

LOW TENSION METHODS FOR FRACTURED RESOURCES

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DEGREE OF MASTER OF SCIENCE**

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June 2009**

I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

Dr. Louis Castanier

Abstract

Water flooding typically recovers about 50% of the original oil in place leaving much oil in the reservoir. Recovery efficiency in fractured reservoirs can be dramatically lower in comparison to conventional reservoirs because water channels selectively from injector to producer leaving considerable oil within the matrix and uncontacted by injected water. An enhanced recovery process is needed to access such oil held in the reservoir matrix. Addition of aqueous surfactants to injection water dramatically reduces oil/water interfacial tension and surfactant may adsorb to oil-wet rock surfaces inducing a shift in wettability that improves the imbibition of water.

At the pore level, capillary forces are responsible for oil trapping and generally dominate over viscous and gravitational forces. Because of the reduction in interfacial tension between oil and water with the addition of surfactant, the role of capillary forces on fluid flow can be minimized. When gravity parameters are large enough to give a Bond number (ratio of gravity to capillary forces) greater than 10, gravitational forces become more dominant and oil held with rock matrix by capillarity may be released as a result of buoyancy.

In this work, we use experiments conducted in two-dimensional micromodels to investigate the effect of gravity at low interfacial tension. The micromodels have the geometrical and topological characteristics of sandstone and the network is etched into silicon. Pore-level mechanics are observed directly via a reflected-light microscope. A screening study of sulfonate and sulfate surfactants was conducted to choose an appropriate system compatible with the light crude oil (27°API). A variety of flow behavior through the microscope is investigated including forced and spontaneous imbibition. Results are illustrated via pore-level photo and image analysis of whole micromodel pictures. Forced displacements are conducted at realistic flow rates to maintain a 1 m/day Darcy velocity and at surfactant concentrations of 0.9% to 1.25%. Forced displacement with a horizontal or vertical positioning of the micromodel yields dramatic improvement of recovery for surfactant injection cases. All the oil retained after a waterflood was recovered by tertiary injection of surfactant solution. In comparison, about 25% oil saturation remained after a waterflood.

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Chapter 1

1. Introduction

Primary recovery processes (e.g. water flooding) leave much oil in the reservoir, especially in fractured reservoirs where water channels to producers leaving oil within the matrix unswept by water. Further recovery requires using an enhanced recovery process. In the reservoir, three forces influence fluid flow: viscous forces, gravitational forces and capillary forces. Capillary forces are related to viscous forces and gravitation forces by the capillary number (Ca) and the Bond number (Bo) respectively. The capillary number and the Bond number are defined as follows:

$$Ca = \frac{\mu_i u_i}{\sigma} \quad (1-1)$$

$$Bo = \frac{\Delta \rho g d^2}{\sigma} \quad (1-2)$$

where μ_i is the injectant viscosity, u_i is the injectant Darcy velocity, σ is the interfacial tension between the two phases (e.g. oil and water), $\Delta \rho$ is the density difference between the two phases, g is the gravity acceleration, and d is the pore diameter. Both Ca and Bo are dimensionless numbers and units should be consistent. Below roughly 10^{-3} for Ca and 10 for Bo, capillary forces dominate (Cinar et al. 2007). Another dimensionless number of equal importance is the mobility ratio (M) that is described as follows:

$$M = \frac{k_{rw} \mu_o}{k_{ro} \mu_w} \quad (1-3)$$

where k_{ri} and μ_i are the relative permeability and viscosity of phase i, respectively. The mobility ratio is defined as the ratio of the displacing fluid mobility to the displaced fluid mobility. A mobility ratio less than or equal to one indicates a more stable (favorable) displacement.

The two principle means to improving recovery are thus to increase Ca and Bo while possibly decreasing M. Surfactant flooding is known to lower IFT and hence, reduce capillary forces responsible for trapping oil. In this work, surfactant flooding in fractured resources is examined by conducting micromodel experiments.

