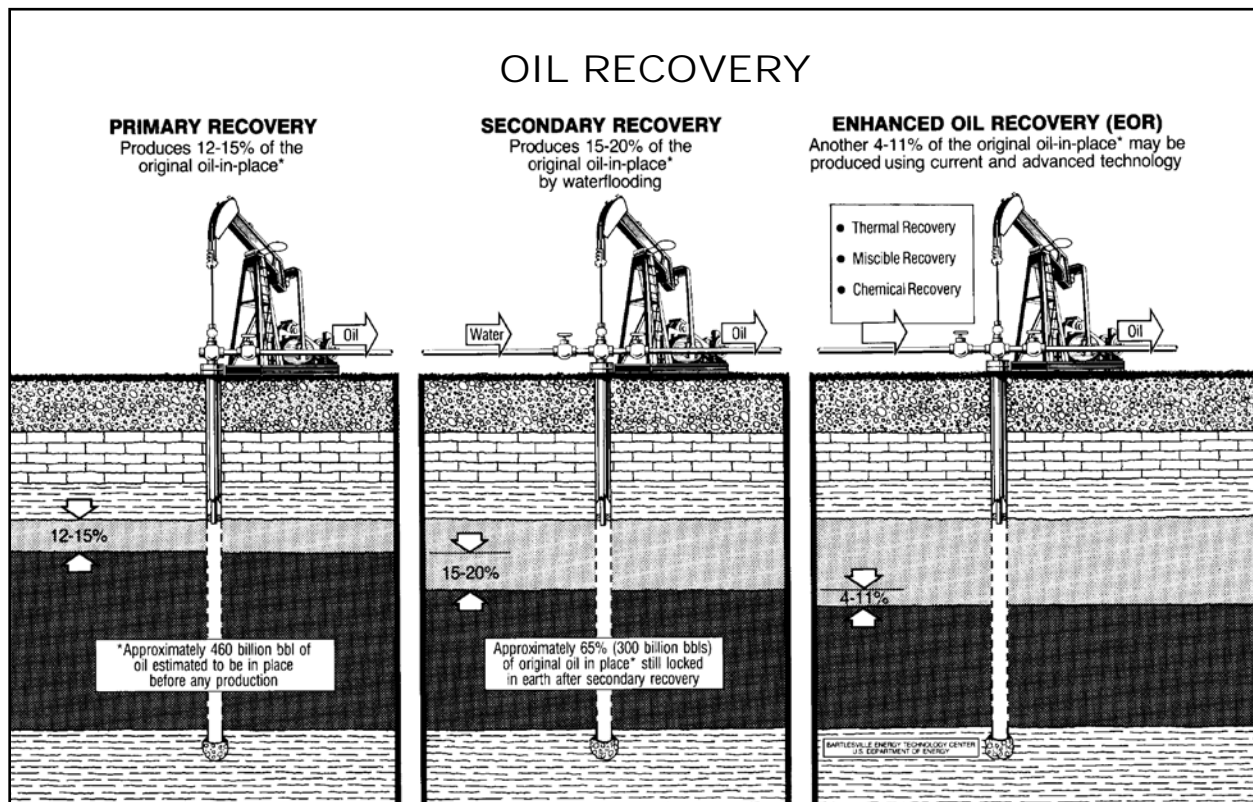
Figure 2. Oil recovery steps.[8]

1.2 Enhanced Oil Recovery

EOR was defined by Lake (1989) as "oil recovery by the injection of materials not normally present in the reservoir".[40] Green and Willhite (1998) have divided EOR processes into 5 categories.[36]

1.2.1 Mobility Control Processes

In mobility control process, water soluble high molecular weight substances called polymers are used to increase the viscosity of injected fluid to increase sweep efficiency of the injected fluid by obtaining favorable mobility ratios (M $\leq$ 1).

1.2.2 Chemical Processes

Reduction of the inter-facial tension (IFT) between oil and water is the scope of chemical processes. Surface active agents, surfactants, are utilized in order to obtain low IFT. The mobility of the surfactant solution is controlled by adding polymers.
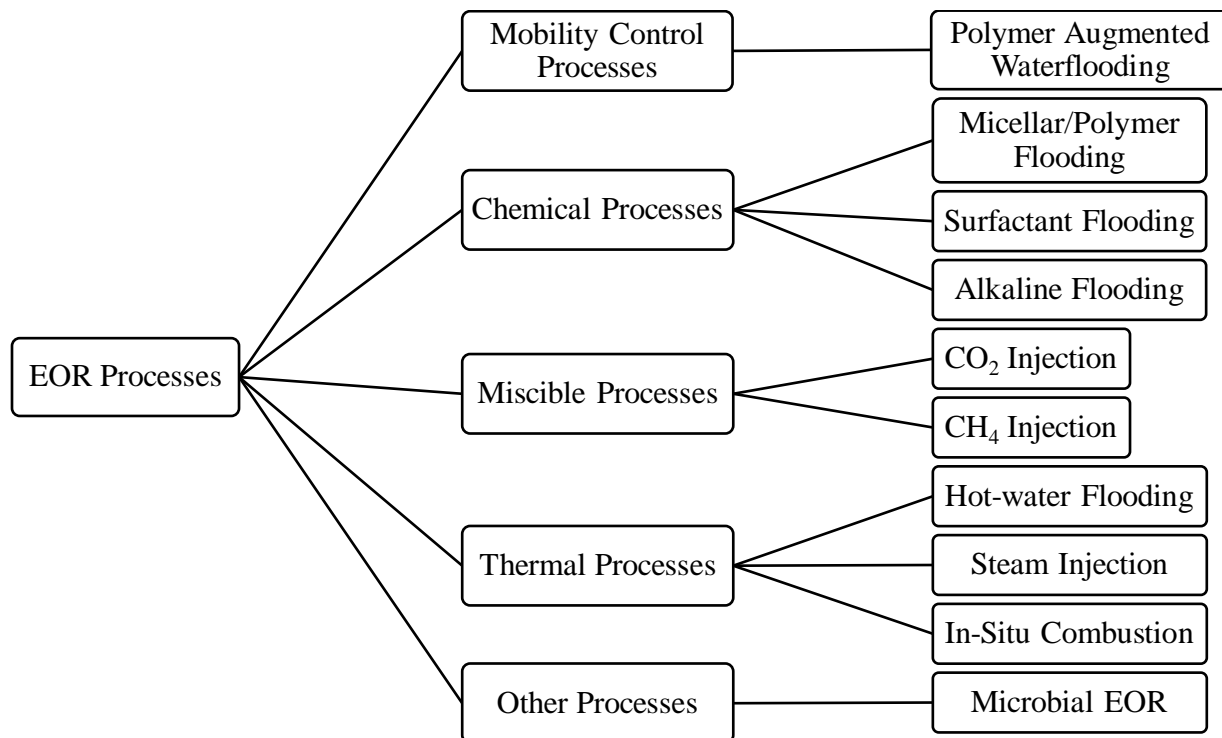
Figure 3. Enhanced oil recovery processes

1.2.3 Miscible Processes

The primary aim of miscible process is to sweep the trapped oil with a fluid which is miscible in oil. When the injected fluid is dissolved, it improves the mobility of oil. Carbon dioxide (CO_2) and dry hydrocarbon gas injection are the most common methods.

1.2.4 Thermal Processes

In thermal process, heat is introduced into a reservoir. The main objective is to increase the mobility of oil by reducing the viscosity. Hot-water flooding, steam injection (cyclic steam stimulation or stem flooding) and in-situ combustion are the main methods.[36]

1.2.5 Other Processes

Microbial EOR: The main mechanism in microbial EOR is the injection of microorganisms which metabolically produce different products such as acids, surfactants, carbon dioxide and hydrogen.[9] These products are utilized to increase recovery by improving the mobility of oil.

Taber et al. (1997) summarized the benchmarks for common EOR methods and stated that these are approximated parameters for good projects.[58]

		Oil Properties			Reservoir Characteristics					
Detail Table in Ref. 16	EOR Method	Gravity (°API)	Viscosity (cp)	Composition	Oil Saturation (% PV)	Formation Type	Net Thickness (ft)	Average Permeability (md)	Depth (ft)	Temperature (°F)
				Gas Injection Methods (Miscible)						
1	Nitrogen and flue gas	>35↗48↗	<0.4↘0.2↘	High percent of C_1 to C_7	>40↗75↗	Sandstone or carbonate	Thin unless dipping	NC	>6,000	NC
2	Hydrocarbon	>23↗41↗	<3↘0.5↘	High percent of C_2 to C_7	>30↗80↗	Sandstone or carbonate	Thin unless dipping	NC	>4,000	NC
3	CO_2	>22↗36↗ ᵃ	<10↘1.5↘	High percent of C_5 to C_{12}	>20↗55↗	Sandstone or carbonate	Wide range	NC	>2,500ᵃ	NC
1–3	Immiscible gases	>12	<600	NC	>35↗70↗	NC	NC if dipping and/or good vertical permeability	NC	>1,800	NC
				(Enhanced) Waterflooding						
4	Micellar/Polymer, ASP, and Alkaline Flooding	>20↗35↗	<35↘13↘	Light, intermediate, some organic acids for alkaline floods	>35↗53↗	Sandstone preferred	NC	>10↗450↗	>9,000↘3,250	>200↘80
5	Polymer Flooding	>15	<150, >10	NC	>50↗80↗	Sandstone preferred	NC	>10↗800↗ ᵇ	<9,000	>200↘140
				Thermal/Mechanical						
6	Combustion	>10↗16→?	<5,000 ↓ 1,200	Some asphaltic components	>50↗72↗	High-porosity sand/sandstone	>10	>50ᶜ	<11,500↘3,500	>100↗135
7	Steam	>8 to 13.5→?	<200,000 ↓ 4,700	NC	>40↗66↗	High-porosity sand/sandstone	>20	>200↗2,540↗ ᵈ	<4,500↘1,500	NC
—	Surface mining	7 to 11	Zero cold flow	NC	>8 wt% sand	Mineable tar sand	>10ᵉ	NC	>3:1 overburden to sand ratio	NC

NC = not critical.
Underlined values represent the approximate mean or average for current field projects.
ᵃSee Table 3 of Ref. 16.
ᵇ>3md from some carbonate reservoirs if the intent is to sweep only the fracture system.
ᶜTransmissibility >20 md-ft/cp
ᵈTransmissibility >50 md-ft/cp
ᵉSee depth.

Figure 4. Criteria for common EOR methods.[58]

1.3 Sea Water Flooding as an EOR Method

At first glance, sea water flooding seems like a secondary recovery method rather than an EOR method. However, it has been proven that in carbonate reservoirs certain parameters such as wettability, capillary pressures, etc. can be altered in favor of oil recovery by the help of potential determining ions present in sea water.[13, 55, 65] Thus, since the chemical and physical properties of a carbonate reservoir can be altered, sea water flooding is an EOR method. Ekofisk field in Norway is an outstanding example of sea water flooding. Primary recovery ratio of the Ekofisk field was estimated as 17% by pressure depletion; however, by the initiation of sea water injection in 1984, expected recovery ratio of the field is now close to 50%.[25, 26]

1.4 Project Objectives

In this project 6 surface active limestone cores from different sections of a reservoir have been studied. The effect of cleaning solvents on wettability has been analyzed. Besides, the effect of sea water and $C_{12}TAB$ (cationic surfactant) on wettability alteration has been examined on these cores.

2) THEORY

Sedimentary rocks comprise almost 70% of the Earth's surface. They can be divided into 4 main groups which are biogenic, biochemical and organic sediments (e.g. limestone, dolomite, coal and oil shale), siliciclastic sediments (e.g. conglomerate, sandstone and mud rock), chemical sediments (e.g. evaporate and ironstone) and volcanic sediments (e.g. ignimbrite and tuff).[64]

The most important reason why sedimentary rocks have being studied is the abundance of economic minerals and organic matter contained within them. "Black gold" and gas are derived from the maturation of organic matter in sediments and migrate to a porous and permeable sedimentary (reservoir) rock.

Among those sedimentary rocks, organic sediments (carbonate rocks) attract the attention because of their hydrocarbon content capability.

2.1 Carbonate Rocks

The formation of carbonate rocks is mainly governed by biological and biochemical processes and diagenesis which is the combination of chemical and physical processes occurring after deposition considerably changes carbonate rocks.[64]

The economic importance of carbonate rocks is because of their organic content and reservoir properties. It is estimated that 40-60% of world's total hydrocarbon production is from carbonate rocks.[33] Ghawar Field, Saudi Arabia and South Pars/North Dome field, Iran & Qatar are the world's largest oil and gas fields respectively which are composed of carbonate rocks.[1, 4]

Three major types of carbonate rocks are chalk, limestone and dolomite. Chalks are mainly composed of soft, white, very fine-grained extremely pure limestone consisting of the remains of skeletal bits of planktonic green algae, associated with varying proportions of larger microscopic fragments of bivalves, foraminifera and ostracods.[2] Limestones mostly consist of calcite ($CaCO_3$) mineral deriving from the remains of organisims such as corals, foraminiferas, sponges, bivalves, etc. The remains of these organisms in the reservoir rock result in high heterogeneity which is a major challenge in oil production and applications of enhanced oil recovery (EOR). Dolomites are originally deposited calcite/aragonite, $CaCO_3$, rich limestones, however, during diagenesis, calcite and/or aragonite is transformed to dolomite, $CaMg(CO_3)_2$.[5] This transformation process is called dolomitization. The best source of dolomite formation is the Mg^{+2} rich ground waters that are warm, tropical near ocean environments.[5]
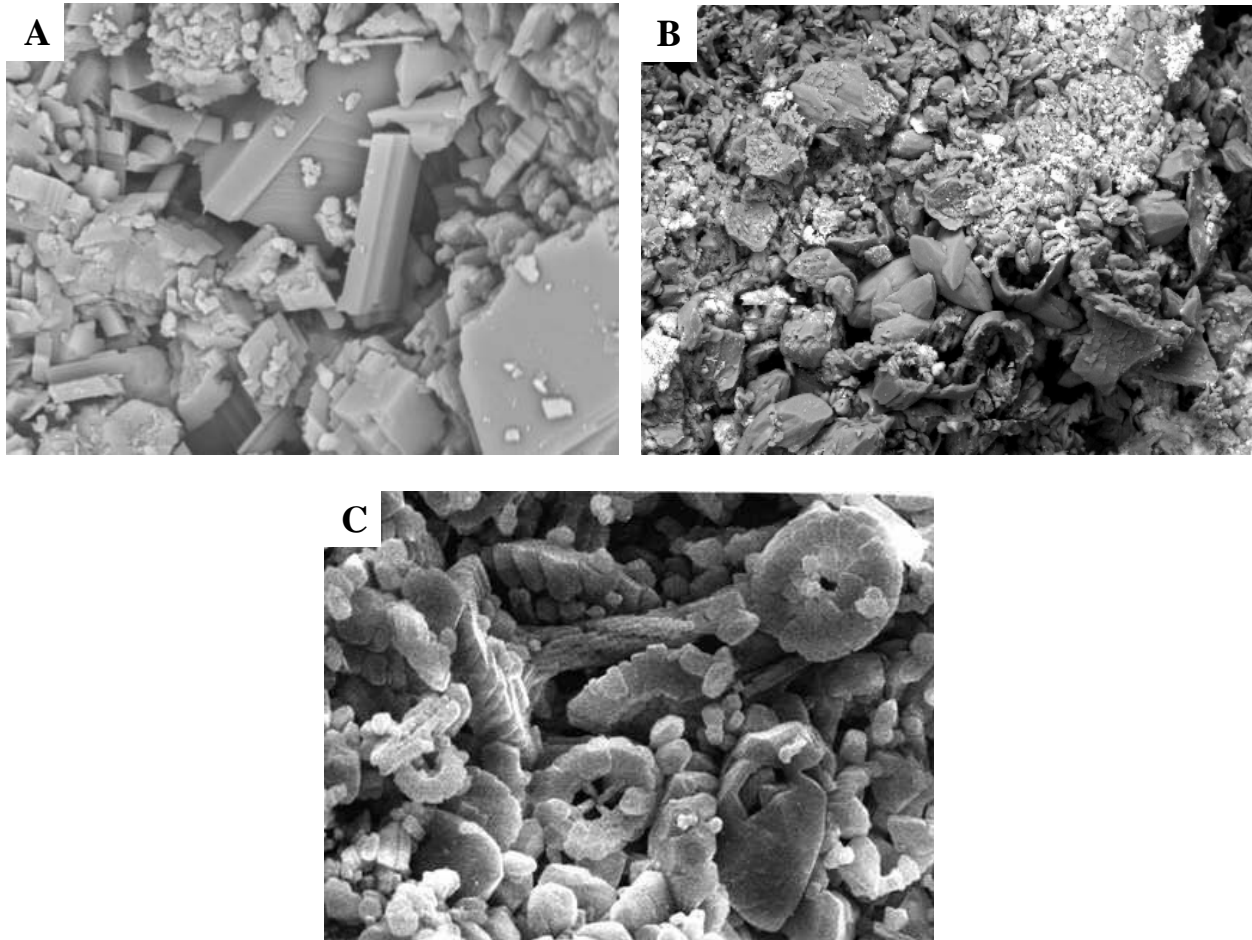
Figure 5. Scanning electron microscope (SEM) photographs of limestone (A)[31], dolomite (B)[35] and chalk (C)[32].

2.2 Wettability

Wettability is defined as the tendency of one fluid to spread or adhere to a solid surface in the vicinity of another immiscible fluid.[21] In a crude oil/brine/rock system, wettability depends on the attraction forces among rock mineral, crude oil and brine. According to Donaldson and Alam (2008), there are four types of wetness system [27]:
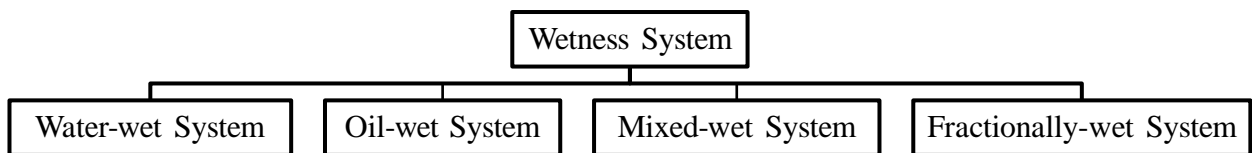
Figure 6. Wetness systems in carbonate reservoirs.

Water-wet System

If more than 50% of the rock surface in oil/brine/rock system is covered by water, it is recognized as water-wet system. In this system, small pores and the surface of larger pores are occupied by water. Initially, water is in continuous phase in the reservoir and oil is present in the larger pores as droplets. [27]

Oil-wet System

Oil-wet system is the reverse of water-wet system. Oil occupies smaller pores and the surface of larger pores. Initially, oil is in continuous phase and water is present in the larger pores as droplets. [27]

Mixed-wet System

According to Salathiel (1973), "mixed wettability is a condition where the small pores in the rock are water-wet and saturated with water, but the larger pores are oil-wet and filled with oil in contact with the pore walls that form a continuous path through the length of the rock". [49]

Fractionally-wet System

According to Donaldson and Alam (2008) fractional wettability term was proposed "to characterize heterogeneous wetting of the pore surfaces where the preferential wetting is randomly distributed throughout the rock". The random distribution of minerals in reservoir rock with different chemical properties might be one of the reasons for fractionally-wet systems. [27]

2.2.1 Wettability of Carbonate Reservoirs

It is estimated that 40-60% of the world's total hydrocarbon production is from carbonate rocks and most of these carbonate reservoirs are naturally fractured.[33] The studies on wettabilitiy of carbonate rocks have showed that majority of carbonate reservoirs have a tendency of being neutral-wet to oil-wet.[19, 63] Oil production from these naturally fractured, oil-wet reservoirs is a great challenge in terms of enhanced oil recovery (EOR) applications. One of the most common EOR techniques for this type of reservoirs is waterflooding in terms of accessibility and costs. However, water flooding in a fractured, oil-wet reservoir is not effective because of the early breakthrough of injected and negative capillary forces. The main recovery mechanism in fractured reservoirs is the imbibition of injected water into the matrix blocks and displacing oil; however, if the capillary pressure in the matrix blocks is negative water cannot

imbibe and displace oil. Thus, the wetness of the reservoir has to be modified towards more water-wet (positive capillary pressure) in order to recover more oil by imbibition of water.

2.2.2 Methods of Wettability Measurement

Wettability measurement methods can be divided into two groups that are qualitative methods and quantitative methods. Qualitative methods are imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance, dye adsorption and quantitative methods are contact angle measurement method, imbibition & forced displacement (Amott) method and USBM wettability method.[11]

The most widely used methods are contact angle method, spontaneous imbibition & forced displacement (Amott) method and USBM wettability method. Besides, a new chromatographic wettability measurement method was developed recently to measure the wetting state in carbonate rocks.

2.2.2.1 Contact Angle Measurement Method

According to Anderson (1986), contact angle method is one of the best wettability measurement methods when pure fluids and artificial cores are used. However, when crude oil is used, because of surface active agents in crude oil, a significant length of time is necessary for a contact angle to reach equilibrium. [11]

Sessile drop and modified sessile drop methods are the two generally used methods in petroleum industry. In sessile drop method, a drop of water or oil is placed onto the flat mineral surface and contact angle is measured.[11] It should be remembered that the angle has to be measured from solid surface to denser liquid. The magnitude of contact angle determines the wetness of surface. A schematic illustration is shown below to measure the wetness of a crude oil/brine/rock system.

θ < 90º surface is water-wet[18]   θ > 90º surface is oil-wet[18]
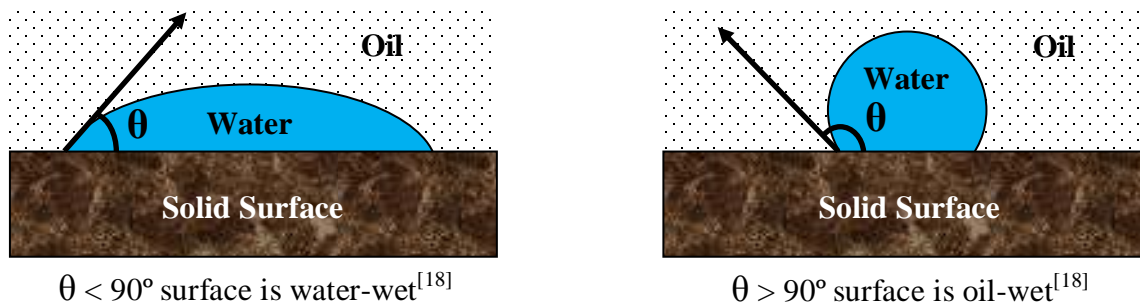
Figure 7. Sessile drop method. Redrawn after Raza et al. (1968). [47]

In modified sessile drop method, an oil drop is placed between two crystals. After aging the oil/crystal interface, the two crystals are displaced parallel to each other. This shifts the oil drop and allows water to move over a portion of the surface previously covered by oil and then contact angles are measured from solid surface.[11]
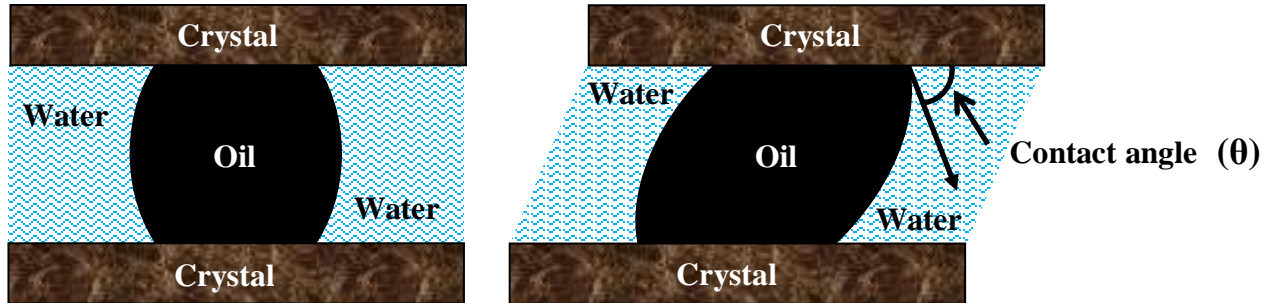
Figure 8. Modified sessile drop method. Redrawn after Craig (1971).[21] If θ < 90°, system is water-wet and system is oil-wet if θ > 90°.