Dilute surfactants were used to lower IFT. Hirasaki and Zhang (2003) showed an improvement in oil recovery when anionic surfactants are injected in a fractured oil-wet carbonate system. They also added sodium carbonate to reduce IFT and surfactant adsorption to rock surfaces. Adibhatla and Mohanty (2006) looked at the effect of gravity for a similar system using also diluted anionic surfactants with sodium carbonate.

In this work, dilute surfactants with sodium carbonates are injected in a micromodel to visualize the improvement of oil recovery in the presence of gravity. Micromodels are made of silicon wafers. The pore network, obtained from an image of a rock thin section, is etched into the wafer. The micromodel is then bonded to glass creating a two-dimensional porous medium. Silicon micromodels are water wet as a result of the bonding process.

Surfactant solutions are injected at one side of the micromodel and monitored optically as they propagate through the micromodel pore network. Reducing capillary forces minimizes their effect on trapping oil at the pore scale. Hence, buoyancy forces become dominant and gravity segregates oil and water. Vertical micromodel experiments are conducted to measure the effect of gravity on oil recovery at low IFT values.

Before conducting the micromodel experiments, a full characterization of surfactant/brine/oil interactions is obtained. Phase separation tests are conducted to study the effect of sodium carbonates and surfactant concentration on samples made of brine and oil. Next, a brief literature review is given. The review is followed by fluid characterization and experimental details. The major experimental findings are conveyed by micromodel images. Discussion and conclusions complete the thesis.

1.1. Literature Review

In this work, micromodel experiments are conducted to investigate the improvement in oil recovery at low interfacial tensions (IFT). Surfactants are used to achieve low IFT along with sodium carbonate to lower adsorption and alter wettability towards water wetness. Sodium carbonates are added to the brine as alkali. They increase the negative charge on rock surfaces making them more water wet. Sodium carbonates are also used to lower surfactant adsorption to rock surfaces. This section provides a set of relevant work found in the literature.

1.1.1. Fluid Characterization

Hirasaki and Zhang (2003) looked at surfactant flooding in fractured, oil-wet, carbonate formations. In such systems, waterflood leads to low recovery as water flows through fractures leaving oil within the matrix. Moreover, rocks retain oil due to capillary forces and because carbonates have prominent irregularities (more surface area), much oil remains. In their work, they studied improvement of oil recovery when using anionic surfactants and sodium carbonates as alkali. Sodium carbonates were chosen as alkali for several reasons. For example, they alter wettability towards water-wetness, lower surfactant adsorption, and produce natural surfactants when reacting with crude oil. Surfactants and sodium carbonates were characterized by looking at the effect of sodium carbonate concentration on a brine/oil system, sodium carbonate concentration on a surfactant solution/oil system, and water-oil ratio (WOR) on a surfactant solution/oil system with a constant concentration of sodium carbonates (Hirasaki & Zhang, 2003).

On another study, Adibhatla and Mohanty (2006) conducted core-flooding experiments and numerical simulations to investigate a surfactant-aided gravity drainage process. They also used anionic surfactants, specifically alkyl ethoxylated surfactants, to lower the IFT. Before conducting the experiment, they followed a surfactant screening procedure proposed by Seethepalli et al (2004). Surfactants were screened based on phase behavior of samples made of oil/diluted surfactants with varying sodium carbonate concentration, IFT values, and wettability; a similar screening methodology was also implemented by Seethepalli et al. It was found that sodium carbonate concentration has to be at an optimum value to give the greatest reduction in IFT. Moreover, the wettability of oil wet surfaces was altered to intermediate to moderate water wet. These two factors: the IFT reduction and the wettability alteration towards water wetness led to an increase in oil recovery to about 60% in 60 days.