2.2.2.2 Amott Method

Amott method [10] is based on spontaneous imbibition and forced displacement of oil and water. Before beginning the experiment, core is prepared by centrifuging or flooding with brine until the residual oil saturation is reached. In other words, initially, the pore volume of core must be occupied by residual oil and brine. After that step, core is immersed in oil and the volume of water, V_{ws}, which is displaced by spontaneous imbibition of oil, is recorded. Then, core is centrifuged or flooded by oil until the residual water saturation is attained and the volume of water displacement, V_{wf}, is recorded. Total volume of displaced water, $V_{wt}=V_{ws}+V_{wf}$, after spontaneous imbibition and forced displacement is calculated. Now, the core is filled with residual water and oil. This time, same procedure is applied with water and the volume of oil displacement by water after spontaneous imbibition, V_{os}, and forced displacement, V_{of}, is recorded and total oil displacement, V_{ot}, by water is calculated.[27]

A modified Amott method called "Amott-Harvey relative displacement index" was used by some researchers [11, 62]. This modified procedure involves an additional step before running the test. The core is centrifuged or flooded first under brine and then under oil until residual water saturation is attained. Remaining procedures are same as in Amott method. Then, Amott-Harvey relative displacement index, I,

$$I = \frac{\dfrac{V_{os}}{\underbrace{V_{os}+V_{of}}_{V_{ot}}} - \dfrac{V_{ws}}{\underbrace{V_{ws}+V_{wf}}_{V_{wt}}}}{}$$

According to this formula, wettability of a core can be scaled in the range from -1 (strongly oil-wet) to +1 (strongly water-wet). According to Cuiec (1984) a system is oil-wet when $-1 \leq I \leq -0.3$, intermediate-wet when $-0.3 < I < 0.3$ and water-wet when $0.3 \leq I \leq 1$. One disadvantage of Amott method is that it is insensitiveness near neutral wettability.[23]

2.2.2.3 USBM (United States Bureau of Mines) Method

In USBM method, required work for one liquid to displace other one is compared. Before running the test, cores are prepared by centrifuging under oil until the residual water saturation is achieved. In other words, core has to be filled with residual water and oil initially. Then, the first step is to centrifuge the core under water until the residual oil saturation is attained. The speed of centrifuge should be increased incrementally until -10 psi capillary pressure is achieved. Simultaneously, water saturation in the core, corresponding to the speed increment, should be calculated by measuring the oil displacement. In the second step, core immersed in oil and water is displaced by oil. As in the first step, capillary pressures (till +10 psi) and water saturations, corresponding to these capillary pressures, are recorded. In USBM method, the required work to displace a liquid is proportional to the area under capillary pressure curve [11, 41, 43] and the ratio of the areas under capillary pressure curves is used to calculate wettability index, W,

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

If a core is water-wet, the area, A_2, under the brine-drive capillary pressure curve is smaller than the area,

Figure 9. USBM method. Redrawn after Donaldson (1969).[28]

A_1, under the oil-drive capillary pressure curve. It is vice versa if a core is oil-wet. When $W > 0$ the core is water-wet, when $W < 0$ the core is oil-wet and when W is near zero it means that the core is neutrally wet.

2.2.2.4 Chromatographic Wettability Test

This method is based on chromatographic separation between SCN^- (the tracer) and SO_4^{-2} (the potential determining ion) as described by Strand et al. (2006).[57] This wettability test can be run on the cores saturated with 100% water as well as the cores having residual oil saturation.

In the case of oil saturated core, initially, the core is flooded by SW-0T (composition is in experimental setup part) that has neither SCN^- nor SO_4^{-2} at a constant rate until residual oil saturation is reached. Then, injected brine is switched to SW-1/2T (without changing the injection rate) in which the molar concentrations of SCN^- and SO_4^{-2} are equal. During injection, SO_4^{-2} adsorbs on the water-wet portions of carbonate surface whereas SCN^- just passes through the core because of its non-adsorbable nature. The effluent is collected and analyzed to determine the relative concentrations of SCN^- and SO_4^{-2}. Then, injected pore volume is plotted against relative concentrations of ions.
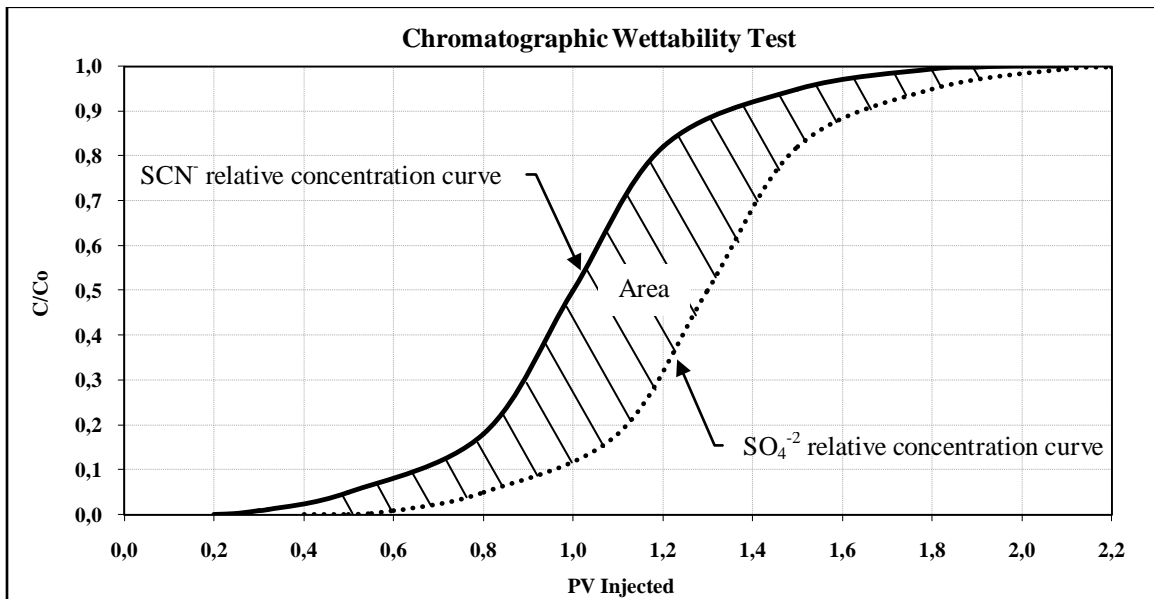
Figure 10. Schematic illustration of the chromatographic wettability test separation between SCN^- and SO_4^{-2}.

The area between tracer curve and sulfate curve is proportional to the water-wet surface of the core. The new wettability index, WI_{New}, is calculated according to the following formula,

$$WI_{New} = \frac{A_{Wett}}{A_{Heptane}}$$

A_{Wett} = The area between thiocyanate, SCN^-, and sulfate, SO_4^{-2}, curves generated by flooding a core aged in crude oil.

$A_{Heptane}$ = The reference area between thiocyanate, SCN^-, and sulfate, SO_4^{-2}, curves generated by flooding a core assumed o be strongly water-wet (saturated with heptanes).

WI_{New} ranges from 0 (completely oil-wet) to 1 (completely water-wet) and 0.5 refers to neutrally-wet.

This new method can be used to observe changes in wetting conditions of the core when it is exposed to different fluids and also to evaluate the efficiency of different cleaning solvents by comparing the result of wettability tests before and after cleaning the core.

2.2.3 Wettability Alteration in Carbonate Reservoirs

Almost 50% of proven oil reserves are in carbonate reservoirs and average recovery from these reservoirs is less than 30%. The reason of low recovery ratio arises from both highly fractured-low permeable and neutral to preferential oil-wet characteristics of carbonate reservoirs.[18] Waterflooding is one of the most common method to improve recovery. However, waterflooding is not effective in fractured-low permeable oil-wet reservoirs. Thus, wettability in the reservoir must be modified towards water-wet to increase recovery by spontaneous imbibition.

It has been reported that up to 40% improvement in oil recovery could be reached by using sea water as imbibing fluid instead of formation brine.[66] This increase in recovery was explained by Zhang et al. (2007) in chalk reservoirs.[68]

2.2.3.1 Wettability Alteration by Sea Water Injection

It has been shown that SO_4^{-2} is a strong potential determining ion towards $CaCO_3$[46] When sulfate ion enters the reservoir, it adsorbs onto positively charged rock surface and as a result rock surface becomes less positively charged compared to the initial condition. Since the surface strength has decreased, more Ca^{+2} ions are able to come closer to the rock surface and

make a connection with the negatively charged carboxylic, R-COO⁻, components. Less carboxylic group on the surface means higher water-wetness and oil recovery.

When the concentration of ions in sea water is examined, it can be seen that Mg^{+2} has the highest concentration among divalent ions (Ca^{+2} and SO_4^{-2}). A study by Zhang et al. (2007) has shown that at high temperatures, Mg^{+2} in sea water acts as a potential determining ion and modifies wetness of the carbonate reservoir towards water-wet within the presence of SO_4^{-2} and Ca^{+2}.[68] The main mechanism behind this wettability modification is the substitution of Ca^{+2} by Mg^{+2}. Korsnes et al. (2006) has showed that Ca^{+2} can substitute Mg^{+2} from the surface of biogenic outcrop chalk at high temperature.[39] After the connection between Ca^{+2} and carboxylic group has established, Mg^{+2} releases the Ca^{+2} & R-COO⁻ compound from the surface at high temperature. Since the carboxylic components have been removed from the surface, the wetting state of the core becomes more water-wet and at the same time oil recovery increases.
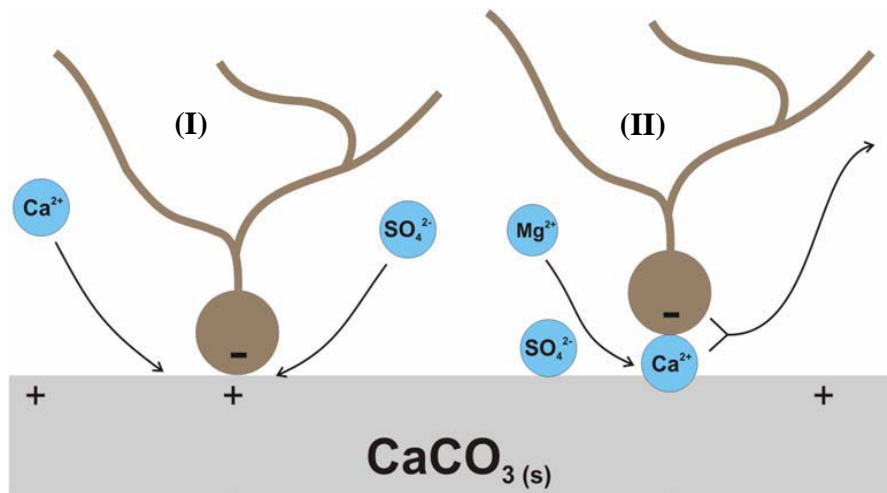
Figure 11. Schematic model of the suggested mechanism for the wettability alteration induced by seawater. **(I)** Proposed mechanism when Ca^{+2} and SO_4^{-2} are active. **(II)** Proposed mechanism when Mg^{+2} and SO_4^{-2} also are active at higher temperatures.[68]

2.2.3.2 Wettability Alteration by Surfactant Injection

It is known that negatively charged carboxylic, R-COO⁻, components have great tendency of adsorbing onto the positively charged carbonate surface.[61] Another method to alter the wetting state of the reservoir towards more water-wet and improve the oil recovery is to break the bond between carboxylic components and carbonate rock surface by injecting surfactant into the formation.

Surfactants are composed of two parts, (1) a non-polar hydrocarbon portion and (2) a polar portion. Since non-polar hydrocarbon portion (tail) interacts weakly with water molecules, it is called hydrophobic. On the other hand, polar portion (head) interacts strongly with water molecules and it is called hydrophilic.[36] Standnes and Austad (2000) have performed comprehensive experiments on both cationic, $R-N^+(CH_3)_3$, and anionic surfactants to observe the effectiveness of surfactant injection on wettability alteration and oil recovery in chalk.[53] They have tested 14 different surfactants and concluded that cationic surfactants are much more effective than anionic surfactants. The mechanism behind the effectiveness of cationic surfactants is their ability of desorbing carboxylic components from the rock surface. This is achieved by forming an ion-pair (not soluble in water but soluble in oil) between the cationic surfactant and carboxylic component.[53] It has been mentioned by Standnes and Austad (2000) that hydrophobic portion of the cationic surfactant has a significant role in altering the wettability of chalk and among the tested cationic surfactants $C_{12}TAB$, $n-C_{12} - N(CH_3)_3BR$, is the most effective one.[53]

2.3 Crude Oil/Brine/Carbonate Rock Interactions

The attractive and/or repulsive forces between oil and rock surface are directly related to the polar components in oil and the surface charge of carbonate rock which depends on the ion concentration of formation brine.

2.3.1 Fractions in Crude Oil

There are mainly four types of fractions in crude oil which are aromatics, saturates, resins and asphaltenes. These fractions are determined with respect to their solubility in different solvents. Aromatics, saturates and resins are soluble in heptane. On the other hand, asphaltenes are not soluble in heptane but soluble in benzene or toluene. It is important to identify crude oil fractions according to their polarity as far as crude oil/rock surface interactions are concerned. Saturates and aromatics are the non-polar fractions, resins are low molecular weight polar fractions and asphaltenes are high molecular weight polar fractions.[15] These polar fractions which are generally called as acid number and base number determine the wetting condition in reservoir.

2.3.2 Effect of Acid and Base Numbers of Crude Oil on Carbonate Rock Surface

The terms acid number and base number are used to refer to the amount of titrant used to neutralize acidic or basic constituent in crude oil. Polar components in crude oil may behave either acidic (becoming negatively charged by donating a proton) or basic (becoming positively charged by gaining a proton).[20] Since surface of carbonate rocks are positively charged, acidic components (negatively charged) like carboxylic acids, $R\text{-}COO^-$, are much more important than basic components (positively charged). The attractive electrostatic force between acidic components and carbonate rock surface is the key parameter in crude oil/carbonate rock surface interaction. Recent studies have showed that the wetting state of carbonate rocks shifts towards oil-wet when the acid number (directly proportional to the negatively charged components in oil) of crude oil increases.[67]

2.3.3 Formation Brine/Carbonate Rock Interaction

Calcite, $CaCO_3$, has zero point of surface charge when pH of the brine is 9-10 and salinity is low. Initially, in carbonate reservoirs, formation brine has high concentration of Ca^{+2} (high salinity) and because of that carbonate surface becomes positively charged (zeta potential studies have showed that at reservoir conditions, high salinity and low pH, calcite is prone to have positively charged surface.[54]) and the water film between oil and rock loses its stability.[56] As a result, negatively charged carboxylic groups, $R\text{-}COO^-$, in oil adsorb strongly onto the positively charged carbonate surface[59] and reservoir wettability changes towards oil-wet.

2.4 Wettability Restoration

In laboratory studies, to simulate reservoir behavior, it is vital to work with the parameters as close as possible to the original reservoir condition. Thus, same reservoir fluids and rock (core sample) must be used at reservoir temperature and pressure. It is easy to get reservoir fluids (oil, gas, brine) and provide required reservoir pressure & temperature in laboratory conditions. However, it is hard to know whether the core sample represents the original reservoir condition or not. The reservoir parameters such as initial and residual fluid saturations, relative permeabilities, capillary pressures etc. are very important and directly depend on the wetting state of the reservoir. Hence, prior to any experiments, the native wetting state of the reservoir must be restored in order to obtain the most realistic results. It has to be

remembered that these results are used in reservoir evaluation programs to assess the fate of reservoirs in terms of development and investment.

2.4.1 Core Preservation

The aim of core preservation is to prevent the alteration of chemical and physical properties of the reservoir in the core sample. According to Skopec (1994) the main challenges in coring and core preservation are (I) designing a drilling fluid program to minimize mud invasion and maximize drilling parameters, (II) selecting a nonreactive core preservation material and preventing fluid loss or absorption of contaminants and (III) applying appropriate core handling and preservation methods based on rock type, degree of consolidation and fluid type.[51]

Coring is a time and money consuming operation; hence, it should be completed as soon as possible. Many companies use oil based drilling mud throughout coring operations because this type of mud can reduce drilling time and cost.[34, 50] However, cores that are cut with oil based mud are generally contaminated and native wetting state of the cores are altered because of the surfactant components in this type of mud. It has been reported that there is no oil based drilling mud that does not cause any wettability alteration in core.[60]

Another challenge starts when the core was brought to the surface. It has to be divided into smaller sections for transportation and simultaneously interaction between the core sections and atmospheric conditions must be eliminated immediately to prevent alteration. According to Bobek et al. (1958), there are mainly two methods which are applicable at the well site to preserve cores. These are (1) wrapping the cores at the well site in polyethylene or polyvinylidene film, then in aluminum foil and sealing the wrapped cores with paraffin or thick plastic container to prevent further evaporation and air invasion, (2) immersing the cores in deoxygenized formation or artificial brine in a glass-lined steel or plastic tube and sealing the package to prevent air invasion and leakage.[16]

During surface preparation of cores, they are inevitably exposed to atmospheric conditions in terms of pressure, temperature and air. Due to pressure drop, some of the light components in oil evaporate and because of air exposure some of the active chemicals are oxidized. Temperature drop, evaporation of light components and oxidization may result in precipitation of the polar components if there are any and this may change the wetting state of the core towards more oil-wet.[45, 48]

Consequently, it is almost impossible to maintain natural wetting state of core sample when contamination during coring, pressure drop and air exposure during surface handling are considered. Hence, prior to any laboratory experiments, to be on the safe side, cores have to be cleaned with proper solvents and the native wetting state of the reservoir should be tried to restore by using corresponding reservoir fluids.

2.4.2 Core Cleaning

In order to restore the native wetting state of the core sample, natural (oil & formation brine) and unnatural (contamination due to coring mud) components have to be extracted from the core by using proper solvents. In other words, at the end of cleaning process, wetting state of the core should be as strongly water-wet as possible. The main challenge in cleaning step is to find the most convenient solvent/s that can dissolve all the organic compounds adsorb onto the surface of core.

2.4.2.1 Extraction Methods

In the literature some of the reported cleaning methods are distillation/extraction (Soxhlet method), flow-through core, centrifuge flushing, gas-driven solvent extraction, supercritical fluid extraction, critical point drying, steam cleaning and firing the core in the presence of oxygen.[34] Among those methods, distillation/extraction (Soxhlet method) and flow-through core are the most commonly used ones in laboratories.

2.4.2.1.1 Distillation/Extraction Method

In this method an apparatus called Soxhlet extractor, invented in 1879 by Franz von Soxhlet, is used.[3] Figure 12. shows the parts of Soxhlet extractor. The core is placed in thimble (4) onto a thick filter paper and then extraction solvent is heated to reflux. The vapor of extraction solvent passes through distillation path (3) and condenses (9). Then, the thimble (4) starts filling with condensed warm solvent in which oil is dissolved. When the chamber is filled with solvent, siphon (6, 7) automatically removes the excessive amount and returns it back to the pot (2). This loop continues until the core is cleaned. This method is being used widely in laboratories and efficient if the core has high permeability. However, if the permeability of the core is low, only the circumference of the core is cleaned and inner center of the core remains contaminated.

1)	Stirrer bar
2)	Extraction solvent pot
3)	Distillation path
4)	Soxhlet thimble
5)	Core sample
6)	Siphon arm inlet
7)	Siphon arm outlet
8)	Expansion adapter
9)	Condenser
10)	Cooling water inlet
11)	Cooling water outlet
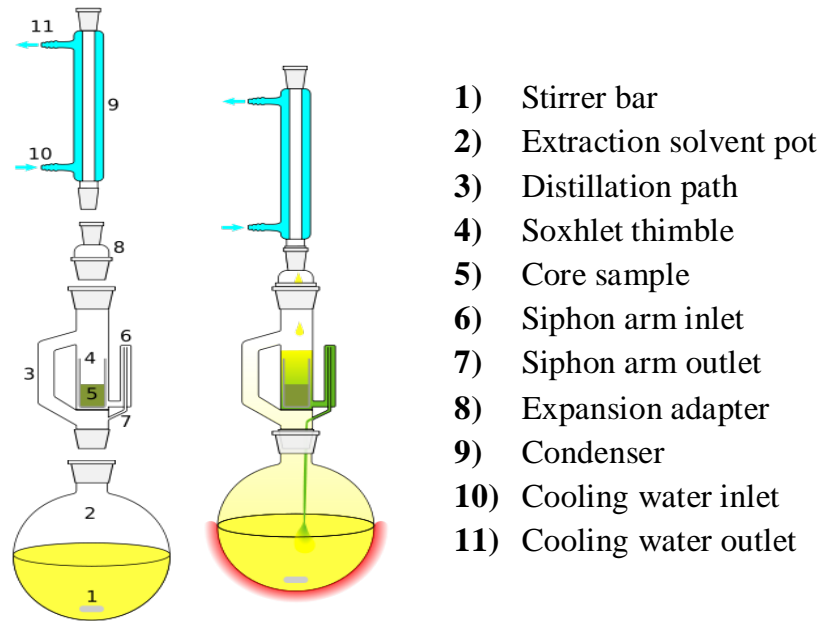
Figure 12. Soxhlet extractor.[3]

2.4.2.1.2 Flow-through Core Method

In this method, core is inserted into a rubber sleeve and put into a steel cylinder (core holder) together with rubber sleeve. After that, confining pressure (pneumatic or hydraulic) is applied between the outside of the rubber sleeve and inside of the core holder so that the rubber sleeve wraps around the core and prevents the passage of solvent through circumference of the core. Then, the solvent is injected and forced to pass through the core by applying required pressure. Effluent is collected at the outlet and clarity is checked visually. Figure 13. shows different parts core flooding setup which is used in flow-through core method. This method is the only applicable and effective one when the permeability of the core is low and high pressure is required to assure the flow through the core.
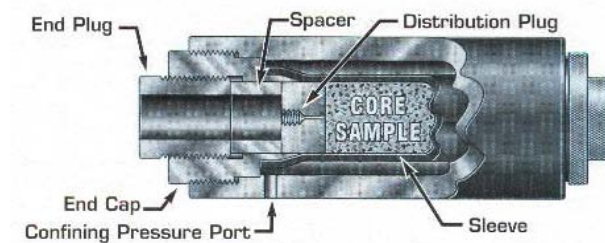
Figure 13. Parts of core flooding setup.[6]
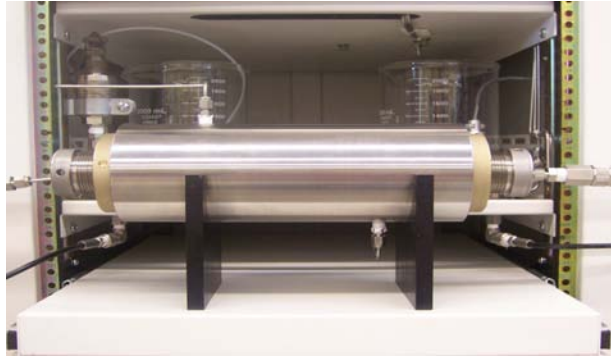
Figure 14. Hassler type core holder used in flow-through core cleaning method.[6]

According to Anderson and Gant, flow-through cleaning is more effective than extraction cleaning because the surface area contacted by solvents is higher in flow-through cleaning.[34]

2.4.2.2 Cleaning Solvents

The selection of proper solvent to clean the core depends on the properties of the oil and rock. Reaction between rock and oil is related to the surface charge of the rock and the acid and base number of the crude oil. It is known that in carbonate reservoirs, water-rock interface is positively charged if the pH is less than 9.5 due to the high Ca^{+2} concentration of formation brine.[54] Thus, the magnitude of acid number, negatively charged polar components, in oil is important as well as the reactivity of carbonate rocks. The main challenge in cleaning carbonate cores is to break the bond between acidic components and rock surface.

It has been reported that toluene is very effective as a cleaning solvent when combined with other solvents such as methanol (CH_3OH) or ethanol (CH_3CH_2OH).[34, 37] Toluene effectively removes the hydrocarbons including asphaltenes and some of the weakly polar components while methanol removes the strongly adsorbed polar components that are responsible for wettability alteration.[12] Anderson and Gant performed some experiments with different solvents to clean dolomite cores and concluded that using mixture of solvents is more effective than using single solvents.[34] The most comprehensive study on cleaning of limestone cores was performed by Cuiec with different single and mixture of solvents. Cuiec concluded that "(1) with regard to pollution by polar crude oils, standard solvents such as chloroform and toluene cannot be used in cleaning porous media, (2) a series of solvents appears to be effective in cleaning limestone cores and (3) for cleaning by a single product, solvents having a basic nature is effective for limestone."[22]

Consequently, it is important to remember that there is not a fixed type of solvent which effectively cleans every limestone, dolomite or chalk core. Determining the proper cleaning solvent (or mixture of solvents) is a trial and error procedure and strictly depends on the crude oil/rock interaction.[34]

2.4.3 Core Aging

After cleaning was completed, the native wetting state of the core can be restored by introducing oil and formation brine. First, the core is 100% saturated with formation brine and then centrifuged or flooded with oil until the residual water saturation is reached. Another method to obtain residual water saturation (RWS) in core is to keep it in a desiccator till the desired RWS is reached.[52] Final step in wettability restoration is aging of the core at reservoir temperature for a sufficient time to establish adsorption equilibrium. The aging time is a controversial subject. Many aging times have been mentioned in the literature and it seems that aging up to1000 hours is the most acceptable one.[12] One other problem in core aging is the effect of residual water on oil/rock interaction. It is known that oil migrates from source rock to reservoir rock where there is already water. Thus, it is important to examine the effect of water on wettability restoration. Experiments performed by Cuiec have shown that the presence of residual water does not prevent but delays the adsorption of polar components in oil onto the rock surface. [22, 24]

3) EXPERIMENTAL MATERIALS & METHODS

3.1 Core Properties

Reservoir limestone cores that have high surface reactivity from different sections of a well were used in this project. Table-1 shows the properties of these cores.

Table-1 Properties of limestone core samples.

Core Zone & Number	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)
C 1-3	8.26	3.80	18	1.3
C 2-4	8.08	3.80	14	0.4
C 4-14	8.08	3.80	16	0.4
C 5-16	7.11	3.80	17	1.0
C 5-18	3.82	3.77	17	-
C 5-20	7.91	3.79	18	-

3.2 Crude Oil Properties

2 different crude oil mixtures were used in experiments. Table-2 shows the properties of oil mixtures and Table-3 shows which oil mixtures were used in the cores during restorations. The mixtures were centrifuged to separate solid particles and heavy components and then they were filtered through 8 µm and 5 µm milipore filter papers. The acid and base numbers of oil mixture were measured by Mettler Toledo DL 55 titrator. Physica UDS200 Universal Dynamic Spectrometer was used to determine the viscosity of oil mixture. The densities were measured by Anton PAAR DMA 4500 density meter.

Table-2 Properties of oil mixtures.

	Acid Number (mgKOH/g oil)	Base Number (mgKOH/g oil)	Density (g/cm^3 at 20 ºC)	Viscosity (cP at 20 ºC)	Asphaltene (g/100 ml)
Oil Mixture-1	0.08	0.35	0.8376	5.8	-
Oil Mixture-2	0.07	0.57	0.84290	6.7	-

Table-3 Used oil mixtures during core restorations.

Core Zone & Number	1st Restoration	2nd Restoration	3rd Restoration
C 1-3	Mixture-1	-	-
C 2-4	Mixture-1	Mixture-1	-
C 4-14	Mixture-1	n-Heptane	-
C 5-16	Mixture-2	Mixture-2	Mixture-2
C 5-18	Mixture-2	Mixture-2	-
C 5-20	Mixture-1	Mixture-2	-

3.3 Brine Properties

During this project different types of synthetic brines have been used for core restoration, spontaneous imbibition and chromatographic wettability tests. Table-4 shows the composition of these brines.

❖ **FW-ØS:** Synthetic limestone formation water without SO_4^{-2}.

❖ **PSW:** Synthetic sea water for spontaneous imbibition test.

❖ **SW-ØT:** Synthetic sea water for chromatographic wettability test without SO_4^{-2} and SCN^-.

❖ **SW-1/2T:** Synthetic sea water in which molar concentrations of SO_4^{-2} and SCN^- are equal for chromatographic wettability test

❖ **PSW-ØNaCl:** Synthetic sea water for spontaneous imbibition test without sodium chloride.

Table-4 Brine composition.

Ion Name	FW-ØS (mole/L)	PSW (mole/L)	SW-ØT (mole/L)	SW-1/2T (mole/L)	PSW-ØNaCl (mole/L)
HCO_3^-	0.003	0.003	0.002	0.002	0.003
Cl^-	3.643	0.662	0.583	0.538	0.136
SO_4^{-2}	0.000	0.032	0.000	0.012	0.032
SCN^-	0.000	0.000	0.000	0.012	0.000
Mg^{+2}	0.076	0.059	0.045	0.045	0.059
Ca^{+2}	0.437	0.010	0.013	0.013	0.010
Na^+	2.620	0.594	0.460	0.427	0.068
Li^+	0.000	0.000	0.000	0.012	0.000
K^+	0.000	0.000	0.010	0.022	0.000
Ba^{+2}	0.000	0.000	0.000	0.000	0.000
Sr^{+2}	0.000	0.000	0.000	0.000	0.000
TDS (g/L)	208.94	42.22	33.39	33.39	11.48
Ion Strength (mole/L)	4.158	0.829	0.643	0.645	0.303

3.4 Core Preparation

All cores had been pre-flooded and saturated with kerosene by the operator company prior to delivery and it was assumed that the cores were not contaminated by drilling mud or any other chemicals. Prior to first restoration, all cores, apart from C 5-20, were cleaned by n-heptane not to disturb original wetting state inside the cores. Core C 5-20 was cleaned with dry toluene and methanol after n-heptane injection. Because of the extraction of oil by pre-flooding with kerosene, asphaltene precipitation was not expected during heptane injection. After cleaning the cores with solvents, distilled water was injected to remove any precipitated salts and sulfate.

Then, all cores were restored according to the procedure described in section 4. Flow-through core method was used in all cleaning processes.

Before second restoration, cores were cleaned with different solvents. Dry toluene and methanol were successively injected through the cores C 1-3, C 2-4 and C 5-18 until the effluent was clear. Sea water at high temperature, 130 ºC, was injected into the cores C 4-14 and C 4-16 to observe the effect of hot sea water on wettability alteration and then they were cleaned with dry toluene and methanol successively. Core C 5-20 was cleaned with kerosene and heptane prior to second restoration.

Before third restoration, core C 5-16 was first cleaned with water saturated toluene and then sea water + 1 weight % $C_{12}TAB$ at 130 ºC.

3.5 Core Saturation Procedure

After cleaning the cores, they were dried at 90 ºC at least over. The next step was to obtain initial water saturation in the cores. Desiccation method was utilized in this project to obtain initial water saturation that was 10%.[52] Thus, after vacuuming the cores to evacuate air, 10 times diluted formation water without sulfate was used to 100% saturate the cores and saturated weights were recorded. The reason of using 10 times diluted formation water was the method selected to attain initial water saturation. In desiccation method, driving mechanism is evaporating the water in the core in a controlled way. Thus, in order to reach 10% initial water saturation, the core had to be 100% saturated with 10 times diluted formation water. Pore volume and dry weight of the core and density of formation water was known so 10% saturated weight of the core was calculated by the following formula:

$$\text{Pore volume, PV} = \frac{\text{Saturated weight of core with 10 times diluted formation water} - \text{Dry weight of core}}{\text{Density of 10 times diluted formation water}}$$

Weight of core with 10% initial water saturation

$$= \left[\text{PV of core} * \underbrace{0.10}_{\substack{\text{Volume occupied by} \\ \text{initial water in core}}} * \text{Density of formation water} \right] + \text{Dry weight of core}$$

After reaching the desired weight, cores were kept in a container for three days in order to reach the saturation equilibrium all over the cores.[52] Then, totally 4 pore volumes of oil (2 PVs from each direction) were injected with a rate of 0.1 ml/min through the cores by using flow

through core method. After saturating the cores with oil, first, they were wrapped in Teflon and then put into the aging cells filled with oil. The aging cells were kept in an oven at 90 ℃ for two weeks.

3.6 Oil Displacement Methods

In this project, spontaneous and forced imbibition methods were used in order to displace oil.

Spontaneous Imbibition: Tests were performed both at room (20 ℃) and reservoir (110 ℃) temperatures in Amott Glasses and steel imbibition cells respectively. Pressure support (10 bars) cells were connected to steel imbibition cells during tests at reservoir temperature. The amount of oil recovery was recorded as a function of time. Figure 15. and Figure 16. show the schematic illustrations of spontaneous imbibition in Amott Glass and steel imbibition cell.

Forced Imbibition: This test was performed on core C 5-18 at reservoir temperature (110 ℃) with a 10 bar back pressure. Injection rate was 0.5 PV/day. FW-ØS was injected through the core and the amount of oil recovery was recorded as a function of time. Figure 17. schematically illustrates core flooding setup.

3.7 Wettability Evaluation

Chromatographic wettability test was used to evaluate the wetting condition of reservoir limestone core before and after exposing them to different cleaning solvents. The area between tracer (SCN^-) and sulfate (SO_4^{-2}) was compared to the initial area which was obtained after mild (kerosene and n-heptane) cleaning.
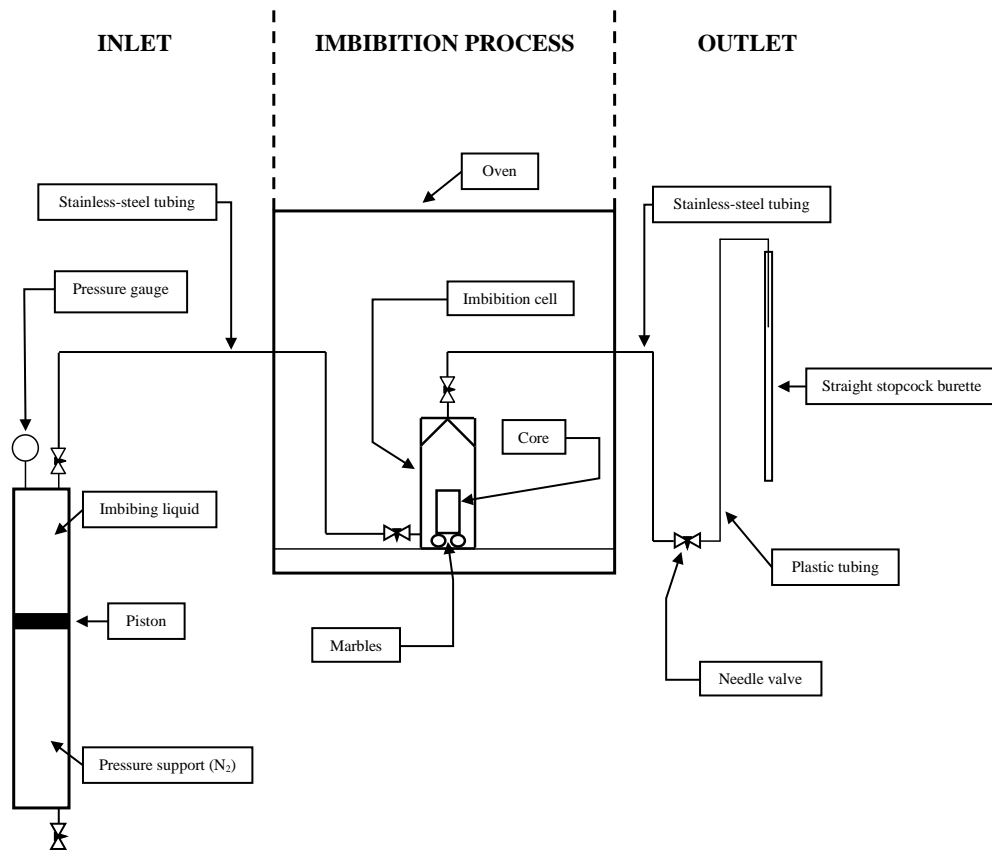
Figure 15. Spontaneous imbibition test at reservoir temperature.
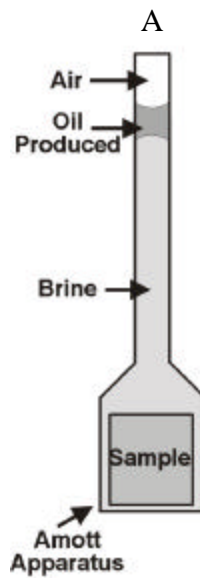
Figure 16. Spontaneous imbibition test in Amott Glass at room temperature.[29]
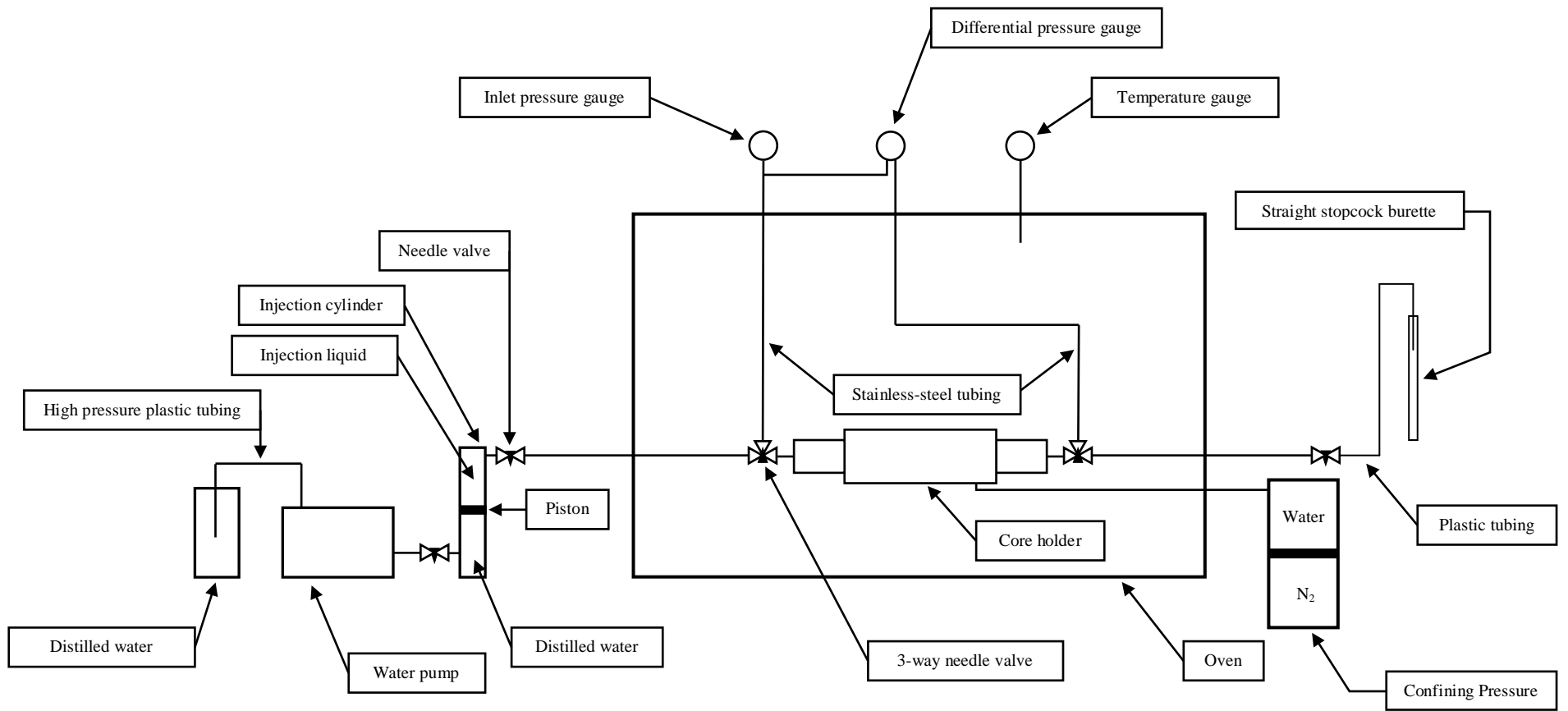
Figure 17. Schematic illustration of core flooding setup.

4) RESULTS & DISCUSSIONS

During previous experiments on limestone cores performed by EOR group in University of Stavanger, a problem has emerged. Two different oil recovery ratios were encountered during spontaneous imbibition tests on the same core. It has been realized that the only different parameter was the type of solvents that were introduced during cleaning the cores.

After cleaning the cores with kerosene and heptane, around 40% of originally oil in place (OOIP) was recovered. On the other hand, around 10% of OOIP was recovered after cleaning with toluene and methanol.

The objective of this thesis is to understand the mechanism behind this recovery difference as well as to compare the effect of different imbibing liquids on oil recovery.

4.1 Wetting State of the Cores

After cleaning with different solvents, chromatographic wettability tests were performed in order to observe the effect of cleaning solvents on wetting state of the cores. The area (A_w) between tracer (SCN^-) and sulfate (SO_4^{-2}) was utilized to specify wetting state of the cores. The term "restoration" used in this thesis includes all procedures (cleaning, obtaining initial water saturation, oil flooding and aging) to mimic original reservoir conditions inside the cores.

Core C 1-3 & C 2-4

In the 1st restoration after mild cleaning (kerosene and n-heptane), first wettability tests were performed to determine the native wetting state of the cores. The area between tracer and sulfate was 0.25 for the core C 1-3 and 0.38 for the core C 2-4 indicating that the native wetting state of the cores was preferentially water-wet. In the 2nd restoration, cores were cleaned with toluene and methanol and then second wettability tests were performed to observe the effect of cleaning solvents (Figure 18. and 19.). No significant difference between the areas before and after cleaning with toluene and methanol was observed. The delay of sulfate was caused by adsorption onto the rock surface at water-wet surfaces.

Core C 4-14

In this core four wettability tests were performed to examine the wetting states (Figure 20.). 1st wettability test was run after mild cleaning (kerosene and n-heptane) to determine the native wetting state inside the core. Result of the test has shown that native wetting state of the core was preferentially water-wet (area, A_w, between tracer and sulfate was 0.50). 2nd wettability

test was performed right after first spontaneous imbibition test to observe the effect of crude oil on core wettability. A reduction in area (from 0.50 to 0.41) was observed indicating that the water-wet fraction inside the core decreased due to the adsorption of polar components onto the rock surface during aging. Austad et al. (2008) has shown that water-wet fraction can be increased up to 30 % by injecting hot sea water.[14] Therefore, after second wettability test, core was tried to be cleaned by injecting hot sea water (130 ℃). After hot sea water injection, 3rd wettability test was run however no significant change in area (from 0.41 to 0.42) was observed. 4th wettability test was performed after cleaning the core with toluene and methanol to examine the effect of these solvents on wetting state. Result of the test has shown a decrease in area (from 0.42 to 0.35) between tracer and sulfate indicating that water-wet area inside the core reduced.

Core C 5-16

Three wettability tests have been conducted on core C 5-16 (Figure 21.). 1st wettability test was run after mild cleaning (kerosene and n-heptane) to determine the native wetting state inside the core. Result of the test has shown that native wetting state of the core was preferentially water-wet (area, A_w, between tracer and sulfate was 0.38). 2nd wettability test was performed after cleaning the core with water saturated toluene. A reduction in area (from 0.38 to 0.24) was observed indicating that wetting state inside the core shifted towards less water-wet. Standnes and Austad (2000) have proved the efficiency of water-soluble cationic surfactants on wettability alteration (oil-wet to water-wet) in low permeable chalks.[53] Therefore, it has been decided to clean the core with PSW at high temperature, 130 ℃. After cleaning the core with PSW + 1 weight % C_{12}TAB, 3rd wettability test was run. Result of the test has shown an increase in area (from 0.24 to 0.30) between tracer and sulfate indicating that wetting state inside the core shifted towards more water-wet.

Core C 5-18 & C 5-20

No wettability tests were run on these cores.