Levitt et al. (2006) proposed another screening methodology of chemical EOR fluids. The screened fluids include surfactants, polymers, co-surfactants and co-solvents. It was found that increasing the length of the hydrophobic part of the surfactants improves its performance in terms of higher solubilization ratio and lower optimum salinity. Propylene oxide (PO), a hydrophobic functional group, is added to the surfactant at different concentrations. Three types of surfactants were investigated: C16-17-(PO)₃-SO₄, C16-17-(PO)₅-SO₄ and C16-17-(PO)₇-SO₄ along with three types of co-surfactants: alcohol propoxy sulfate (APS), C15-18 internal olefin sulfonate (IOS) and C20-24 alpha olefin sulfonate (AOS). The fluids are evaluated by conducting phase behavior tests at different temperatures on samples made of surfactant/oil/brine. The testing criteria include the high stability and the low viscosity of the microemulsion phase, and the great reduction in the interfacial tension (IFT). It was found that C15-18 IOS with the 7 PO surfactant is the optimum mixture for low temperature dolomite reservoirs. For high temperatures (above 60°C), IOS hydrolyzes and sulfonate co-surfactants (e.g. AOS) are recommended. The researchers also concluded that adding sodium carbonate lowers IFT even more and reduces equilibration time.

Wellington and Richardson worked on designing surfactant flooding systems to obtain the greatest possible oil recovery using 40 anionic, 25 cationic, and 120 surfactant combinations. To maximize the recovery, surfactant concentration is kept at an optimum value at which oil and water phases are solely present with no microemulsion phase. Moreover, the mobility of the surfactant flood is kept below oil mobility by injecting polymer, to enhance displacement efficiency. Surfactants were screened based on cloud point, the “maximum temperature at which a single-phase solution exists,” and IFT measurements. It was found that the optimum concentration, for the examined surfactants, is about 0.4wt%. With such concentration, about one pore volume of surfactant solution is effective in displacing all residual oil in sand packs with less than 0.1 pore volume of surfactant loss. Moreover, it was found that the amount of undisplaced oil increases with loss of surfactants in a surfactant flood. Hence, adsorption control is highly recommended in designing surfactant flooding processes (Wellington & Richardson, 1997). Osterloh and Jante used polyethylene glycol (PEG) additives to lower adsorption of a surfactant/polymer system. By conducting core-flooding experiments,

they concluded that PEG-1000 has lowered adsorption the most compared to the other glycols (Osterloh & Jante, 1992).

Gupta and Mohanty looked at the effect of temperature on a surfactant flooding process in a carbonate system. It was found that increasing the temperature causes the rock matrix to become more water wet which was also reported by Wang and Gupta (1995), Hamouda and Gomari (2006), Schembre et. al. (2006), and Hjelmeland and Larronda (1986). Hence, oil recovery increases as temperature increases in surfactant flooding. The wettability alteration towards water wetness by an increase in temperature is interpreted by two reasons. The first is adsorption of crude oil components to the solid surface causing the surface to become more oil wet decreases as temperature increases. Another reason is that the activity of calcium ions on the solid surface also decreases with an increase in temperature. (Gupta & Mohanty, 2007).

1.1.2. Micromodel Experiments

Micromodels are two-dimensional systems that consist of an etched silicon wafer bonded to a glass wafer. The silicon wafer can be etched with any desired network. An inherent limitation in micromodels comes from the fact that they are two dimensional and more care should be taken in extrapolating the experimental results to the three-dimensional space. However, they provide an excellent means of optically visualizing displacement mechanisms and interactions of injected phases at a representative pore scale.

Feng et al. in 2004 conducted micromodel experiments to study water-alternating gas (WAG) displacement mechanisms. They found that WAG displacement mechanisms differ than water-oil or gas-oil displacement mechanisms. Oil becomes an intermediate phase between water, occupying small pores, and gas, occupying large pores (in a water-wet micromodel). Expansion of gas helps displace oil. Such realization had to be visualized, by conducting a micromodel experiment (Feng et al. 2004).