These wettability tests have shown that native wetting state of the cores were preferentially water-wet and successive injection of toluene and methanol had a negative effect on water-wet fraction inside the cores.
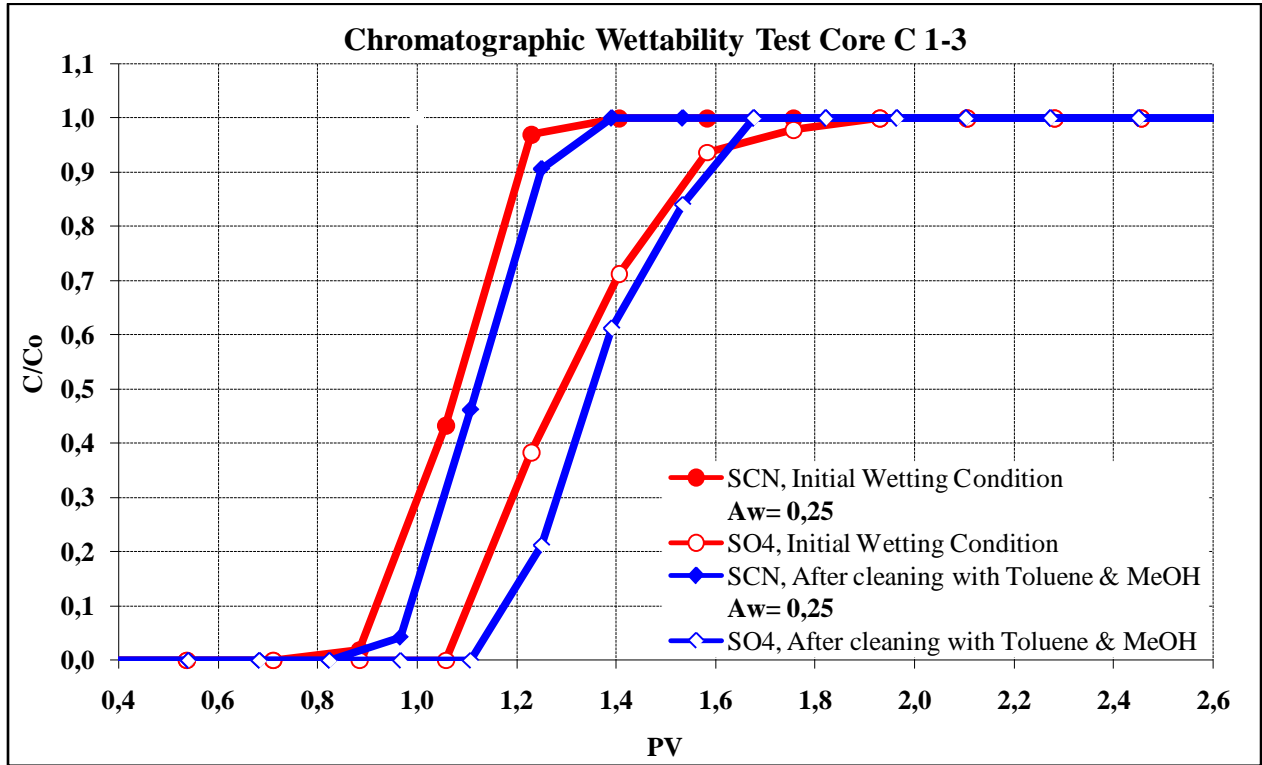
Figure 18. Wetting state of core C 1-3 before and after cleaning with Toluene & Methanol.
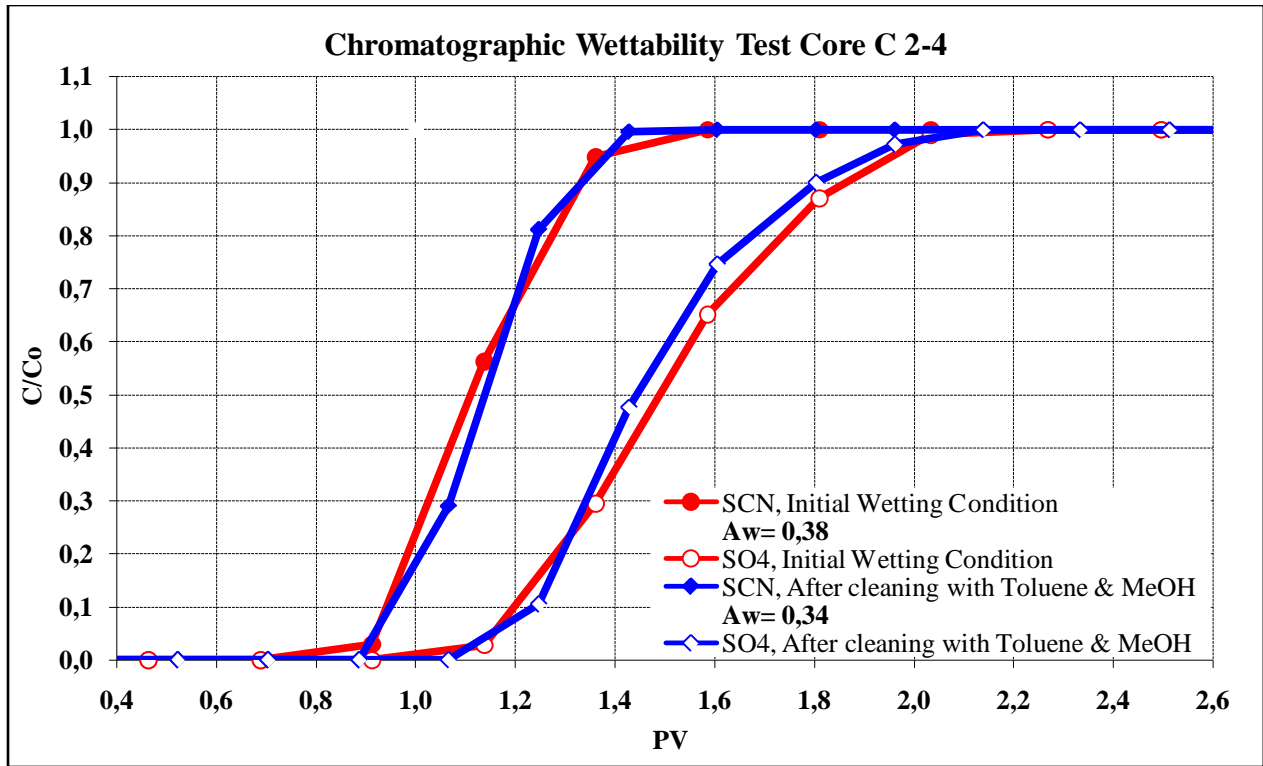
Figure 19. Wetting state of core C 2-4 before and after cleaning with Toluene & Methanol.
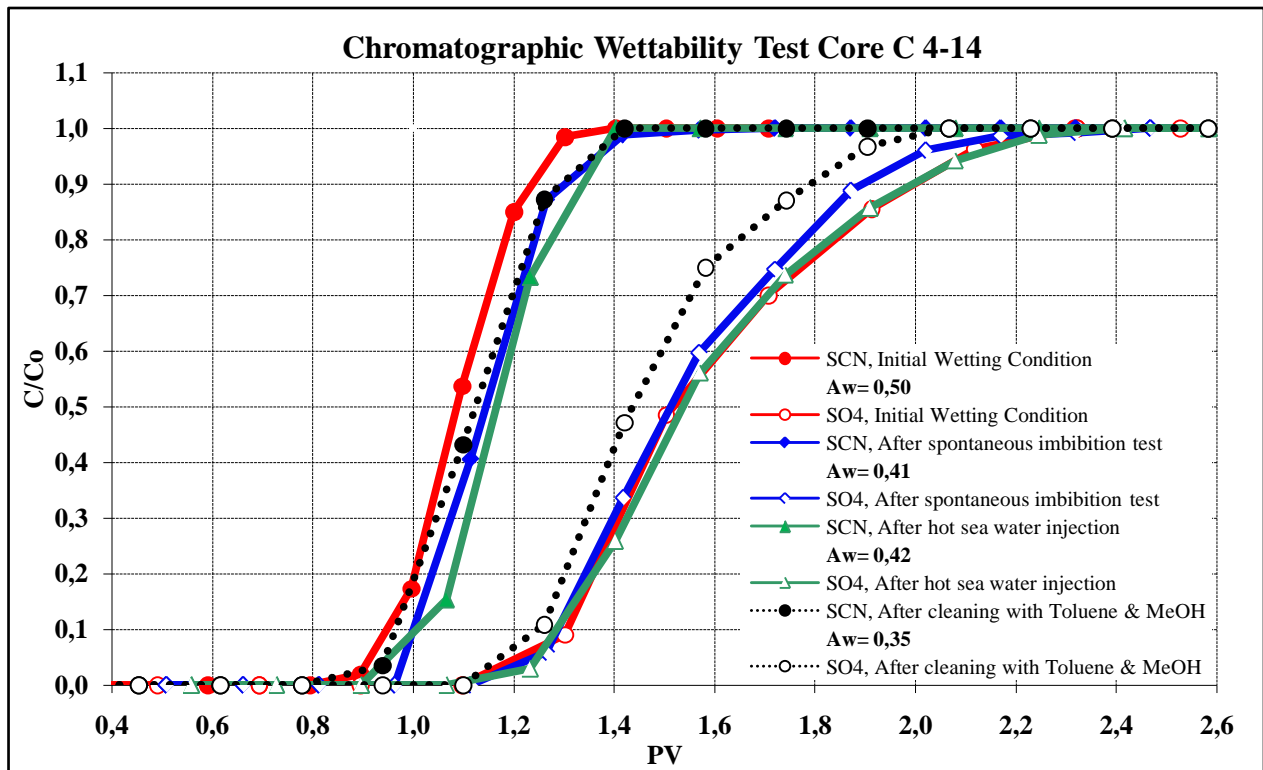
Figure 20. Wetting state of core C 4-14 before and after multiple cleaning procedures.
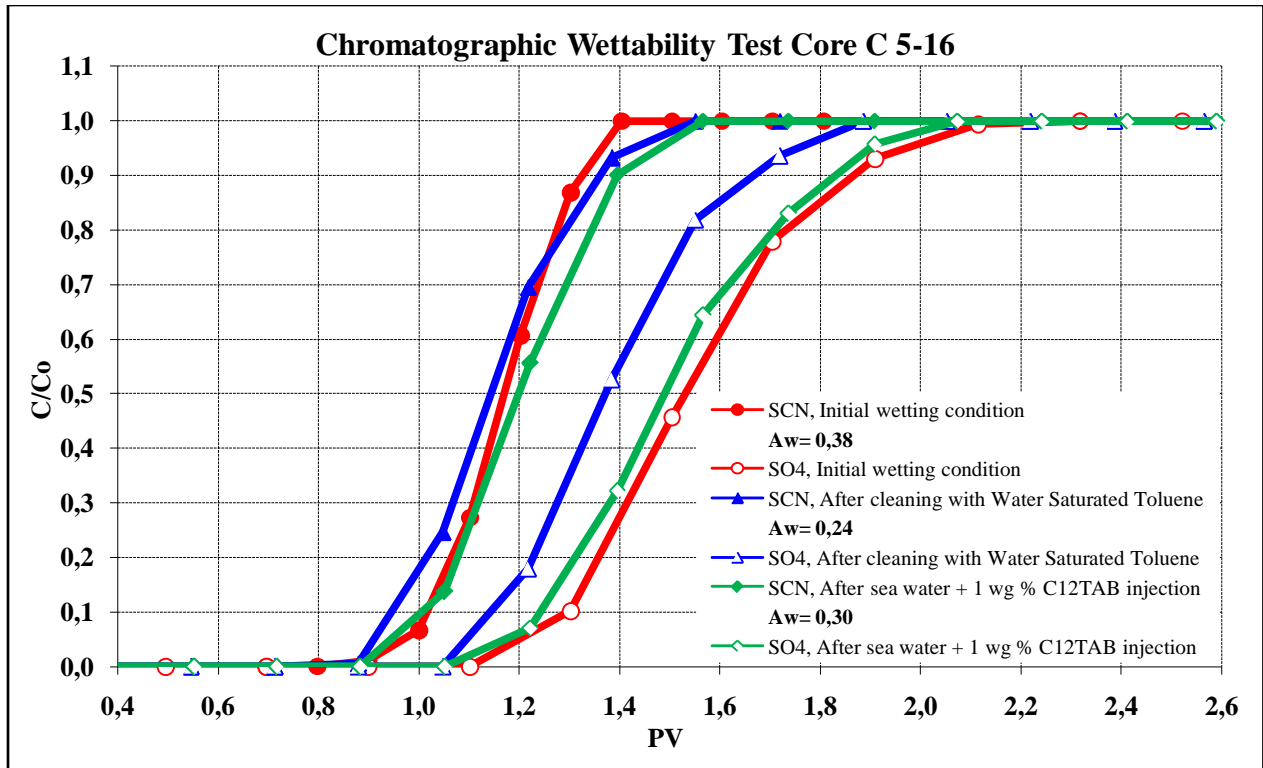
Figure 21. Wetting state of core C 5-16 before and after multiple cleaning procedures.

4.2 Oil Displacement

4.2.1 Spontaneous Imbibition Test with 100% Heptane Saturated Cores

Spontaneous imbibition of injected brine is the main driving mechanism in oil production from a fractured carbonate reservoir. Imbibition of water into the reservoir block is possible if the capillary pressure in the block is positive. Spontaneous imbibition tests were performed on cores C 4-14 and C 5-16 in order to observe capillary pressures after cleaning the cores with toluene and methanol. N-heptane was used as the non-wetting reference oil.

Core C 4-14

After cleaning the core with toluene and methanol in 2nd restoration, core was saturated 100% with n-heptane. Spontaneous imbibition (SI) test was performed at room temperature. Distilled water was used as imbibing liquid. 42% of originally oil in place (OOIP) was recovered within 2.6 days (Figure 22.).
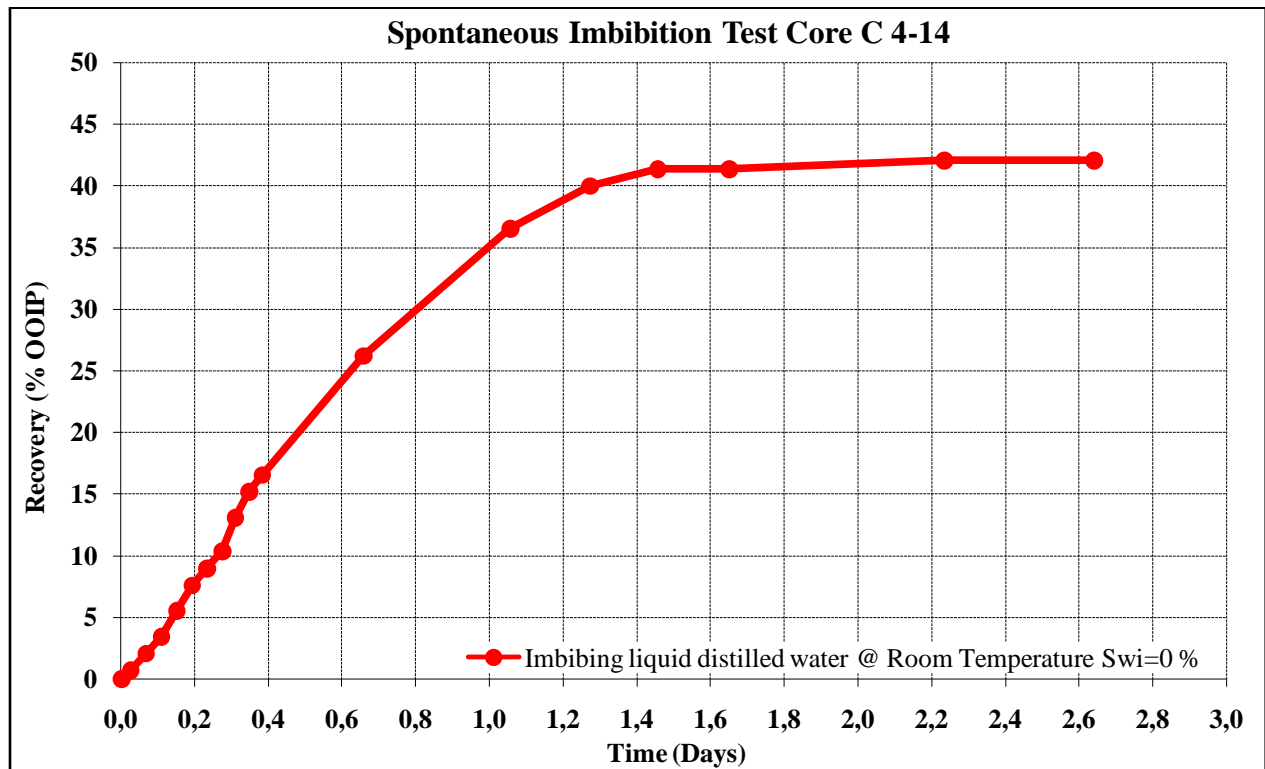
Figure 22. SI test on core C 4-14 at room temperature after cleaning the core with toluene and methanol without initial water saturation.

Core C 5-16

A spontaneous imbibition test was run after cleaning the core with PSW + 1 weight % C_{12}TAB in 2nd restoration at room temperature. Core was saturated 100% with n-heptane. Distilled water was used as imbibing liquid. Around 51% of OOIP was recovered in 0.8 days (Figure 23.).
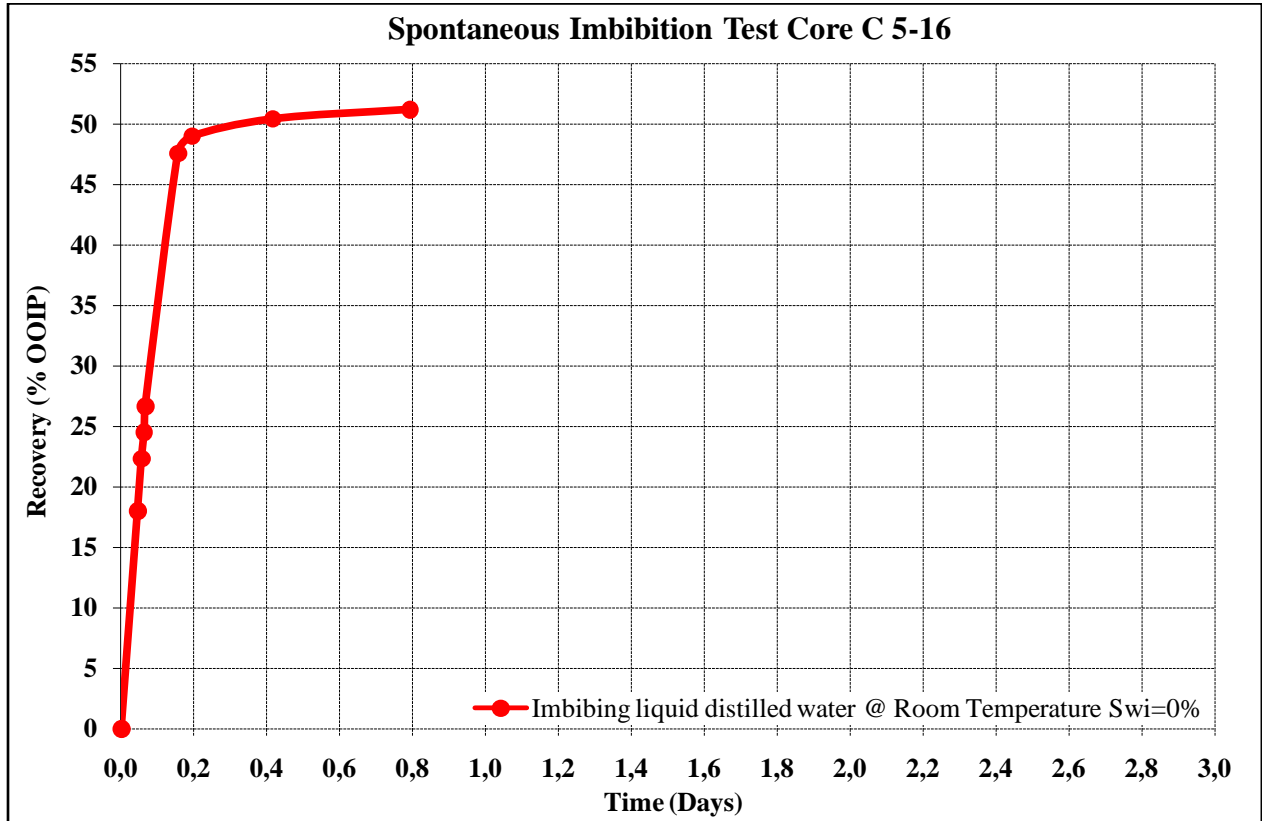
Figure 23. SI test on core C 5-16 at room temperature after cleaning the core with PSW + 1 weight % C_{12}TAB without initial water saturation.

Tests have shown that there were capillary pressures in both cores indicating that the cores were preferentially water-wet. However, recovery rates were quite different. This difference could be associated with different pore structures and/or different wetting states after cleaning with different solvents inside the cores.

4.2.2 Spontaneous Imbibition Tests

Spontaneous imbibition (SI) tests were performed at reservoir temperature, 110 ºC, using different imbibing brines. In all of the cores 10% initial water saturation was stablized before oil flooding. After that 4 PV of oil was flooded through the cores (2 PV from each direction). Cores have been aged in crude oil at 90 ºC for two weeks prior to SI tests.

Core C 1-3

One spontaneous imbibition test was run after 1st restoration. Core was cleaned with kerosene and n-heptane. Oil mixture-1 has been used in the test as reservoir oil. Formation fluid without sulfate (FW-ØS) has been used as imbibing liquid. Almost 45% of OOIP was recovered after 10 days (Figure 24.).
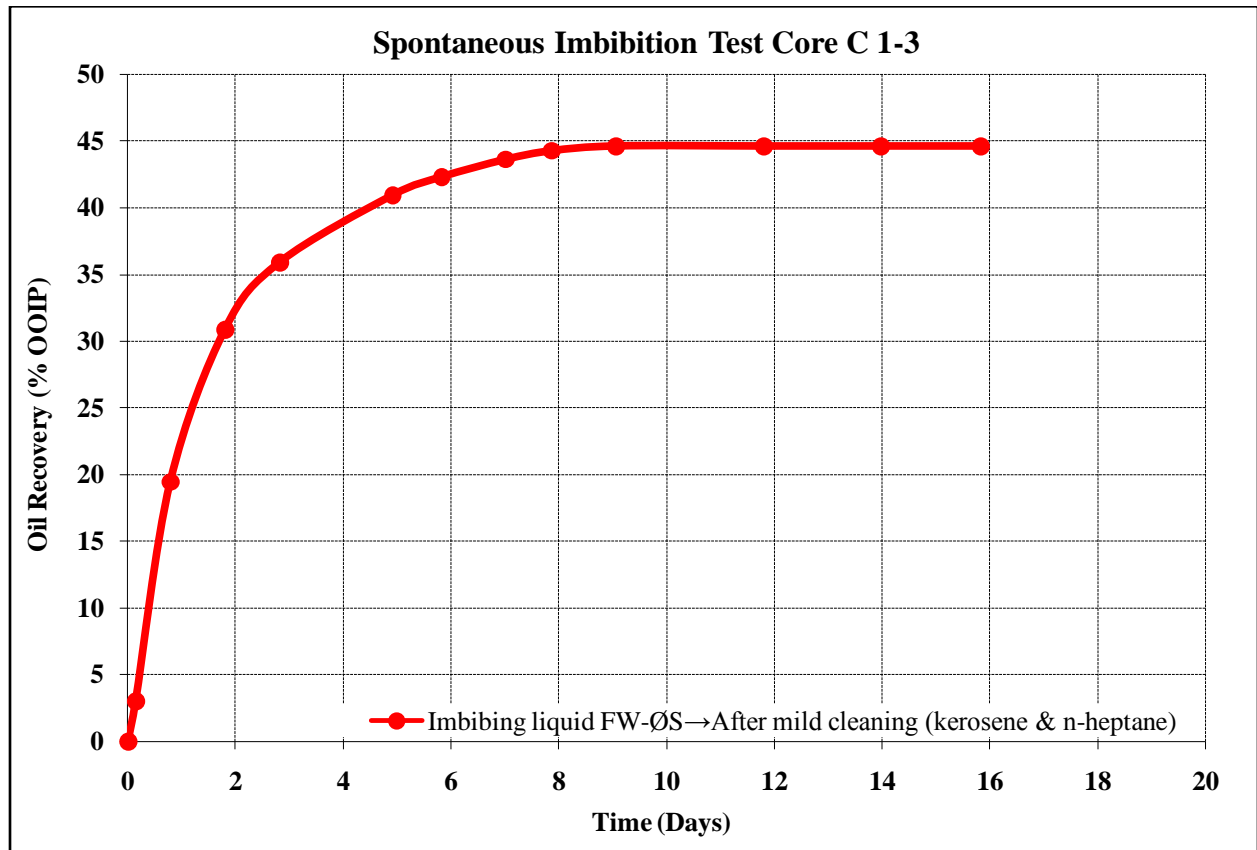
Figure 24. SI test on core C 1-3 at reservoir temperature after mild cleaning.

Core C 2-4

Two spontaneous imbibition tests were run on this core (Figure 25.). In both tests oil mixture-1 was used as reservoir oil.

In the 1st restoration, core was cleaned with kerosene and n-heptane. Oil recovery has reached the plateau after 38 days with a 33% recovery of OOIP. This recovery was consistent with the result of 1st wettability test on this core (Figure 19.) where A_w=0.38 indicating that the core was preferentially water-wet.

In the 2nd restoration, core was cleaned with toluene and methanol. Recovery was about 4% of OOIP in 7 days. Even though the result of 2nd wettability test on this core (Figure 19.) has shown that core was less water-wet than the initial condition, core acted as not water-wet during spontaneous imbibition test.

There was 29% difference in recovery between two tests even though the same imbibing liquid (FW-ØS) was used.
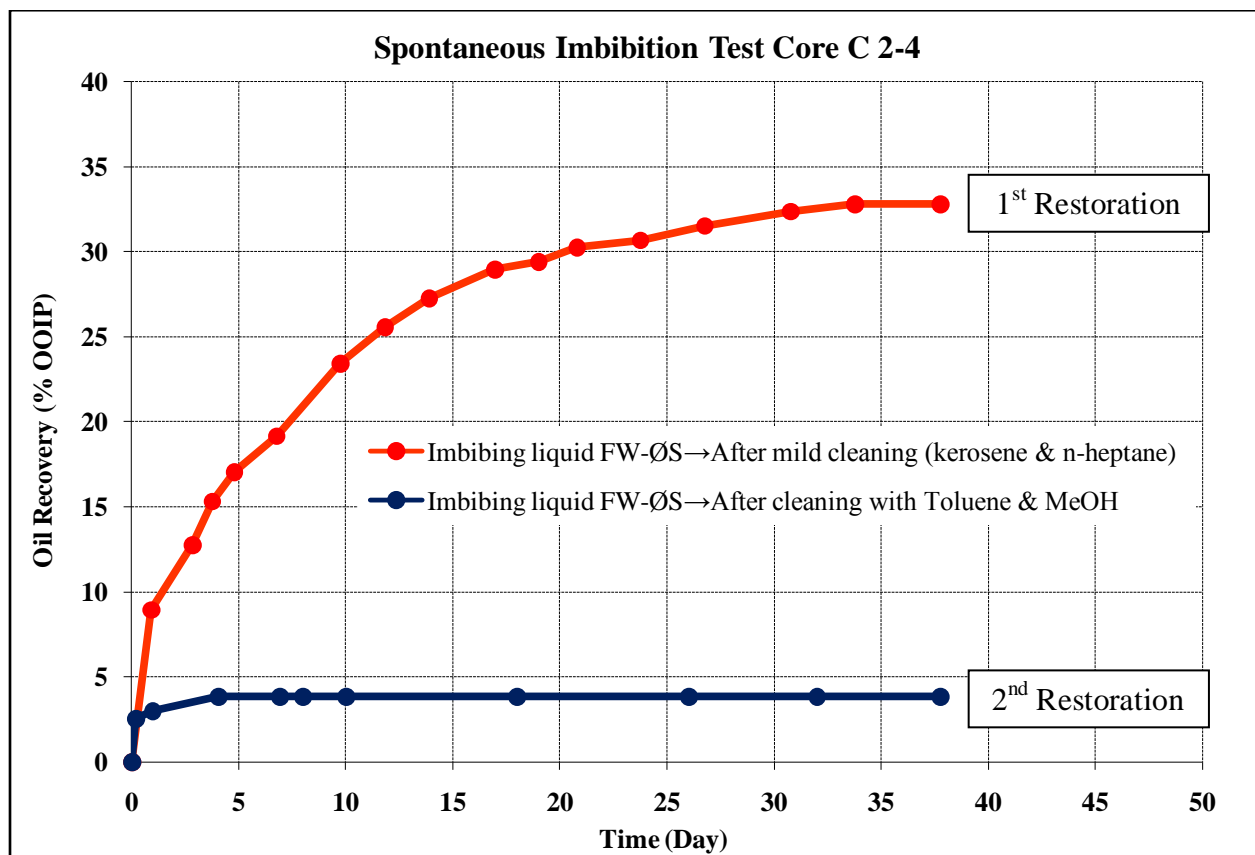
Figure 25. SI test on core C 2-4 at reservoir temperature after cleaning with different solvents.

Core C 4-14

Spontaneous imbibition test was conducted after mild cleaning (kerosene & n-heptane). Oil mixture-1 has been used in the test as reservoir oil. Formation fluid without sulfate (FW-ØS) has been used as imbibing liquid. Almost 41% of OOIP was recovered in 27 days (Figure 26.). This recovery was consistent with the result of 1st wettability test on this core (Figure 20.) where A_w=0.50 indicating that the core was preferentially water-wet.
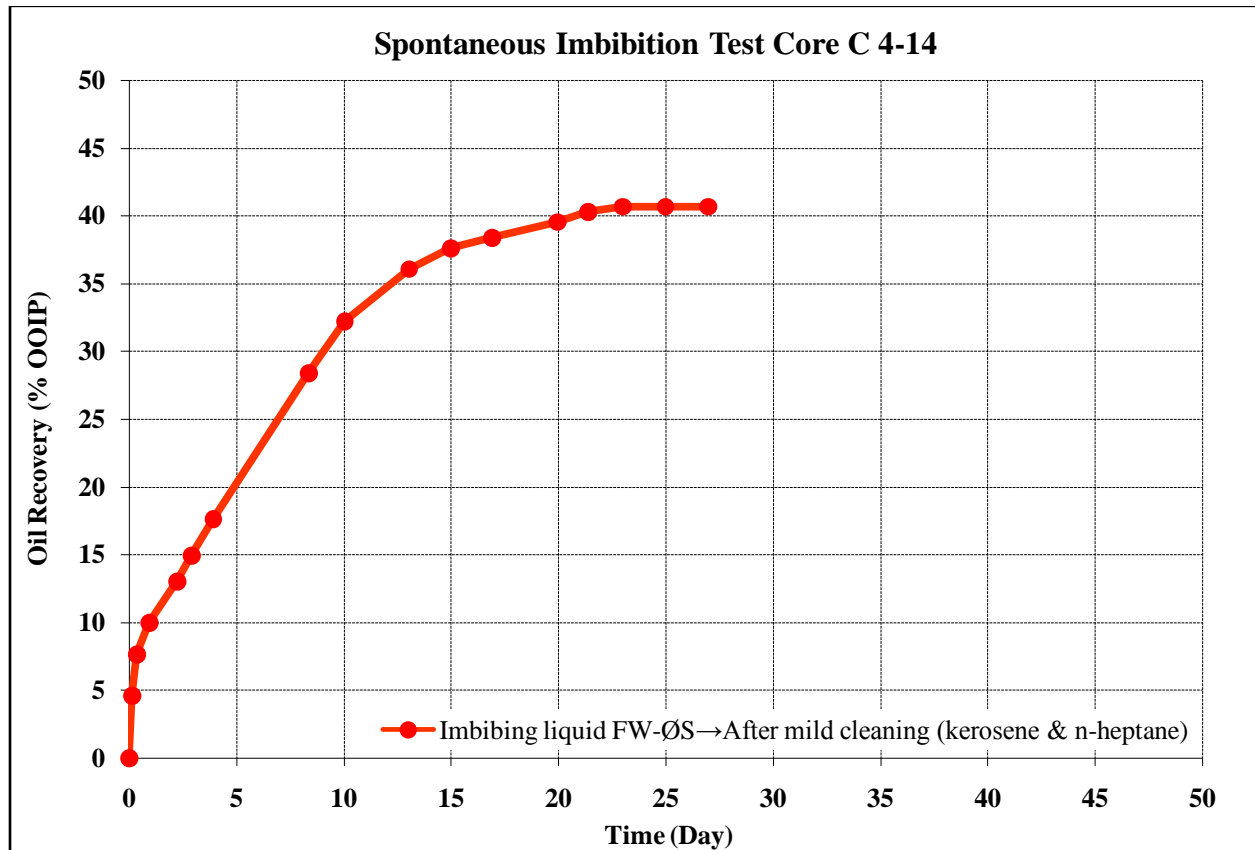
Figure 26. SI test on core C 4-14 at reservoir temperature after mild cleaning with kerosene & n-heptane.

Core C 5-16

Three spontaneous imbibition tests at reservoir temperature were performed on this core (Figure 27.). In all tests oil mixture-2 was used as reservoir oil.

In the 1st restoration, core was cleaned with kerosene and n-heptane. Initially, formation water without sulfate (FW-ØS) has been used as imbibing liquid. Oil recovery has reached the plateau in 8 days with a 42% recovery of OOIP.

In the 2nd restoration, core was cleaned with toluene and methanol. Again, formation water without sulfate (FW-ØS) has been used as imbibing liquid.

There is a significant difference (36%) between first and second spontaneous imbibition tests in terms of oil recovery even though the same imbibing liquid (FW-ØS) was used. This significant recovery difference shows that cleaning these limestone cores which have high surface reactivity with toluene and methanol changes wetting state (towards less water-wet) inside the cores.
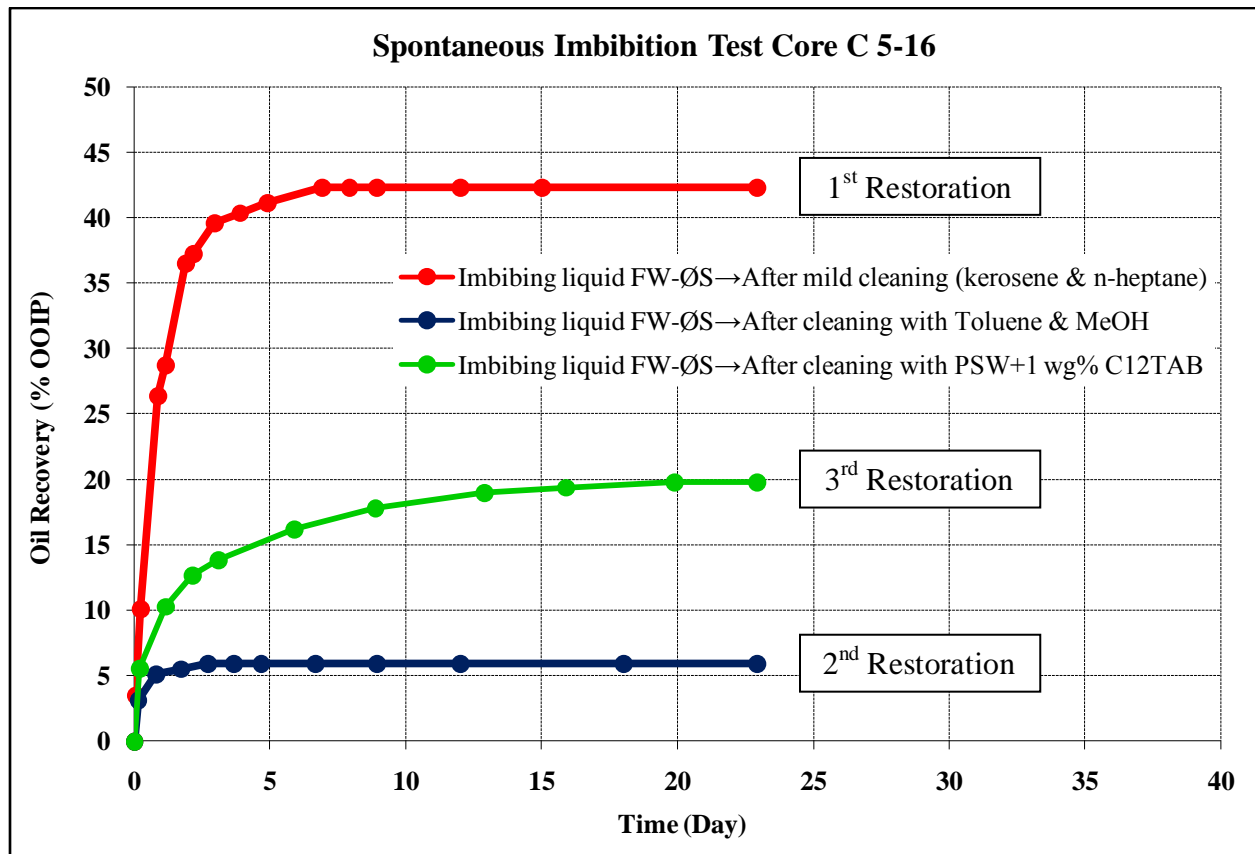
Figure 27. SI test on core C 5-16 at reservoir temperature after cleaning with different solvents.

In 3rd restoration, it has been decided to clean the core with PSW + 1 weight % C_{12}TAB at 130 ºC due to the wettability modifying potential of C_{12}TAB. As a result, oil recovery has reached the plateau in 23 days with 20% recovery of OOIP. FW-ØS was used as imbibing liquid.

Consequently, cleaning the core with sea water+1 weight % C_{12}TAB has modified the wetting state inside the core towards more water-wet. This result has been supported by chromatographic wettability test results of this core (See Figure 21.).

Core C 5-20

Two spontaneous imbibition tests were performed on this core (Figure 28.). Before 1ˢᵗ restoration, core was initially cleaned with kerosene & n-heptane and then toluene and methanol. Oil recovery has reached the plateau in 22 days with a 37% recovery of OOIP.
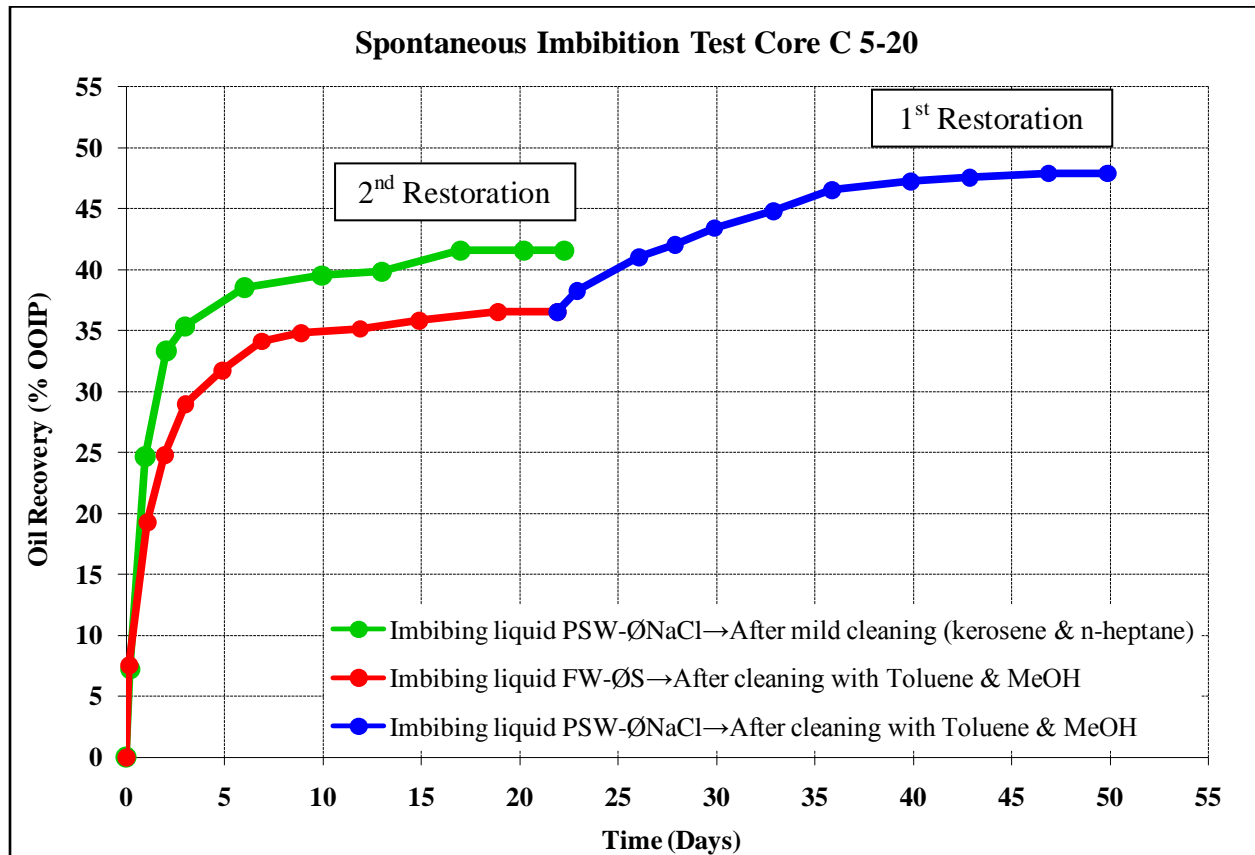
Figure 28. SI test on core C 5-20 at reservoir temperature after cleaning with different solvents.

This high recovery can be explained by usage of kerosene and n-heptane as the first cleaning solvents. Heptane injection had removed most of the oil inside the core therefore the amount of dissolved oil in toluene and methanol has decreased which means that the amount of acidic component, responsible from changing wettability towards oil-wet, in oil has reduced. Under the light of previous experiments, it can be concluded that if the core had been cleaned only with toluene and methanol, recovery would have been below 10% of OOIP. After FW-ØS, imbibing liquid has been switched to PSW-ØNaCl to observe the effect of smart water on wettability alteration and 11% additional recovery was obtained. Totally, 48% oil recovery was attained in 50 days.

In the 1st restoration, PSW-ØNaCl was used after FW-ØS. In the 2nd restoration, it has been decided to perform a spontaneous imbibition test by using only PSW-ØNaCl as imbibing liquid. The objective was to compare oil recoveries between 1st and 2nd restorations.

In the 2nd restoration, core was cleaned with only kerosene and heptane. Oil recovery has reached the plateau in 22 days with a 42% recovery of OOIP which was 6% less than 1st spontaneous imbibition test.

The wettability tests have shown symmetric tracer curves suggesting homogeneous cores with good pore connectivity. Sulfate curves after mild cleaning had stretched section (tail) at the end part of the effluent curve indicating that the small pores were water-wet. It has been observed that this stretched section decreased after exposing cores to successive toluene and methanol injection indicating that water-wet fraction in smaller pores decreased due to the adsorption of polar components during toluene and methanol injection.

During cleaning most of the oil inside the core was removed during toluene injection. However, some oil may have been trapped inside the pores partly due to surrounded water film.
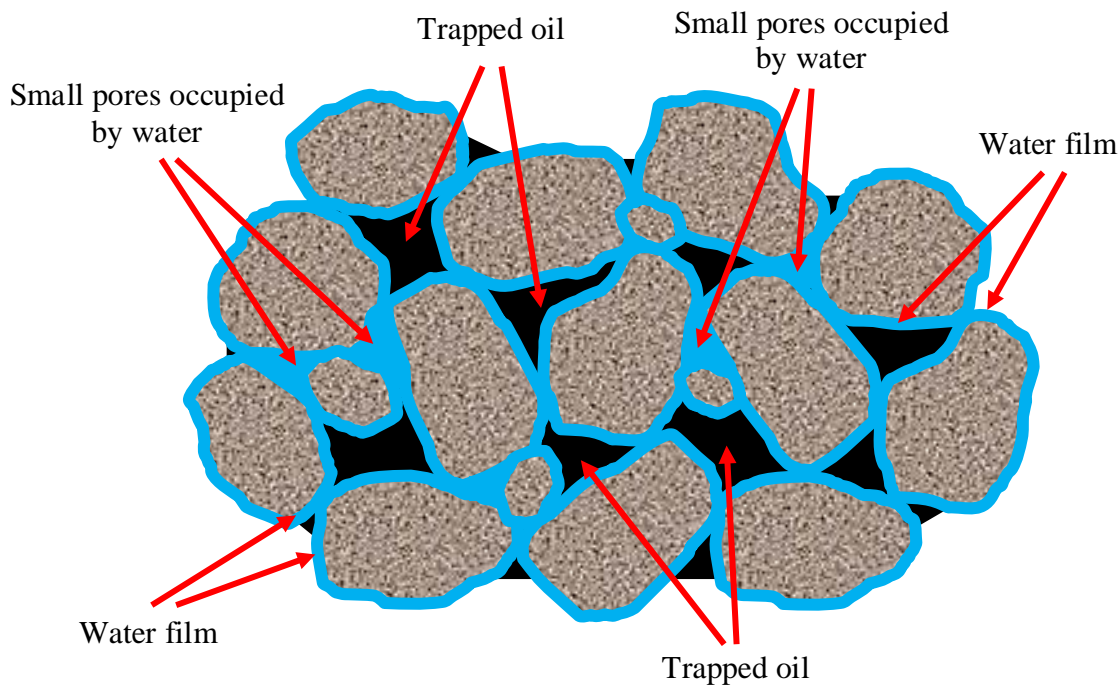
Figure 29. Schematic illustration of oil and water distribution in pores.

Because of the immiscibility with water and high capillary pressures, toluene may not have swept oil in these pores. On the other hand, methanol is miscible with both oil and water, so methanol injection removed some of the oil, water in small pores and water film on the surface of larger pores. By removal of water, rock surface became vulnerable to the polar components inside oil. Successive toluene and methanol injection kept dissolving the oil remains inside the core. Due to the high surface reactivity of the cores, polar components inside the dissolved oil may have adsorbed onto the surface of the smaller pores which were initially water-wet. Since smaller pores were responsible for the capillary forces inside the cores, re-distribution of wetness (towards less water-wet) inside these pores caused low oil recovery during spontaneous imbibition tests after cleaning the cores with toluene and methanol.

This wettability re-distribution might be less significant in viscous flooding (forced imbibition) in which imbibing liquid is forced to pass through all pores inside the core. Therefore, to prove this theory, two forced imbibition tests were conducted on the same core after cleaning the core with different solvents

4.2.3 Forced Imbibition Tests

Two forced imbibition (viscous flooding) tests were performed on core C 5-18 at reservoir temperature, 110 ℃, (Figure 30.). The properties of the core and crude oil were given in experimental materials and methods part.