Rangel-German and Kovscek (2006) conducted micromodel experiments to investigate matrix-fracture transfer mechanisms of two phases. The wafers were etched with a representative Berea sandstone pore network (matrix) with two channels on two opposite sides of the network (fractures). The experiments were conducted by injecting the wetting phase (water) into the fracture and visualizing how it imbibes into the matrix. They showed that imbibition of wetting phase into the matrix is proportional to the volume of injected water at low injection rates and proportional to the square root of time at high flow rates. These results were concluded by microscopically monitoring the transient imbibition process.

The paper by Riaz et al (2007) showed the importance of M to fluid dynamics by monitoring core-flooding experiments with a CT scanner and conducting numerical simulations. Their work demonstrated how M is directly related to the stability of the injectant. Aktas et al (2008) and Buchgraber et al (2009) show how to modify M towards a more stable front by injecting associative polymers. They used micromodels similar to those ones described above. Associative polymers are used to lower the mobility of the

injectant and the overall mobility ratio. They showed that injecting associative polymers stabilizes the displacement front and thereby improving oil recovery. The experiments were conducted on two-dimensional silicon micromodels similar to the ones used by Rangel-German and Kovscek (2006). The aqueous phase of the associative polymers was forcedly imbibed into the micromodel from one side and the recovered oil was collected from the other side (Aktas et al. 2008).

Silicon and glass micromodels are naturally water wet. To make them oil wet, they are treated with hexadecyltrimethylammonium bromide (Hirasaki & Zhang, 2003).

Chapter 2

2.Fluid Characterization

A phase behavior study was carried out similar to the study of Hirasaki and Zhang (2003). Four tests were conducted by preparing samples of oil/brine/dilute surfactant to study the effect on IFT of the following:

- Increasing sodium carbonate concentration without surfactants
- Increasing sodium carbonate concentration at a constant surfactant concentration
- Increasing water-oil ratio (WOR) at a constant surfactant and sodium carbonate concentrations
- Increasing surfactant concentration at a constant sodium carbonate concentration

The IFT measurements were obtained using a spinning drop tensiometer. The following section presents the surfactants that were included in the study along with a brief description of the spinning drop tensiometer. The results of the phase behavior tests are discussed afterwards.

2.1. Surfactant Screening

In this work, three surfactants were evaluated based on their interfacial tension reduction (IFT): ONYXIDE 200 and PETROSTEP S-3A from STEPAN and NEODOL 25-3 from Shell Chemical.

ONYXIDE 200 is composed of 78.5% 1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol and 21.5% water (78.5% active). ONYXIDE 200 has the following properties:

- Flash Point: > 201°F
- Boiling Point: 212°F
- Density: 1.15 g/ml
- Percent Volatile (% w/w): 21.5
- pH: 10.5 (as is)
- Solubility in Water: Miscible (STEPAN, 2006)

PETROSTEP S-3 A is an internal olefin sulfonate (60.72% active). It has the following properties:

- Appearance @ 70 F: Brown liquid
- Flash Point: > 201°F
- Boiling Point: >212°F
- Density: 8.6 lb/gal

- Percent Volatile (% w/w): 35
- pH: 10-11.5 (10% aqueous)
- Solubility in Water: soluble (STEPAN, 2006)

NEODOL 25-3 (100% active) is made of ethylene oxide and pure C12-C15 NEODOL alcohol with a 3:1 molar ratio respectively. NEODOL 25-3 has the following properties:

- Flash Point: 325°F
- Pour Point: 41°F
- Density: 0.908 g/ml
- Kinematic Viscosity (@40°C): 17 cSt (ShellChemicals, 2006)