In the 1st restoration, core was mildly cleaned with kerosene & n-heptane. During the test, formation water without sulfate (FW-ØS) was used as injected fluid. Totally, 48% of OOIP was recovered after injecting 2.57 PV. In the 2nd restoration, core was cleaned with toluene and methanol and then same procedures and parameters were applied on the core as in the first restoration. Throughout the second test same liquid (FW-ØS) was injected. Totally, 54% of OOIP was recovered after injecting 1.93 PV.

The 6% recovery difference between the tests could be due to different wetting condition inside the core after cleaning with toluene and methanol compared to the mild cleaning with kerosene & n-heptane. Morrow and Mason (2001) have stated that higher oil recovery can be achieved when the wetting state inside the core is mixed-wet compared to strongly water-wet system.[44] According to this theory wetting state inside the core may have become mixed-wet after cleaning the core with toluene and methanol. In strongly water-wet systems, less oil is recovered due to the snap-off mechanism inside the pores.
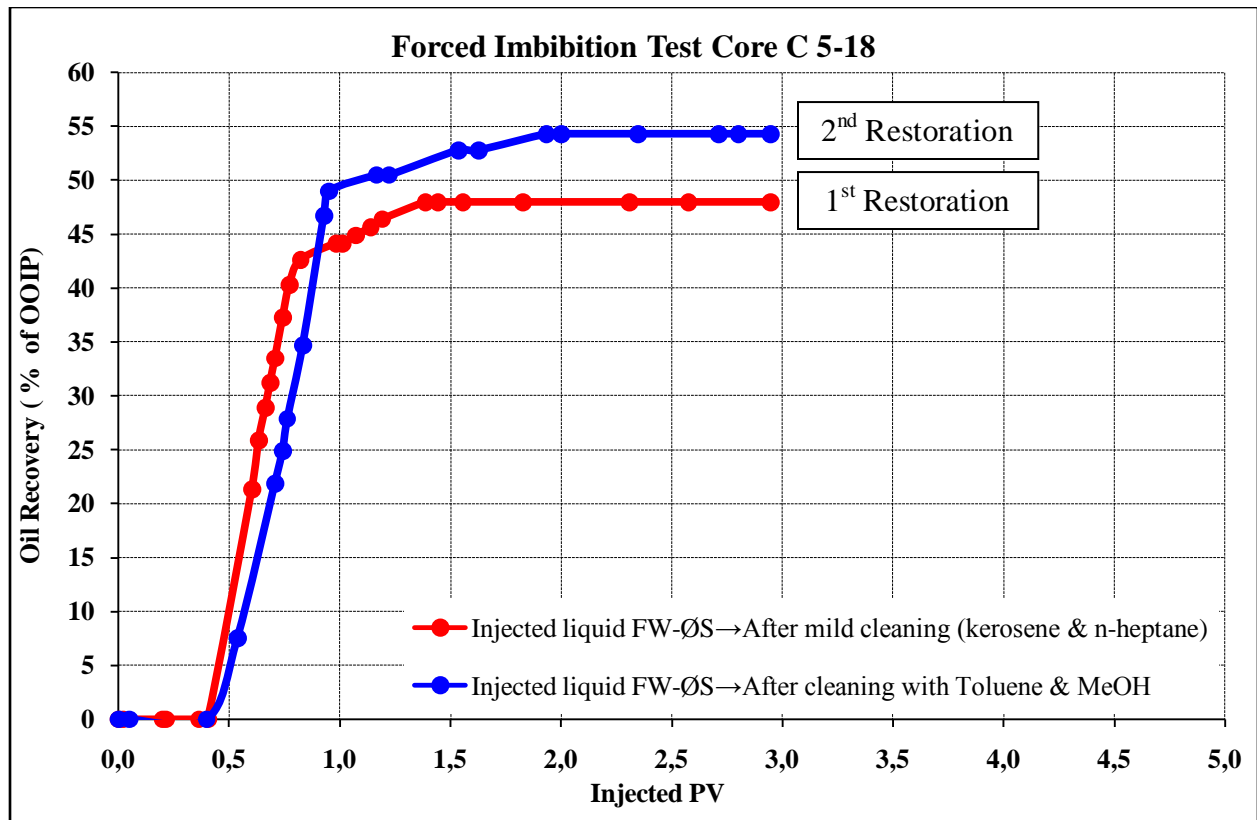
Figure 30. Forced imbibition test on core C 5-20 at reservoir temperature after cleaning with different solvents.

4.3 Effect of Imbibing Brine on Oil Recovery

During spontaneous imbibition tests of the cores C 2-4 and C 5-16 different imbibing liquids were utilized as a tertiary method in order to increase the oil recovery by modifying wetting state inside the cores.

4.3.1 Effect of Sea Water on Oil Recovery

During spontaneous imbibition tests on core C 5-16 after cleaning with different solvents, imbibing liquid was switched to PSW after oil recovery has reached the plateau with formation water without sulfate (FW-ØS) (Figure 31.). In the first spontaneous imbibition test, after 1st restoration, 5.83% additional recovery was obtained after switching imbibing liquid to PSW. In the second spontaneous imbibition test, after 2nd restoration, 26% additional recovery was obtained after switching imbibing liquid to PSW. In the third spontaneous imbibition test, after 3rd restoration, 7.92% additional recovery was obtained after switching imbibing liquid to PSW.

Oil recovery mechanism by sea water is associated with wettability determining ions (SO_4^{-2}, Ca^{+2} and Mg^{+2}) and theory behind this mechanism was described in previous sections of this thesis.

The lowest recovery (5.83%) by PSW was attained in first spontaneous imbibitions after 1st restoration. Since the core was mildly cleaned with kerosene and n-heptane in 1st restoration, the amount of oil adsorbed onto the rock surface was low meaning that there was not much oil on the surface of the rock for SO_4^{-2} and Ca^{+2} to remove. Therefore, it was plausible to attain the lowest recovery after introducing PSW as imbibing liquid.

The highest recovery (26%) by PSW was attained in second spontaneous imbibitions after 2nd restoration. Since the core was cleaned with toluene and methanol in 2nd restoration, the amount of oil adsorbed onto the rock surface was much higher compared to the 1st restoration meaning that there was more oil on the surface of the rock for SO_4^{-2} and Ca^{+2} to remove. Hence, it was reasonable to attain the highest recovery after introducing PSW as imbibing liquid.
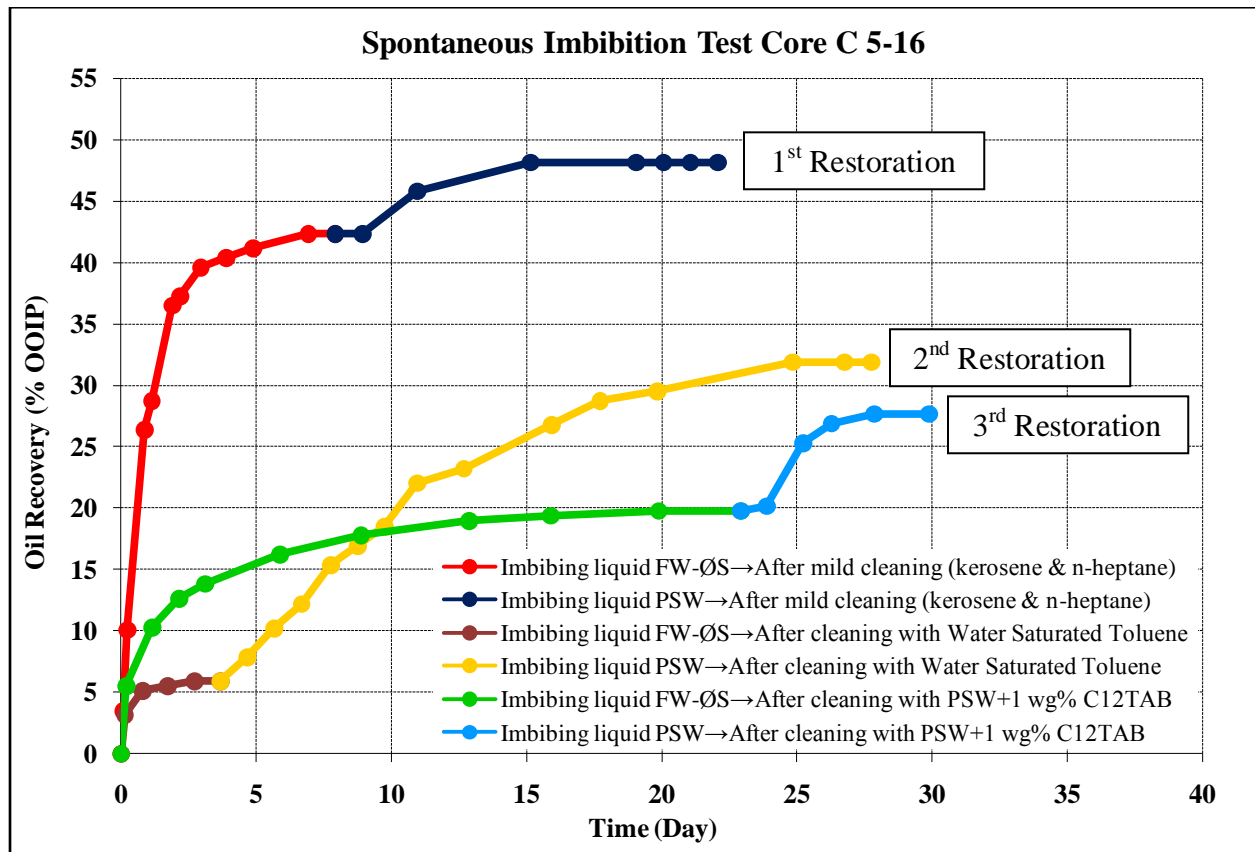
Figure 31. SI test on core C 5-16 at reservoir temperature after cleaning with different solvents.

In the 3rd restoration core was cleaned with PSW + 1 weight% C$_{12}$TAB. The result of spontaneous imbibition tests with FW-ØS has shown that water-wet fraction inside the core was between the first and second restorations. Therefore, it was expected to get an oil recovery value between the first and second tests after switching imbibing liquid to PSW. As a result, 7.92% additional oil recovery was obtained by PSW which fulfilled the expectation.

4.3.2 Effect of Surfactant (C$_{12}$TAB) on Oil Recovery

C$_{12}$TAB has two positive effects on oil recovery. The first effect is the ability of connection with negatively charged oil components on rock surface because of its positively charged structure. The second one is the ability of reducing inter-facial tension between oil and water.

In the third spontaneous imbibition test on core C 5-16, after PSW, imbibing liquid was switched to PSW + 1 weight% C$_{12}$TAB (Figure 32.). 18.6% additional oil recovery was obtained after introducing PSW + 1 weight% C$_{12}$TAB as imbibing liquid. This additional recovery has confirmed the wettability modification (towards more water-wet) ability of C$_{12}$TAB.
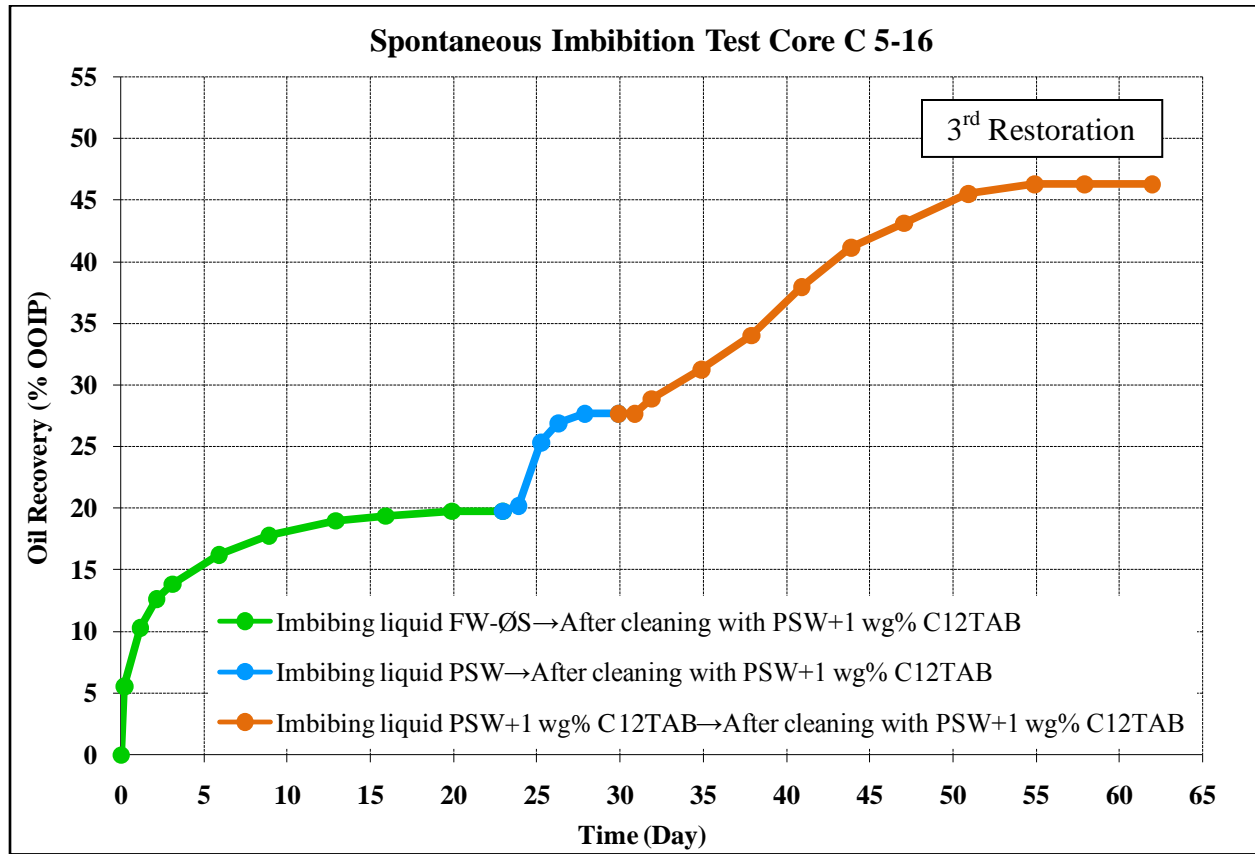
Figure 32. SI test on core C 5-16 at reservoir temperature after cleaning with PSW + 1 weight% C$_{12}$TAB.

4.3.3 Effect of Modified Sea Water (PSW-ØNaCl)

In order to observe the effect of modified sea water on oil recovery, during second spontaneous imbibition test on core C 2-4 imbibing liquid was switched to PSW-ØNaCl after FW-ØS (Figure 33.). 34.08% additional oil recovery was obtained after introducing PSW-ØNaCl as imbibing liquid.
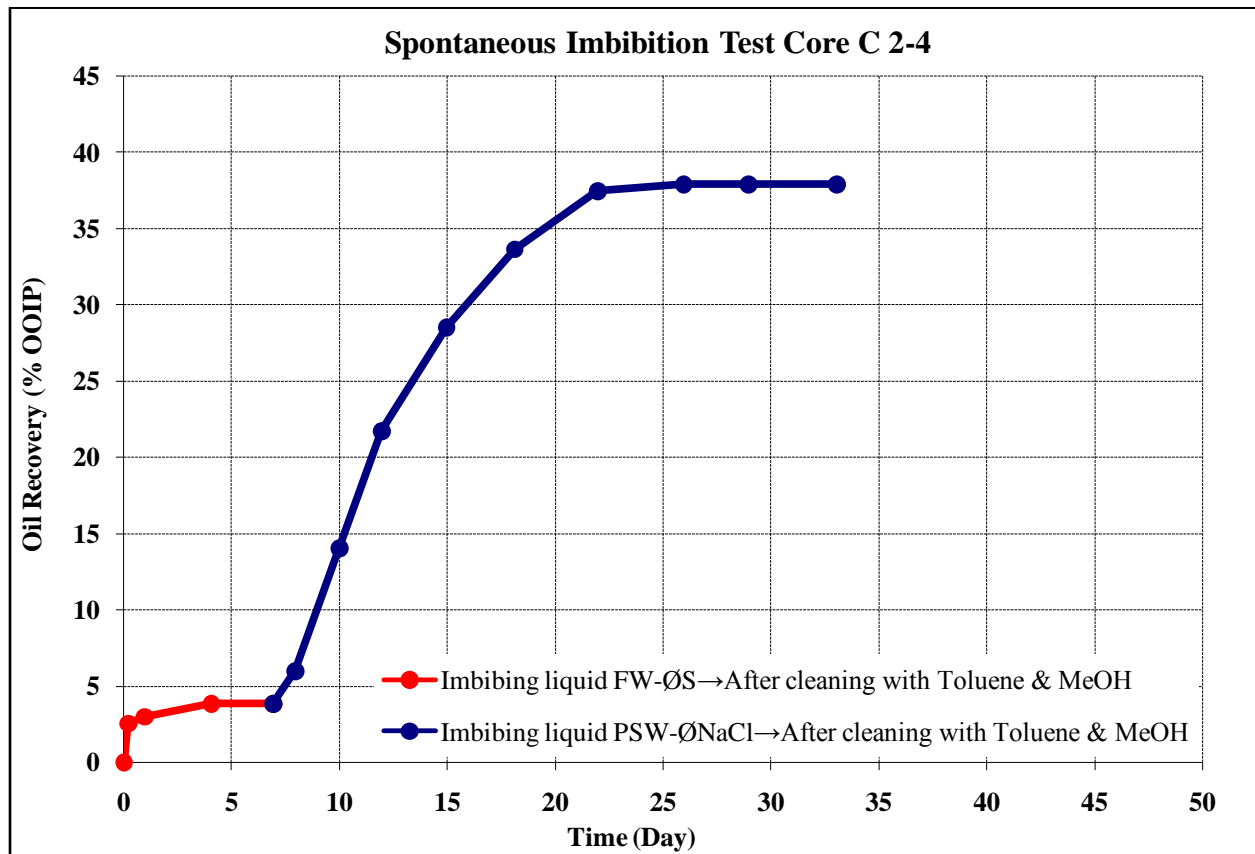
Figure 33. SI test on core C 2-4 at reservoir temperature after cleaning with toluene and methanol.

Fathi et al. (2009) has shown that it is possible to obtain higher oil recovery by using sea water without sodium chloride (PSW-ØNaCl) instead of sea water (PSW) based on the spontaneous imbibition experiments with chalk cores.[30]

Two cores were compared to observe the recovery difference between PSW and PSW-ØNaCl (Figure 34.). Even though the cores were different, their oil recovery behavior after cleaning with toluene and methanol was same meaning that they had the same wetting state. Thus, it was convenient to compare the oil recoveries after switching imbibing liquids to PSW

and PSW-ØNaCl. In core C 5-16, imbibing liquid was switched to PSW after FW-ØS. 26% additional oil recovery was attained by using PSW. In core C 2-4, imbibing liquid was switched to PSW-ØNaCl after FW-ØS. As a result, 34.08% additional oil recovery was obtained. Consequently, more oil was recovered (8.08%) just by using PSW-ØNaCl as imbibing liquid which was consistent with the study of Fathi et al.
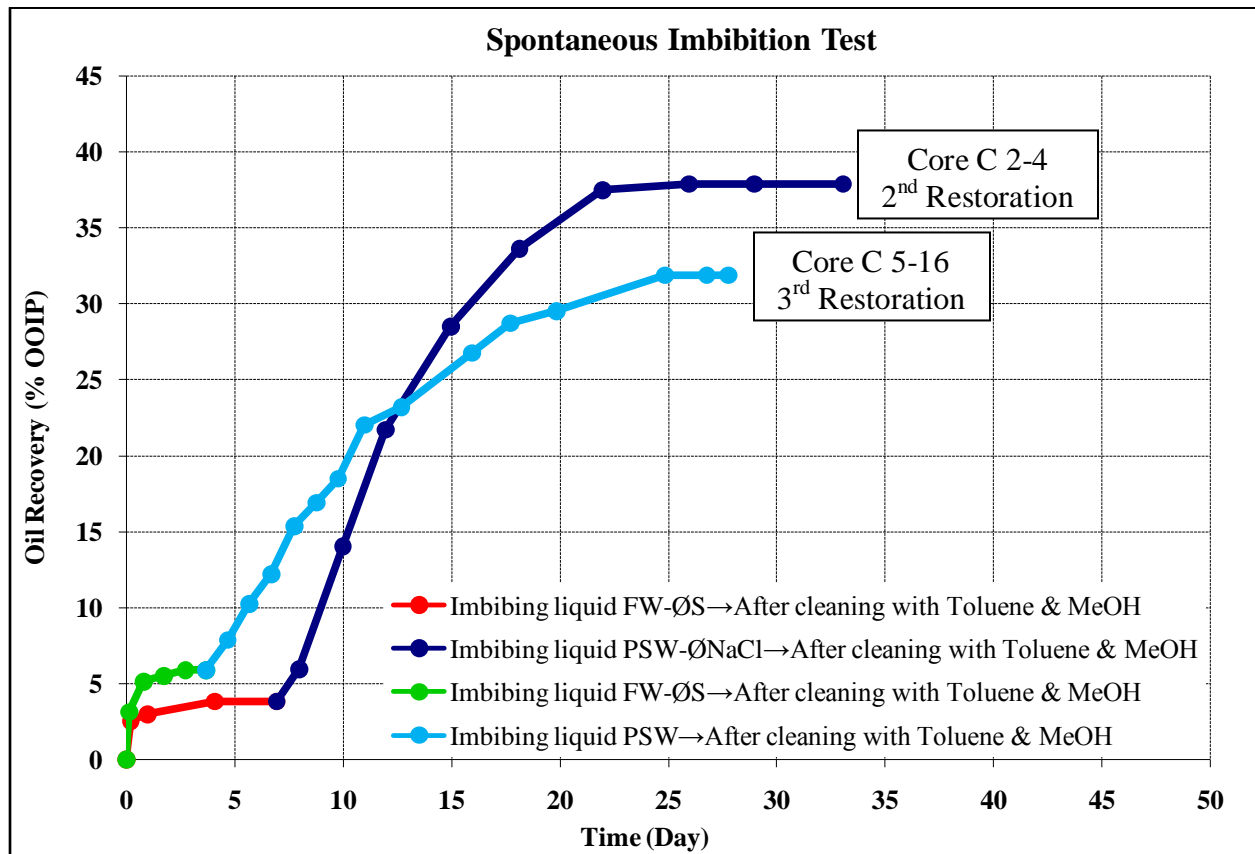
Figure 34. SI tests on core C 2-4 and C 5-16 at reservoir temperature after cleaning with toluene and methanol.

5) CONCLUSION

The surface reactivity of carbonate reservoirs has crucial effect on wetting state of the cores. It is important to perform experiments on cores whose wetting states are close to the wetting state of the reservoir. Therefore, extra attention should be paid on the core preparation procedures of cores that have high surface reactivity. In this project, samples from a fractured, low permeable limestone reservoir with high surface reactivity were used. The results of the experimental study can be summarized as below:

➢ The wetting states of the mildly cleaned cores with (kerosene & n-heptane) were preferentially water-wet. This was verified by both chromatographic and spontaneous imbibition tests.