The IFT was measured using a spinning drop tensiometer shown on Figure 2-1. The basic principle of a tensiometer is measuring the width of an elongated oil drop submersed in a brine/surfactant solution. Both the oil drop and the brine are injected by a syringe into a capillary tube. The tube is placed inside the tensiometer and rotated about the longitudinal axis. The following formula is used to calculate the IFT (σ)

$$\sigma = \frac{1}{4} \Delta \rho \omega^2 r^3 \quad (2-1)$$

Where $\Delta \rho$ is the density difference between oil and brine/surfactant solution in $\frac{\text{kg}}{\text{m}^3}$, r is the elongated oil drop radius in meters and

$$\omega = \frac{2\pi}{\frac{f}{1000}}$$

with f as the angular velocity read from the tensiometer in $\frac{\text{msec}}{\text{shaft rev}}$. The measurements were obtained for oil/brine systems with different surfactant concentrations. It has to be noted that the capillary tubes have to be cleaned before usage. They are flushed with decane followed by acetone.

2.2. Phase Behavior Tests

This work is different than previous works discussed in the literature. It studies pore level displacement mechanisms with surfactant flooding by conducting micromodel experiments. A fracture is simulated by injecting along one side of the micromodel and allowing spontaneous imbibition to occur. Experiments are also conducted vertically to see the effect of gravity at low IFT values.

There are three types of fluids in this work: brine, oil, and surfactant. Brine is composed of sodium chloride, magnesium chloride, and calcium chloride. Concentrations of these salts are shown on Table 2-1.

Oil was obtained from two different reservoirs: sandstone (27.3°API) and carbonate (27.0°API) reservoirs. Two surfactants are used in this study: ONYXIDE 200 from Stepan Company and NEODOL 25-3 from Shell Chemical Company.

Four phase separation tests were conducted, similar to those described in the paper by Hirasaki and Zhang (2003), to study the effect of sodium carbonate concentration, water-oil ratio, and surfactant concentration. Samples of solutions with oil from a sandstone reservoir were prepared. The samples were then heated in an oven for a week to a temperature of 210°F.

2.2.1. Increasing Sodium Carbonate Concentration

In this test, 10 ml of oil (sandstone and carbonate oil; 5 samples for each) were added to 10 ml of brine with increasing concentration of sodium carbonates. Figure 2-2 shows the samples before being heated and Figure 2-3 shows the samples after they were taken out of the oven. White precipitates of calcium carbonates were observed when the samples were prepared. Most of the precipitates dissolved in the aqueous phase after heating the samples. However, these precipitates might block the micromodel network pores and throats and thus calcium chloride was not added to the brine. More sodium chloride was added to compensate for the chloride ions. The new composition is shown on Table 2-2.

The aqueous phase was yellowish in color after heating the samples. This indicates that some oil phase components dissolved in the brine. Samples of the brine were centrifuged at 50 rpm for one hour to see if more than one phase is present in the aqueous phase. Only one phase is found in the brine.

Figure 2-4 shows the IFT measurements for the samples for both oil types. It can be clearly seen that increases in sodium carbonate concentration lowers the IFT as previously suggested by Hirasaki and Zhang (2003).

2.2.2. Increasing Sodium Carbonates Concentration with a Constant Surfactant Concentration

Samples of 10 ml of sandstone oil were added to 10 ml of brine with a constant concentration of ONYXIDE 200 (0.20vol%) and an increasing concentration of sodium carbonates. Less precipitates formed in this test than those formed in the previous one. The surfactant in the brine helps dissolve the precipitates. Figure 2-5 shows the samples upon preparation and Figure 2-6 shows the samples after being heated.

Figure 2-7 shows the IFT measurements with two different surfactants. It roughly observed the same result from the previous test that sodium carbonates lower the IFT.

2.2.3. Increasing Water-Oil Ratios (WOR):

The purpose of this test is to study the effect of increasing WOR on phase separation. Samples were prepared with brine, a constant concentration of ONYXIDE 200

(0.20vol%) and sodium carbonates (0.2 M). Figure 2-8 shows the samples before being heated and Figure 2-9 shows the samples afterwards. Right after preparing the samples, a microemulsion phase was formed. The height of the microemulsion phase increases as WOR increases. After heating the samples, the microemulsion phase disappeared. This was a motivation to conduct a thermal stability test by heating oil/surfactant samples at 210°F and different time intervals. This test was made for ONYXIDE 200 and NEODOL 25-3.