➢ After cleaning the cores with toluene and methanol, chromatographic wettability tests have shown that cores were preferentially water-wet. However, negligible imbibition of formation brine (FW-ØS) was observed.

➢ Approximately 40% of OOIP was recovered from mildly cleaned cores. On the other hand, recovery was below 10% from the cores which were cleaned with toluene and methanol. This difference in recovery was explained by the wettability alteration inside the cores as a result of water removal in smaller pores and re-distribution of surface active crude oil components by successive injection of toluene and methanol.

➢ Forced imbibition tests have shown that cleaning the cores with different solvents does not have dramatic effect on oil recovery. 48% (after mild cleaning) and 56% (after cleaning with toluene and methanol) of OOIP were recovered from the same core.

➢ In limestones with high surface reactivity, oil recovery can be increased by using sea water (PSW) due to wettability alteration.

➢ The potentioal of $C_{12}TAB$ (cationic surfactant)as a wettability modifier (towards more water-wet) has also been proved by performing chromatographic wettability and spontaneous imbibition tests.

➢ Improvement in oil recovery can be obtained by using sea water without sodium chloride (PSW-ØNaCl) instead of sea water (PSW) in limestone cores.

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REFERENCES

[1]   http://en.wikipedia.org/wiki/Ghawar_Field.

[2]   http://www.kabrna.com/cpgs/rocks/sedimentary/chalk.htm.

[3]   http://en.wikipedia.org/wiki/Soxhlet_extractor#cite_ref-1.

[4]   http://en.wikipedia.org/wiki/South_Pars/North_Dome#cite_ref-0.

[5]   http://www.galleries.com/minerals/carbonat/dolomite/dolomite.htm.

[6]   http://www.temcoinstruments.com/products_detail.asp?ProductID=34.

[7]   http://en.wikipedia.org/wiki/George_Clemenceau.

[8]   http://www.netl.doe.gov/technologies/oil-gas/publications/eordrawings/BW/bwp.PDF.

[9]   http://www.netl.doe.gov/technologies/oil-gas/publications/eordrawings/BW/bwmf.pdf.

[10]   Amott, E., "*Observations Relating to the Wettability of Porous Rock"*, 1959.

[11]   Anderson, W., "*Wettability Literature Survey- Part 2: Wettability Measurement*", SPE Journal of Petroleum Technology, Vol. 38 **11** (1986), 1246-1262.

[12]   Anderson, W. G., "*Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability*", SPE Journal of Petroleum Technology, Vol. 38 **10** (1986), 1125-1144.

[13]   Austad, T., Strand, S., Høgnesen, E. J. and Zhang, P., "*Seawater as IOR Fluid in Fractured Chalk"*, SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, 2005.

[14]   Austad, T., Strand, S., Puntervold, T. and Ravari, R. R., "*New Method to Clean Carbonate Reservoir Cores by Sea Water"*, Society of Core Analysts, Abu Dhabi, UAE, 2008.

[15]   Basu, S. and Sharma, M. M., "*Investigating the Role of Crude-Oil Components on Wettability Alteration Using Atomic Force Microscopy*", SPE Journal, Vol. 4 **3** (1999), 235-241.

[16]   Bobek, J. E., Mattax, C. C. and Denekas, M. O., "*Reservoir Rock Wettability - Its Significance and Evaluation"*, 1958.

[17]   http://www.oilcrisis.com/Campbell/.

[18]   Borchardt, J. K. and Yen, T. F., "*Oil Field Chemistry : Enhanced Recovery and Production Stimulation / John K. Borchardt, Editor, Teh Fu Yen, Editor"*, American Chemical Society, Washington, DC, 1989.

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i Stavanger

[19] Chilingar, G. V. and Yen, T. F., "*Some Notes on Wettability and Relative Permeabilities of Carbonate Reservoir Rocks*", Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, Vol. 7 **1** (1993), 67 - 75.

[20] Chukwudeme, E. A., "*Impact of Acid-Base Numbers on Wettability Alteration in Carbonate Reservoir"*, E.A. Chukwudeme, 2006.

[21] Craig, F. F., "*The Reservoir Engineering Aspects of Waterflooding"* Vol. vol. 3, SPE., New York, 1971.

[22] Cuiec, L. E., "*Restoration of the Natural State of Core Samples"*, Fall Meeting of the Society of Petroleum Engineers of AIME, Dallas, Texas, 1975.

[23] Cuiec, L. E., "*Rock/Crude-Oil Interactions and Wettability: An Attempt to Understand Their Interrelation"*, SPE Annual Technical Conference and Exhibition, Houston, Texas, 1984.

[24] Cuiec, L. E., "*Study of Problems Related to the Restoration of the Natural State of Core Samples*", Vol. 16 **4** (1977).

[25] http://www.npd.no/engelsk/cwi/pbl/en/index.htm. Then→ Fields → All fields → Ekofisk.

[26] http://search.datapages.com/data/specpubs/fieldst3/data/a018/a018/0001/0000/0001.htm.

[27] Donaldson, E. C. and Alam, W., "*Wettability"*, Gulf Publ. Co., Houston, Tex., 2008.

[28] Donaldson, E. C., Thomas, R. D. and Lorenz, P. B., "*Wettability Determination and Its Effect on Recovery Efficiency*", Vol. 9 **1** (1969), 13 - 20.

[29] http://www2.ggl.ulaval.ca/personnel/paglover/CD%20Contents/Formation%20Evaluation%20English/Chapter%207.PDF

[30] Fathi, S. J., Austad, T. and Strand, S., ""*Smart Water" As a Wettability Modifier in Chalk: The Effect of Salinity and Ionic Composition*", Energy & Fuels, Vol. 24 **4**, 2514-2519.

[31] http://www.interfacehs.sp.senac.br/en/articles.asp?ed=1&cod_artigo=20&pag=1.

[32] http://geo.rhul.ac.uk/cabinet01/drawer08.htm.

[33] Flügel, E., "*Microfacies of Carbonate Rocks: Analysis, Interpretation and Application"*, Springer, Berlin, 2004.

[34] Gant, P. L. and Anderson, W. G., "*Core Cleaning for Restoration of Native Wettability*", SPE Formation Evaluation, Vol. 3 **1** (1988), 131-138.

[35] http://www.i-pi.com/~diana/slime/corrosion/dolomite/.

[36] Green, D. W. and Willhite, G. P., "*Enhanced Oil Recovery"* Vol. vol. 6, Society of Petroleum Engineers., Richardson, TX, 1998.

[37] Grist, D. M., Langley, G. O. and Neustadter, F. L., "*The Dependence of Water Permeability on Core Cleaning Methods in the Case of Some Sandstone Samples*", Vol. 14 **2** (1975).

[38] Itoh, S., "*China's Surging Energy Demand: Trigger for Conflict or Cooperation with Japan?*", East Asia, Vol. 25 **1** (2008), 79-98.

[39] Korsnes, R., Strand, S., Hoff, Ø., Pedersen, T., Madland, M. and Austad, T., "*Does the Chemical Interaction between Seawater and Chalk Affect the Mechanical Properties of Chalk?*", Eurock 2006: Multiphysics Coupling and Long Term Behaviour in Rock Mechanics, 2006, pp. 427-434.

[40] Lake, L. W., "*Enhanced Oil Recovery"*, Prentice Hall, Englewood Cliffs, N.J., 1989.

[41] Leverett, M. C., "*Capillary Behavior in Porous Solids*", (1941).

[42] Morgenthau, H., "*Politics among Nations : The Struggle for Power and Peace"*, Mcgraw-Hill, New York, 1985.

[43] Morrow, N. R., "*Physics and Thermodynamics of Capillary Action in Porous Media*", Industrial & Engineering Chemistry, Vol. 62 **6** (1970), 32-56.

[44] Morrow, N. R. and Mason, G., "*Recovery of Oil by Spontaneous Imbibition*", Current Opinion in Colloid & Interface Science, Vol. 6 **4** (2001), 321-337.

[45] Mungan, N., "*Certain Wettability Effects in Laboratory Waterfloods*", SPE Journal of Petroleum Technology, Vol. 18 **2** (1966), 247-252.

[46] Pierre, A., Lamarche, J. M., Mercier, R., Foissy, A. and Persello, J., "*Calcium as Potential Determining Ion in Aqueous Calcite Suspensions*", Journal of Dispersion Science and Technology, Vol. 11 **6** (1990), 611 - 635.

[47] Raza, S. H., Treiber, L. E. and Archer, D. L., "*Wettability of Reservoir Rocks and Its Evaluation*", Journal Name: Prod. Mon.; (United States); Journal Volume: 32:4   (1968), Medium: X; Size: Pages: 2-4, 6-7.

[48] Richardson, J. G., Jr., F. M. P. and Osoba, J. S., "*Differences in Behavior of Fresh and Aged East Texas Woodbine Cores*", (1955).

[49] Salathiel, R. A., "*Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks*", SPE Journal of Petroleum Technology, Vol. 25 **10** (1973), 1216-1224.

Universitetet
i Stavanger

[50] Shute, J. and Alldredge, G., "*Conoco Cuts North Sea Drilling Time by 40%*", Journal Name: World Oil; (United States); Journal Volume: 195:1 (1982), Medium: X; Size: Pages: 78-87.

[51] Skopec and A., R., "*Proper Coring and Wellsite Core Handling Procedures: The First Step toward Reliable Core Analysis*" Vol. 46, Society of Petroleum Technology, Richardson, TX, 1994.

[52] Springer, N., Korsbech, U. and Aage, H. K., "*Resistivity Index Measurement without the Porous Plate: A Desaturation Technique Based on Evaporation Produces Uniform Water Saturation Profiles and More Reliable Results for Tight North Sea Chalk*", International Symposium of the Society of Core Analysts, Pau, France, 2003.

[53] Standnes, D. C. and Austad, T., "*Wettability Alteration in Chalk: 2. Mechanism for Wettability Alteration from Oil-Wet to Water-Wet Using Surfactants*", Journal of Petroleum Science and Engineering, Vol. 28 **3** (2000), 123-143.

[54] Strand, S., "*Wettability Alteration in Chalk: A Study of Surface Chemistry*", UiS, 2005.

[55] Strand, S., Austad, T., Puntervold, T., HÃ¸gnesen, E. J., Olsen, M. and Barstad, S. M. F., "*"Smart Water" For Oil Recovery from Fractured Limestone: A Preliminary Study*", Energy & Fuels, Vol. 22 **5** (2008), 3126-3133.

[56] Strand, S., Høgnesen, E. J. and Austad, T., "*Wettability Alteration of Carbonates--Effects of Potential Determining Ions (Ca^{2+} and SO_4^{2-}) and Temperature*", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 275 **1-3** (2006), 1-10.

[57] Strand, S., Standnes, D. C. and Austad, T., "*New Wettability Test for Chalk Based on Chromatographic Separation of Scn^- and So_4^{2-}*", Journal of Petroleum Science and Engineering, Vol. 52 **1-4** (2006), 187-197.

[58] Taber, J. J., Martin, F. D. and Seright, R. S., "*Eor Screening Criteria Revisited - Part 1: Introduction to Screening Criteria and Enhanced Recovery Field Projects*", SPE Reservoir Engineering, Vol. 12 (1997).

[59] Thomas, M., M., Clouse, A., J., Longo and M., J., "*Adsorption of Organic Compounds and Carbonate Minerals. Iii: Influence on Dissolution Rates*" Vol. 109, Elsevier, Amsterdam, 1993.

[60] Thomas, D. C., Hsing, H. and Menzie, D. E., "*Evaluation of Core Damage Caused by Oil-Based Drilling and Coring Fluids*", SPE Annual Technical Conference and Exhibition, Houston, Texas, 1984.

[61] Thomas, M. M., Clouse, J. A. and Longo, J. M., "*Adsorption of Organic Compounds on Carbonate Minerals: 1. Model Compounds and Their Influence on Mineral Wettability*", Chemical Geology, Vol. 109 **1-4** (1993), 201-213.

[62] Trantham, J. C. and Clampitt, R. L., "*Determination of Oil Saturation after Waterflooding in an Oil-Wet Reservoir the North Burbank Unit, Tract 97 Project*", SPE Journal of Petroleum Technology, Vol. 29 **5** (1977), 491-500.

[63] Treiber, L. E. and Owens, W. W., "*A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs*", Vol. 12 **6** (1972), 531-540.

[64] Tucker, M. E., "*Sedimentary Petrology: An Introduction to the Origin of Sedimentary Rocks*", Blackwell Science, Oxford, 2001.

[65] Tweheyo, M. T., Zhang, P. and Austad, T., "*The Effects of Temperature and Potential Determining Ions Present in Seawater on Oil Recovery from Fractured Carbonates*", SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, 2006.

[66] Webb, K. J., Black, C. J. J. and Tjetland, G., "*A Laboratory Study Investigating Methods for Improving Oil Recovery in Carbonates*", International Petroleum Technology Conference, Doha, Qatar, 2005.

[67] Zhang, P. and Austad, T., "*The Relative Effects of Acid Number and Temperature on Chalk Wettability*", SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, 2005.

[68] Zhang, P., Tweheyo, M. T. and Austad, T., "*Wettability Alteration and Improved Oil Recovery by Spontaneous Imbibition of Seawater into Chalk: Impact of the Potential Determining Ions Ca^{2+}, Mg^{2+}, and SO_4^{2-}*", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 301 **1-3** (2007), 199-208.

APPENDIX

A. Procedures performed on core C 1-3

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C.

➢ Saturation with distilled water and permeability measurement.

➢ Drying at 90 ˚C. Dry weight was 208.92 gr.

➢ Wettability test + distilled water injection

➢ Drying at 90 ˚C. Dry weight was 208.57 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 225.39 gr.

➢ Pore volume was 16.57 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging at 90 ˚C for 2 weeks.

➢ Weight of core after aging was 222.93 gr.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Total recovery was 44.67% of OOIP.

Table-5 Core C 1-3 spontaneous imbibition test data after first restoration.

Originally Oil in Place (ml)		14,888		
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Recovery (%)
17:20	21.12.2009	0,00	0,00	0,00
21:00	21.12.2009	0,15	0,45	3,02
12:15	22.12.2009	0,79	2,90	19,48
12:30	23.12.2009	1,80	4,60	30,90
13:00	24.12.2009	2,82	5,35	35,93
15:15	26.12.2009	4,91	6,10	40,97
13:00	27.12.2009	5,82	6,30	42,32
17:30	28.12.2009	7,01	6,50	43,66
14:00	29.12.2009	7,86	6,60	44,33
18:30	30.12.2009	9,05	6,65	44,67
12:30	02.01.2010	11,80	6,65	44,67
16:45	04.01.2010	13,98	6,65	44,67
13:00	06.01.2010	15,82	6,65	44,67

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Second Restoration

- Cleaning with dry toluene and methanol.
- Distilled water injection to get rid of SO_4^{-2}.
- Drying at 90 ˚C. Dry weight was 208.45 gr.
- Wettability test was performed.

B. Procedures performed on core C 2-4

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C. Dry weight was 214.24 gr.

➢ Saturation with FW-ØT. Saturated weight was 227.54 gr.

➢ Wettability test + washing out with distilled water + permeability measurement.

➢ Drying at 90 ˚C. Dry weight was 214.16 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 227.38 gr.

➢ Pore volume was 13.041 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90˚C.

➢ Weight of core after aging was 225.48 gr.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Total recovery with FW-ØS was 32.80% of OOIP.

Table-6 Core C 2-4 spontaneous imbibition test data after first restoration.

Originally Oil in Place (ml)		11,737		
Time (Hour)	**Date**	**Time (Day)**	**Oil Production (ml) Imbibing liquid FW-ØS**	**Oil Recovery (%)**
15:00	15.01.2010	0,00	0	0
12:43	16.01.2010	0,90	1,05	8,95
10:50	18.01.2010	2,83	1,5	12,78
09:15	19.01.2010	3,76	1,8	15,34
09:57	20.01.2010	4,79	2	17,04
09:15	22.01.2010	6,76	2,25	19,17
09:00	25.01.2010	9,75	2,75	23,43
10:36	27.01.2010	11,82	3	25,56
12:22	29.01.2010	13,89	3,2	27,26
14:15	01.02.2010	16,97	3,4	28,97
14:45	03.02.2010	18,99	3,45	29,39
09:45	05.02.2010	20,78	3,55	30,25
09:07	08.02.2010	23,75	3,6	30,67
09:09	11.02.2010	26,76	3,7	31,52
09:16	15.02.2010	30,76	3,8	32,38
09:10	18.02.2010	33,76	3,85	32,80
09:12	22.02.2010	37,76	3,85	32,80

Second Restoration

➤ Cleaning with dry toluene and methanol.

➤ Drying at 90 ˚C. Dry weight is 214.00 gr.

➤ Saturation with 10 times diluted FW-ØS. Saturated weight was 227.32 gr.

➤ Pore volume was 13.03 ml.

➤ Wettability test + washing out with distilled water.

➤ Drying at 90 ˚C. Dry weight is 213.98 gr.

➤ Saturation with 10 times diluted FW-ØS. Saturated weight was 227.20 gr.

➤ Pore volume was 13.04 ml.

➤ Desiccation to get 10% initial water saturation.

➤ Vacuuming and 2 PV oil flooding from each direction.

➤ Aging for 2 weeks at 90˚C.

➤ Weight of core after aging was 225.31 gr.

➤ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➤ Recovery with FW-ØS was 3.83% of OOIP.

➤ Imbibing liquid was switched to PSW-ØNaCl.

➤ 34.8% additional recovery was achieved with PSW-ØNaCl.

➤ Imbibing liquid was switched to PSW+1 weight % C_{12}TAB.

➤ 2.13% additional recovery was achieved with PSW+1 weight % C_{12}TAB.

➤ Totally 40.04% of OOIP was recovered.

Table-7 Core C 2-4 spontaneous imbibition test data after second restoration.

Originally Oil in Place (ml)	11,737						
Time (Hour)	**Date**	**Time (Day)**	**Oil Production (ml) Imbibing liquid FW-ØS**	**Oil Production (ml) Imbibing liquid PSW- ØNaCl**	**Oil Production (ml) Imbibing liquid PSW+C$_{12}$TAB**	**Total Oil Production (ml)**	**Oil Recovery (%)**
10:15	07.04.2010	0,00	0,00	-	-	0,00	0,00
14:50	07.04.2010	0,19	0,30	-	-	0,30	2,56
09:37	08.04.2010	0,97	0,35	-	-	0,35	2,98
11:30	11.04.2010	4,05	0,45	-	-	0,45	3,83
08:22	14.04.2010	6,92	0,45	-	-	0,45	3,83
09:00	15.04.2010	7,95	-	0,25	-	0,70	5,96
09:47	17.04.2010	9,98	-	1,20	-	1,65	14,06
09:00	19.04.2010	11,95	-	2,10	-	2,55	21,73
09:00	22.04.2010	14,95	-	2,90	-	3,35	28,54
13:07	25.04.2010	18,12	-	3,50	-	3,95	33,65
09:17	29.04.2010	21,96	-	3,95	-	4,40	37,49
08:54	03.05.2010	25,94	-	4,00	-	4,45	37,91
09:00	06.05.2010	28,95	-	4,00	-	4,45	37,91
11:15	10.05.2010	33,04	-	4,00	-	4,45	37,91
15:40	11.05.2010	34,14	-	-	0,00	4,45	37,91
14:15	13.05.2010	35,23	-	-	0,00	4,45	37,91
15:50	15.05.2010	37,29	-	-	0,05	4,50	38,34
14:54	18.05.2010	40,25	-	-	0,20	4,65	39,62
10:00	21.05.2010	43,05	-	-	0,25	4,70	40,04

C. Procedures performed on core C 4-14

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C. Dry weight was 206.02 gr.

➢ Saturation with SW-ØT. Saturated weight was 220.78 gr.

➢ Pore volume was 14.16 ml.

➢ Permeability measurement.

➢ Drying at 90 ˚C. Dry weight was 205.78 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 220.45 gr.

➢ Pore volume was 14.47 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90˚C.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Recovery with FW-ØS was 40.7% of OOIP.

➢ Imbibing liquid was switched to PSW-ØNaCl+ ØCaCl$_2$+4xSO$_4^{-2}$.

➢ 5.4% additional recovery was achieved with PSW-ØNaCl+ ØCaCl$_2$+4xSO$_4^{-2}$.

➢ Totally 46.07% of OOIP was recovered.

➢ First wettability test was performed.

➢ PSW was injected at 130˚C.

➢ Second wettability test was performed.

Table-8 Core C 4-14 spontaneous imbibition test data after first restoration.

Originally Oil in Place (ml)	13,023					
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Production (ml) Imbibing liquid PSW-ØNaCl+ØCaCl$_2$+4xSO$_4^{-2}$	Total Oil Production (ml)	Oil Recovery (%)
11:00	22.09.2009	0,00	0,00	-	0,00	0,00
14:20	22.09.2009	0,14	0,60	-	0,60	4,61
19:40	22.09.2009	0,36	1,00	-	1,00	7,68
09:30	23.09.2009	0,94	1,30	-	1,30	9,98
16:40	24.09.2009	2,24	1,70	-	1,70	13,05
09:00	25.09.2009	2,92	1,95	-	1,95	14,97
09:00	26.09.2009	3,92	2,30	-	2,30	17,66
20:00	30.09.2009	8,38	3,70	-	3,70	28,41
12:00	02.10.2009	10,04	4,20	-	4,20	32,25
12:00	05.10.2009	13,04	4,70	-	4,70	36,09
10:30	07.10.2009	14,98	4,90	-	4,90	37,63
09:00	09.10.2009	16,92	5,00	-	5,00	38,39
10:00	12.10.2009	19,96	5,15	-	5,15	39,55
20:00	13.10.2009	21,38	5,25	-	5,25	40,31
10:30	15.10.2009	22,98	5,30	-	5,30	40,70
10:30	17.10.2009	24,98	5,30	-	5,30	40,70
10:30	19.10.2009	26,98	5,30	-	5,30	40,70
15:00	20.10.2009	28,17	5,30	-	5,30	40,70
10:10	21.10.2009	28,97	-	0,10	5,40	41,47
10:20	22.10.2009	29,97	-	0,45	5,75	44,15
10:20	23.10.2009	30,97	-	0,55	5,85	44,92
10:20	26.10.2009	33,97	-	0,65	5,95	45,69
10:00	28.10.2009	35,96	-	0,70	6,00	46,07
11:00	30.10.2009	38,00	-	0,70	6,00	46,07
11:00	02.11.2009	41,50	-	0,70	6,00	46,07

Second Restoration

➢ Cleaning with dry toluene and methanol.

➢ Distilled water injection with the rate to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C. Dry weight was 205.23 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 219.85 gr.

➢ Pore volume was 14.42 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Heptane flooding.

➢ Spontaneous imbibition test with FW-ØS at room temperature was performed. Total recovery was 40.7% with initial water saturation in 0.36 days. N-heptane was used as oil.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C. Dry weight was 204.92 gr.

➢ Saturation with heptane. Saturated weight was 214.84 gr.