Figure 2-10 shows the effect of WOR on IFT while Figure 2-11 shows the results of the thermal stability test. Figure 2-10 shows that the WOR has no major effect on the IFT. This is helpful because in the micromodel experiment, surfactant solution contacted the oil at variable WOR which can be disregarded since it has no effect on IFT. Figure 2-11 shows that both surfactants have tolerated the high temperature of 210°F.

2.2.4. Increasing Surfactant Concentration with a constant sodium carbonate concentration

10 ml of oil were added to 10 ml of brine with a constant concentration of sodium carbonates (0.20 M) and an increasing volumetric concentration of ONYXIDE 200. Figure 2-12 shows the samples upon preparation and Figure 2-13 shows the samples after being heated. No separation of phases took place in this test. It can be seen from Figure 2-14 NEODOL 25-3 is the most promising surfactant in terms of reducing IFT, then S-3A. At 1 vol% of NEODOL 25-3, crude-oil/water tension is 0.085 mN/m.

Table 2-1: Brine composition.

Compound	Concentration (g/l)
NaCl	16.699
MgCl ₂	1.278
CaCl ₂	4.792

Table 2-2: New brine composition.

Compound	Concentration (g/l)
NaCl	21.746
MgCl ₂	1.278

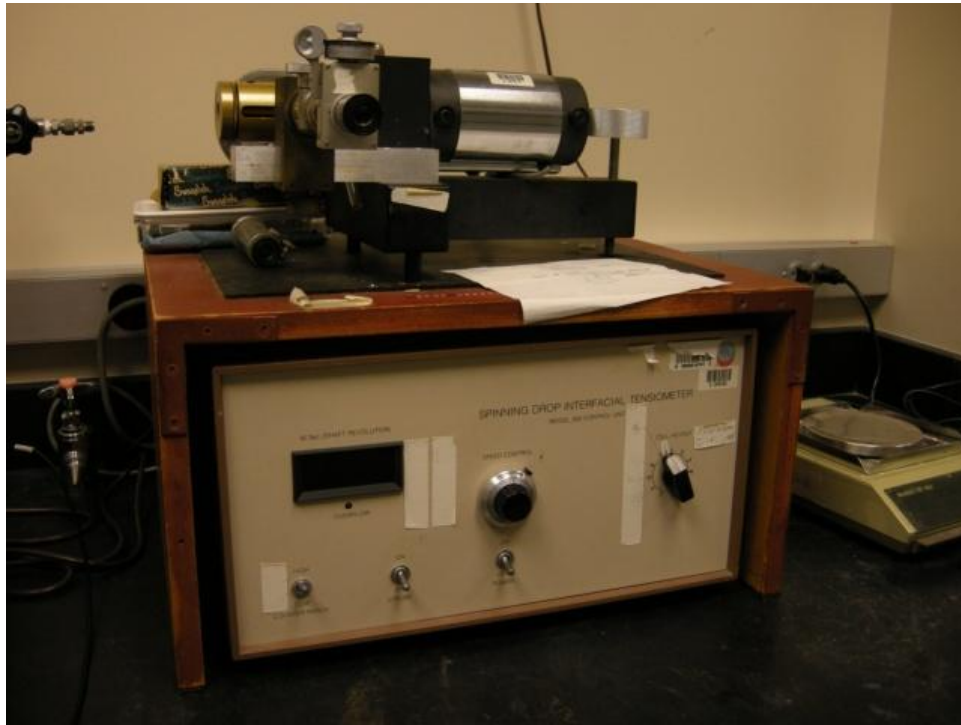


Figure 2-1: Tensiometer used for measuring IFT.

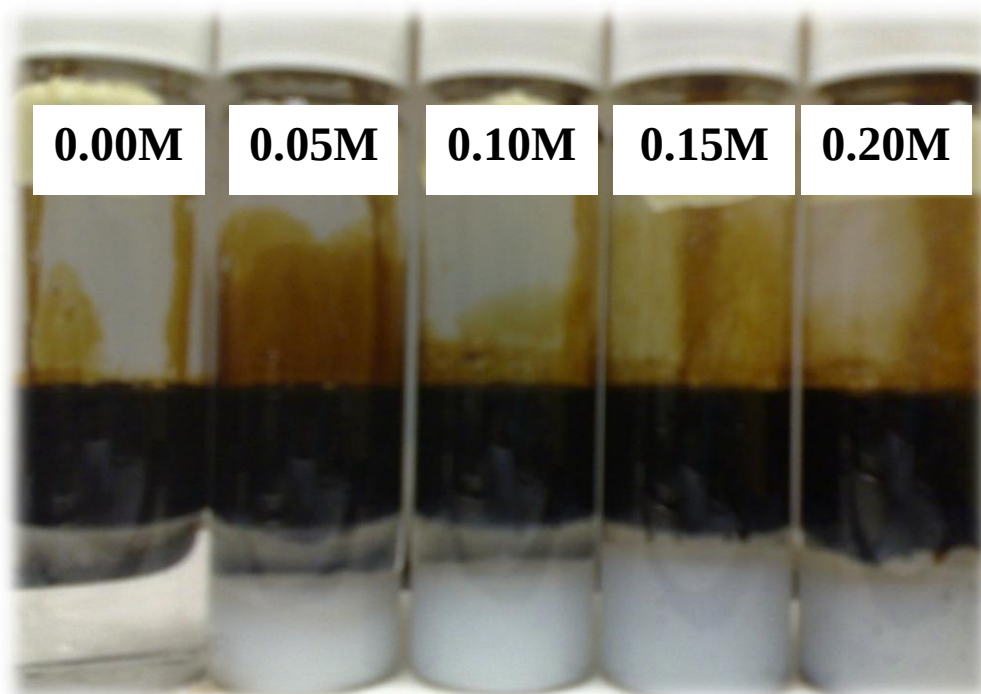


Figure 2-2: Samples made of oil/brine with increasing concentration of sodium carbonates before being heated.