➢ Pore volume was 14.50 ml.

➢ Spontaneous imbibition test with distilled water at room temperature was performed. Total recovery was 42.07 % without initial water saturation in 2.64 days. N-heptane was used as oil.

➢ Saturation with SW-ØT.

➢ Wettability test was performed.

Table-9 Core C 4-14 spontaneous imbibition test data at room temperature with n-heptane and 10% initial water saturation after second restoration.

Originally Oil in Place (ml)		13,023		
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Recovery (%)
13:10	15.12.2009	0,00	0,00	0,00
14:02	15.12.2009	0,04	0,60	4,61
14:32	15.12.2009	0,06	1,30	9,98
15:00	15.12.2009	0,08	1,80	13,82
15:40	15.12.2009	0,10	2,70	20,73
17:20	15.12.2009	0,17	4,70	36,09
18:05	15.12.2009	0,20	5,00	38,39
18:20	15.12.2009	0,22	5,10	39,16
20:06	15.12.2009	0,29	5,30	40,70
21:52	15.12.2009	0,36	5,30	40,70

Table-10 Core C 4-14 spontaneous imbibition test data at room temperature with n-heptane and without initial water saturation after second restoration.

Originally Oil in Place (ml)		14,50		
Time (Hour)	**Date**	**Time (Day)**	**Oil Production (ml) Imbibing liquid DW**	**Oil Recovery (%)**
09:24	19.02.2010	0,00	0,00	0,00
10:00	19.02.2010	0,03	0,10	0,69
11:00	19.02.2010	0,07	0,30	2,07
12:00	19.02.2010	0,11	0,50	3,45
13:00	19.02.2010	0,15	0,80	5,52
14:00	19.02.2010	0,19	1,10	7,59
15:00	19.02.2010	0,23	1,30	8,97
16:00	19.02.2010	0,28	1,50	10,34
16:50	19.02.2010	0,31	1,90	13,10
17:45	19.02.2010	0,35	2,20	15,17
18:35	19.02.2010	0,38	2,40	16,55
01:10	20.02.2010	0,66	3,80	26,21
10:45	20.02.2010	1,06	5,30	36,55
15:56	20.02.2010	1,27	5,80	40,00
20:20	20.02.2010	1,46	6,00	41,38
01:00	21.02.2010	1,65	6,00	41,38
15:00	21.02.2010	2,23	6,10	42,07
00:45	22.02.2010	2,64	6,10	42,07

D. Procedures performed on core C 5-16

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C. Dry weight was 178.57 gr.

➢ Saturation with FW-ØT. Saturated weight was 192.79 gr.

➢ Wettability test + washing out with distilled water + permeability measurement.

➢ Drying at 90 ˚C. Dry weight was 178.17 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 192.37 gr.

➢ Pore volume was 14 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90˚C.

➢ Weight of core after aging was 189.00 gr.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Recovery with FW-ØS was 42.34% of OOIP.

➢ Imbibing liquid was switched to SW.

➢ 5.8% additional recovery was achieved with SW.

➢ Imbibing liquid was switched to PSW-ØNaCl.

➢ No additional recovery was achieved with PSW-ØNaCl.

➢ Temperature was increased to 130˚C.

➢ 1.55% additional recovery was achieved with PSW-ØNaCl at 130 ˚C.

➢ Totally 49.72% of OOIP was recovered.

Table-11 Core C 5-16 spontaneous imbibition test data after first restoration.

Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Production (ml) Imbibing liquid PSW	Oil Production (ml) Imbibing liquid PSW-ØNaCl	Oil Production (ml) Imbibing liquid PSW-ØNaCl at 130 ˚C	Total Oil Production (ml)	Oil Recovery (%)
	Originally Oil in Place (ml)	12,871						
13:00	24.08.2009	0,00	0,00	-	-	-	0,00	0,00
14:30	24.08.2009	0,06	0,45	-	-	-	0,45	3,50
18:20	24.08.2009	0,22	1,30	-	-	-	1,30	10,10
09:45	25.08.2009	0,86	3,40	-	-	-	3,40	26,42
16:15	25.08.2009	1,14	3,70	-	-	-	3,70	28,75
10:30	26.08.2009	1,90	4,70	-	-	-	4,70	36,52
17:10	26.08.2009	2,17	4,80	-	-	-	4,80	37,29
11:30	27.08.2009	2,94	5,10	-	-	-	5,10	39,62
10:15	28.08.2009	3,89	5,20	-	-	-	5,20	40,40
10:15	29.08.2009	4,89	5,30	-	-	-	5,30	41,18
11:00	31.08.2009	6,92	5,45	-	-	-	5,45	42,34
11:00	01.09.2009	7,92	-	0,00	-	-	5,45	42,34
11:00	02.09.2009	8,92	-	0,00	-	-	5,45	42,34
12:00	04.09.2009	10,96	-	0,45	-	-	5,90	45,84
16:15	08.09.2009	15,14	-	0,75	-	-	6,20	48,17
14:15	12.09.2009	19,05	-	0,75	-	-	6,20	48,17
14:15	13.09.2009	20,05	-	0,75	-	-	6,20	48,17
14:15	14.09.2009	21,05	-	0,75	-	-	6,20	48,17
14:15	15.09.2009	22,05	-	0,75	-	-	6,20	48,17
14:15	16.09.2009	23,05	-	-	0,00	-	6,20	48,17
14:15	17.09.2009	24,05	-	-	0,00	-	6,20	48,17
14:15	18.09.2009	25,05	-	-	0,00	-	6,20	48,17
14:15	19.09.2009	26,05	-	-	0,00	-	6,20	48,17
14:15	20.09.2009	27,05	-	-	0,00	-	6,20	48,17
14:15	21.09.2009	28,05	-	-	-	0,15	6,35	49,34
11:00	23.09.2009	29,92	-	-	-	0,20	6,40	49,72
11:00	24.09.2009	30,92	-	-	-	0,20	6,40	49,72
11:00	25.09.2009	31,92	-	-	-	0,20	6,40	49,72

Wettability Test and Second Restoration

➢ Cleaning with kerosene & n-heptane and distilled water.

➢ Drying at 90 ˚C. Dry weight was 178.82 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 188.61 gr.

This PV (9.66) was not plausible hence it was decided to clean the core with toluene and methanol

➢ After cleaning with dry toluene and methanol, distilled water was injected and Ca^{+2} concentration at the outlet was checked.

➢ Drying at 90 ˚C. Dry weight was 177.70 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 192.00 gr.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90˚C.

➢ Weight of core after aging was 190.08 gr.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Recovery with FW-ØS was 5.9% of OOIP.

➢ Imbibing liquid was switched to PSW.

➢ 26% additional recovery was achieved with PSW.

➢ Totally 31.9% of OOIP was recovered.

Table-12 Core C 5-16 spontaneous imbibition test data at room temperature with n-heptane and without initial water saturation after second restoration.

Originally Oil in Place (ml)		13,87		
Time (Hour)	**Date**	**Time (Day)**	**Oil Production (ml) Imbibing liquid DW**	**Oil Recovery (%)**
15:40	12.02.2010	0,00	0,0	0,00
16:45	12.02.2010	0,03	2,5	18,02
17:00	12.02.2010	0,07	3,1	22,34
17:10	12.02.2010	0,11	3,4	24,51
17:16	12.02.2010	0,15	3,7	26,67
19:25	12.02.2010	0,19	6,6	47,57
20:20	12.02.2010	0,23	6,8	49,01
01:38	13.02.2010	0,28	7,0	50,45
10:40	13.02.2010	0,31	7,1	51,17

Table-13 Core C 5-16 spontaneous imbibition test data after second restoration.

Originally Oil in Place (ml)		12,696				
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Production (ml) Imbibing liquid PSW	Total Oil Production (ml)	Oil Recovery (%)
15:45	27.11.2009	0,00	0,00	-	0,00	0,00
19:00	27.11.2009	0,14	0,40	-	0,40	3,15
14:00	28.11.2009	0,79	0,65	-	0,65	5,12
12:00	29.11.2009	1,71	0,70	-	0,70	5,51
12:00	30.11.2009	2,71	0,75	-	0,75	5,91
11:00	01.12.2009	3,67	0,75	-	0,75	5,91
11:00	02.12.2009	4,67	-	0,25	1,00	7,88
11:00	03.12.2009	5,67	-	0,55	1,30	10,24
11:00	04.12.2009	6,67	-	0,80	1,55	12,21
13:00	05.12.2009	7,75	-	1,20	1,95	15,36
13:00	06.12.2009	8,75	-	1,40	2,15	16,93
13:00	07.12.2009	9,75	-	1,60	2,35	18,51
18:00	08.12.2009	10,96	-	2,05	2,80	22,05
11:10	10.12.2009	12,67	-	2,20	2,95	23,24
17:20	13.12.2009	15,93	-	2,65	3,40	26,78
12:00	15.12.2009	17,71	-	2,90	3,65	28,75
15:00	17.12.2009	19,83	-	3,00	3,75	29,54
15:00	22.12.2009	24,83	-	3,30	4,05	31,90
13:00	24.12.2009	26,75	-	3,30	4,05	31,90
13:00	25.12.2009	27,75	-	3,30	4,05	31,90

Third Restoration

➢ Cleaning with water saturated toluene and heptane afterwards.

➢ After distilled water injection, first wettability test was performed.

➢ SW + C_{12}TAB was injected at 130˚C with the rate 3 PV/day.

➢ Distilled water was injected to remove C_{12}TAB.

➢ Second wettability test was performed.

➢ Drying after wettability test at 90 ˚C.

➢ Saturation with heptane 100 %.

➢ Spontaneous imbibition test with distilled water at room temperature without initial water saturation was performed. Total recovery was 51.17% of OOIP in 0.79 days. N-heptane was used as oil.

➢ Drying at 90 ˚C. Dry weight was 176.80 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 191.03 gr.

➢ PV was 14.04 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90˚C.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Recovery with FW-ØS was 19.78% of OOIP.

➢ Imbibing liquid was switched to PSW.

➢ 7.92% additional recovery was achieved with PSW.

➢ Imbibing liquid was switched to PSW+1 weight % C_{12}TAB.

➢ 18,6% additional recovery was achieved with PSW+1 weight % C_{12}TAB.

➢ Totally 46.30% of OOIP was recovered.

Table-14 Core C 5-16 spontaneous imbibition test data after third restoration.

Originally Oil in Place (ml)		12,636					
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid FW-ØS	Oil Production (ml) Imbibing liquid PSW	Oil Production (ml) Imbibing liquid PSW+1 WT%C_{12}TAB	Total Oil Production (ml)	Oil Recovery (%)
12:00	09.03.2010	0,00	0,00	-	-	0,00	0,00
16:27	09.03.2010	0,19	0,70	-	-	0,70	5,54
15:30	10.03.2010	1,15	1,30	-	-	1,30	10,29
15:11	11.03.2010	2,13	1,60	-	-	1,60	12,66
14:16	12.03.2010	3,09	1,75	-	-	1,75	13,85
09:10	15.03.2010	5,88	2,05	-	-	2,05	16,22
08:55	18.03.2010	8,87	2,25	-	-	2,25	17,81
09:04	22.03.2010	12,88	2,40	-	-	2,40	18,99
09:00	25.03.2010	15,88	2,45	-	-	2,45	19,39
09:04	29.03.2010	19,88	2,50	-	-	2,50	19,78
10:06	01.04.2010	22,92	2,50	-	-	2,50	19,78
09:08	02.04.2010	23,88	-	0,05	-	2,55	20,18
17:35	03.04.2010	25,23	-	0,70	-	3,20	25,72
18:30	04.04.2010	26,27	-	0,90	-	3,40	27,30
08:38	06.04.2010	27,86	-	1,00	-	3,50	28,09
09:07	08.04.2010	29,88	-	1,00	-	3,50	28,09
08:53	09.04.2010	30,87	-	-	0,00	3,50	28,09
08:53	10.04.2010	31,87	-	-	0,15	3,65	29,28
08:57	13.04.2010	34,87	-	-	0,45	3,95	31,66
09:04	16.04.2010	37,88	-	-	0,80	4,30	34,43
09:47	19.04.2010	40,91	-	-	1,30	4,80	38,38
09:00	22.04.2010	43,88	-	-	1,70	5,20	41,55
13:32	25.04.2010	47,06	-	-	1,95	5,45	43,53
09:35	29.04.2010	50,90	-	-	2,25	5,75	45,90
09:28	03.05.2010	54,89	-	-	2,35	5,85	46,69
09:36	06.05.2010	57,90	-	-	2,35	5,85	46,69
11:15	10.05.2010	61,97	-	-	2,35	5,85	46,69

E. Procedures performed on core C 5-18

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Drying at 90 ˚C. Dry weight was 97.45 gr.

➢ Saturation with FW-ØS. Saturated weight was 105.15 gr.

➢ Pore volume was 6.74 ml.

➢ Aging for 3 days with FW-ØS.

➢ Distilled water injection to determine SO_4^{-2}, Ca^{+2} and Mg^{+2} concentrations.

➢ Drying at 90 ˚C. Dry weight was 96.44 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 103.84 gr.

➢ Pore volume was 7.3 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging for 2 weeks at 90 ˚C.

➢ Weight of core after aging was 102.83 gr.

➢ Forced imbibition test was performed by injecting FW-ØS at 110 ˚C.

➢ Total recovery was 47.95% of OOIP.

Table-15 Core C 5-18 forced imbibition test data after first restoration.

Time	Date	Cumulative Time (Day)	Injected Pore Volume	Inlet Pressure (Bar)	Differential Pressure (mBar)	Cumulative Production (ml)	Oil Recovery (%)
	Originally Oil in Place (ml)		6,57				
20:40	08.03.2010	0,00	0,00	11,45	..	0,00	0,00
21:51	08.03.2010	0,05	0,02	10,44	390	0,00	0,00
08:42	09.03.2010	0,50	0,20	11,50	119	0,00	0,00
09:42	09.03.2010	0,54	0,21	11,10	207	0,00	0,00
18:42	09.03.2010	0,92	0,36	11,78	262	0,00	0,00
21:14	09.03.2010	1,02	0,40	12,01	279	0,00	0,00
09:17	10.03.2010	1,53	0,60	12,11	470	1,40	21,31
11:13	10.03.2010	1,61	0,63	11,97	452	1,70	25,88
13:07	10.03.2010	1,69	0,66	11,77	271	1,90	28,92
14:20	10.03.2010	1,74	0,68	10,78	452	2,05	31,20
15:38	10.03.2010	1,79	0,71	10,57	353	2,20	33,49
17:50	10.03.2010	1,88	0,74	11,27	409	2,45	37,29
19:40	10.03.2010	1,96	0,77	12,15	266	2,65	40,33
22:40	10.03.2010	2,08	0,82	12,27	96	2,80	42,62
8:25	11.03.2010	2,49	0,98	11,90	0	2,90	44,14
10:07	11.03.2010	2,56	1,01	12,27	26	2,90	44,14
13:54	11.03.2010	2,72	1,07	12,24	28	2,95	44,90
17:55	11.03.2010	2,89	1,14	11,46	1	3,00	45,66
21:05	11.03.2010	3,02	1,19	12,55	325	3,05	46,42
9:00	12.03.2010	3,51	1,39	12,49	341	3,15	47,95
12:22	12.03.2010	3,65	1,44	11,84	372	3,15	47,95
19:14	12.03.2010	3,94	1,55	11,84	372	3,15	47,95
11:45	13.03.2010	4,63	1,83	12,38	324	3,15	47,95
17:05	14.03.2010	5,85	2,31	12,41	372	3,15	47,95
09:18	15.03.2010	6,53	2,57	11,95	242	3,15	47,95
07:45	16.03.2010	7,46	2,94	12,22	294	3,15	47,95

Second Restoration

- Cleaned with dry toluene and methanol.
- Drying at 90 ˚C. Dry weight was 96.20 gr.
- Saturation with 10 times diluted FW-ØS. Saturated weight was 103.65 gr.
- Pore volume was 7.35 ml.
- Desiccation to get 10% initial water saturation.
- Vacuuming and 2 PV oil flooding from each direction.
- Aging for 2 weeks at 90˚C.
- Weight of core after aging was 102.68 gr.
- Forced imbibition test was performed by injecting FW-ØS at 110 ˚C.
- Recovery was 54.27% of OOIP.
- Injected liquid was switched to PSW.
- No additional recovery was achieved with PSW-ØNaCl.
- Injected liquid was switched to PSW+1 weight % C_{12}TAB.
- 3% additional recovery was achieved with PSW+1 weight % C_{12}TAB.
- Total recovery was 57.29% of OOIP.

Table-16 Core C 5-18 forced imbibition test data after second restoration.

Time	Date	Cumulative Time (Day)	Injected Pore Volume	Inlet Pressure (Bar)	Differential Pressure (mBar)	Cumulative Production (ml)	Oil Recovery (%)
Originally Oil in Place (ml)			6,633				
10:34	19.04.2010	0,00	0,00	-	-	0,00	0,00
13:26	19.04.2010	0,12	0,05	5,84	414	0,00	0,00
11:00	20.04.2010	1,02	0,40	6,76	141	0,00	0,00
19:35	20.04.2010	1,38	0,54	-	-	0,50	7,54
06:00	21.04.2010	1,81	0,71	7,32	513	1,45	21,86
08:03	21.04.2010	1,90	0,74	7,54	647	1,65	24,88
09:21	21.04.2010	1,95	0,76	7,54	647	1,85	27,89
13:39	21.04.2010	2,13	0,83	7,50	643	2,30	34,68
19:30	21.04.2010	2,37	0,93	7,58	-	3,10	46,74
20:53	21.04.2010	2,43	0,95	7,24	378	3,25	49,00
10:08	22.04.2010	2,98	1,17	6,98	126	3,35	50,51
13:36	22.04.2010	3,13	1,22	6,61	50	3,35	50,51
08:58	23.04.2010	3,93	1,54	7,04	178	3,50	52,77
14:30	23.04.2010	4,16	1,63	7,06	268	3,50	52,77
09:17	24.04.2010	4,95	1,93	6,72	140	3,60	54,27
13:27	24.04.2010	5,12	2,00	6,86	225	3,60	54,27
10:39	25.04.2010	6,00	2,35	6,79	219	3,60	54,27
09:01	26.04.2010	6,94	2,71	6,86	119	3,60	54,27
14:30	26.04.2010	7,16	2,80	6,96	176	3,60	54,27
08:46	27.04.2010	7,92	3,10	6,91	203	3,60	54,27
09:00	29.04.2010	9,93	3,88	6,66	106	3,60	54,27
09:04	30.04.2010	10,94	4,27	6,47	89	3,60	54,27
15:24	01.05.2010	12,20	4,77	6,90	158	3,60	54,27
09:48	03.05.2010	13,97	5,46	6,90	72	3,70	55,78
08:54	04.05.2010	14,93	5,83	6,72	38	3,80	57,29
09:59	05.05.2010	15,98	6,24	6,74	40	3,80	57,29

F. Procedures performed on core C 5-20

First Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Distilled water injection to get rid of SO_4^{-2}.

➢ Drying at 90 ˚C.

➢ Cleaning with toluene and methanol.

➢ Drying at 90 ˚C. Dry weight was 196.84 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 212.92 gr.

➢ Pore volume was 16.11 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging at 90 ˚C for 2 weeks.

➢ Weight of core after aging was 210.53 gr.

➢ Spontaneous imbibition test with FW-ØS at 110 ˚C was performed.

➢ Recovery with FW-ØS was 36.55% of OOIP.

➢ Imbibing liquid was switched to PSW-ØNaCl.

➢ 11.38% additional recovery was achieved with PSW-ØNaCl.

➢ Totally 47.93% of OOIP was recovered.

Table-17 Core C 5-20 spontaneous imbibition test data after first restoration.

Originally Oil in Place (ml)	14,499					
Time (Hour)	**Date**	**Time (Day)**	**Oil Production (ml) Imbibing liquid FW-ØS**	**Oil Production (ml) Imbibing liquid PSW-ØNaCl**	**Total Oil Production (ml)**	**Oil Recovery (%)**
12:03	03.02.2010	0,00	0,00	-	0,00	0,00
15:53	03.02.2010	0,16	1,10	-	1,10	7,59
13:35	04.02.2010	1,06	2,80	-	2,80	19,31
10:45	05.02.2010	1,95	3,60	-	3,60	24,83
12:11	06.02.2010	3,01	4,20	-	4,20	28,97
09:32	08.02.2010	4,90	4,55	-	4,55	31,73
09:15	10.02.2010	6,88	4,95	-	4,95	34,14
09:13	12.02.2010	8,88	5,05	-	5,05	34,83
09:16	15.02.2010	11,88	5,10	-	5,10	35,17
09:10	18.02.2010	14,88	5,20	-	5,20	35,86
09:12	22.02.2010	18,88	5,30	-	5,30	36,55
09:39	25.02.2010	21,90	5,30	-	5,30	36,55
09:56	26.02.2010	22,91	-	0,25	5,55	38,28
13:10	01.03.2010	26,05	-	0,65	5,95	41,04
09:38	03.03.2010	27,90	-	0,80	6,10	42,07
09:38	05.03.2010	29,90	-	1,00	6,30	43,45
09:09	08.03.2010	32,88	-	1,20	6,50	44,83
09:09	11.03.2010	35,88	-	1,45	6,75	46,55
09:10	15.03.2010	39,88	-	1,55	6,85	47,24
08:55	18.03.2010	42,87	-	1,60	6,90	47,59
09:04	22.03.2010	46,88	-	1,65	6,95	47,93
09:00	25.03.2010	49,87	-	1,65	6,95	47,93

Second Restoration

➢ Cleaning with kerosene & n-heptane.

➢ Drying at 90 ˚C. Dry weight is 196.63 gr.

➢ Saturation with 10 times diluted FW-ØS. Saturated weight was 212.86 gr.

➢ Pore volume was 16.01 ml.

➢ Desiccation to get 10% initial water saturation.

➢ Vacuuming and 2 PV oil flooding from each direction.

➢ Aging at 90 ˚C for 2 weeks.

➢ Weight of core after aging was 210.66 gr.

➢ Spontaneous imbibition test with PSW-ØNaCl at 110 ˚C was performed.

➢ Total recovery with PSW-ØNaCl was 41.64% of OOIP.

Table-18 Core C 5-20 spontaneous imbibition test data after first restoration.

Originally Oil in Place (ml)		14,410		
Time (Hour)	Date	Time (Day)	Oil Production (ml) Imbibing liquid PSW-ØNaCl	Oil Recovery (%)
09:50	23.04.2010	0,00	0,00	0,00
14:08	23.04.2010	0,18	1,05	7,29
09:21	24.04.2010	0,98	3,55	24,64
10:54	25.04.2010	2,04	4,80	33,31
09:05	26.04.2010	2,97	5,10	35,39
09:08	29.04.2010	5,97	5,55	38,51
08:54	03.05.2010	9,96	5,70	39,56
09:00	06.05.2010	12,97	5,75	39,90
09:00	10.05.2010	16,97	6,00	41,64
14:15	13.05.2010	20,18	6,00	41,64
15:50	15.05.2010	22,24	6,00	41,64