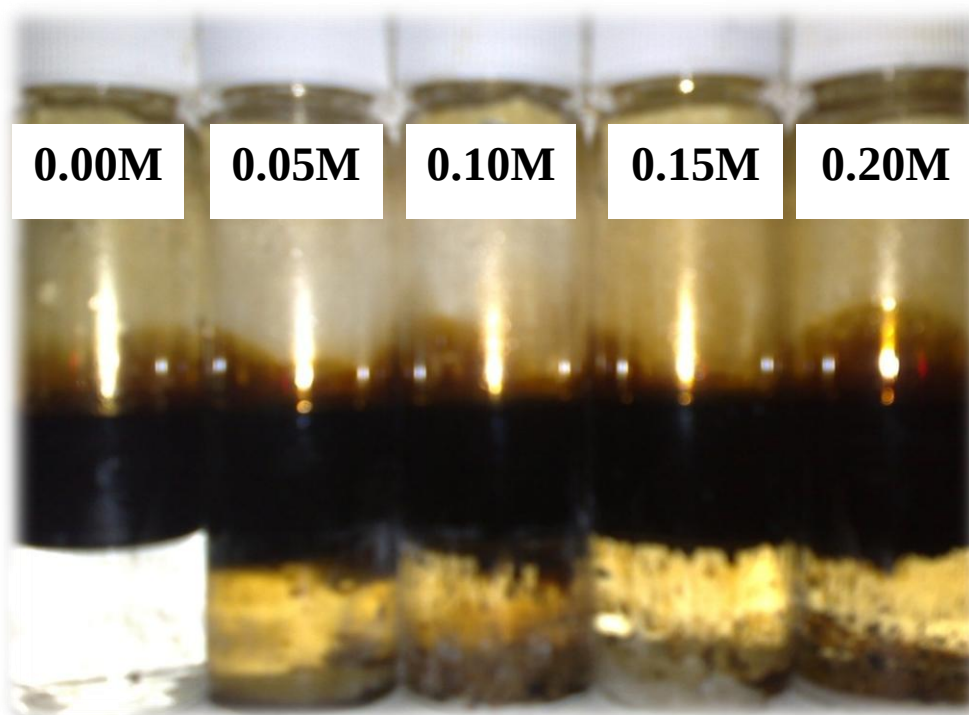


Figure 2-3: Samples made of oil/brine with increasing concentration of sodium carbonates after being heated.

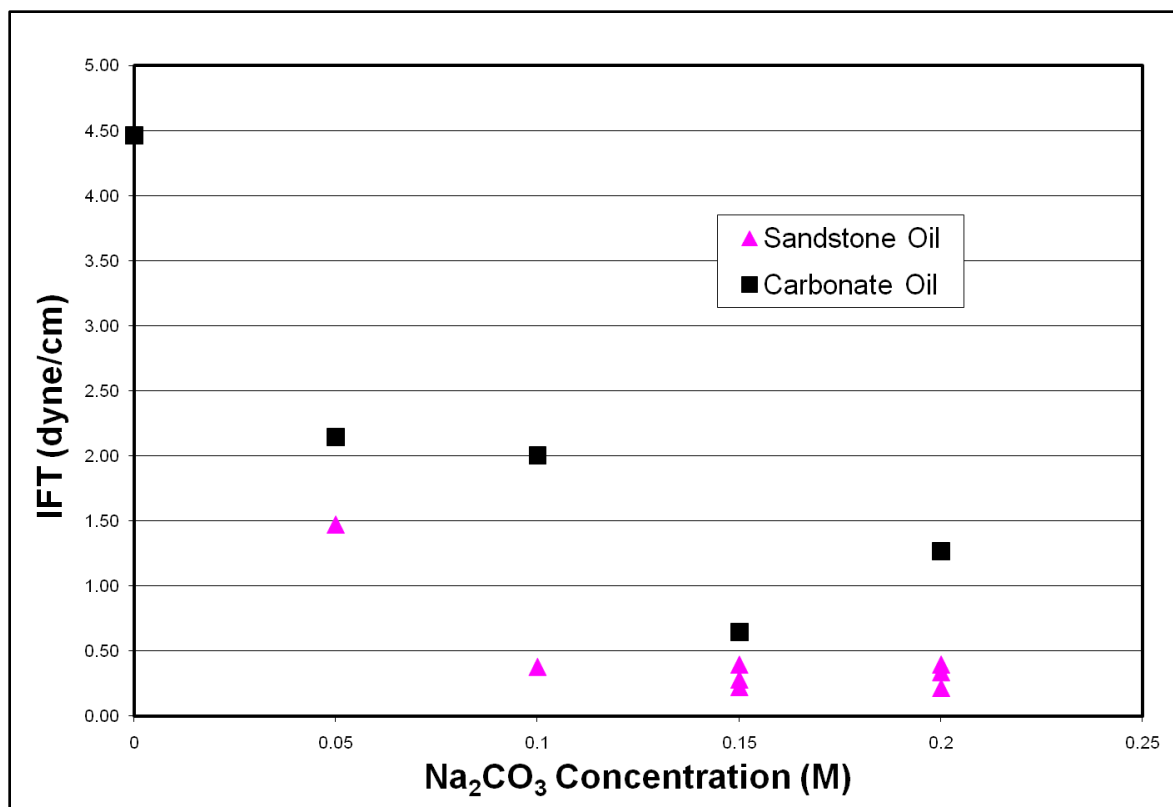


Figure 2-4: Sodium carbonate reduces IFT.

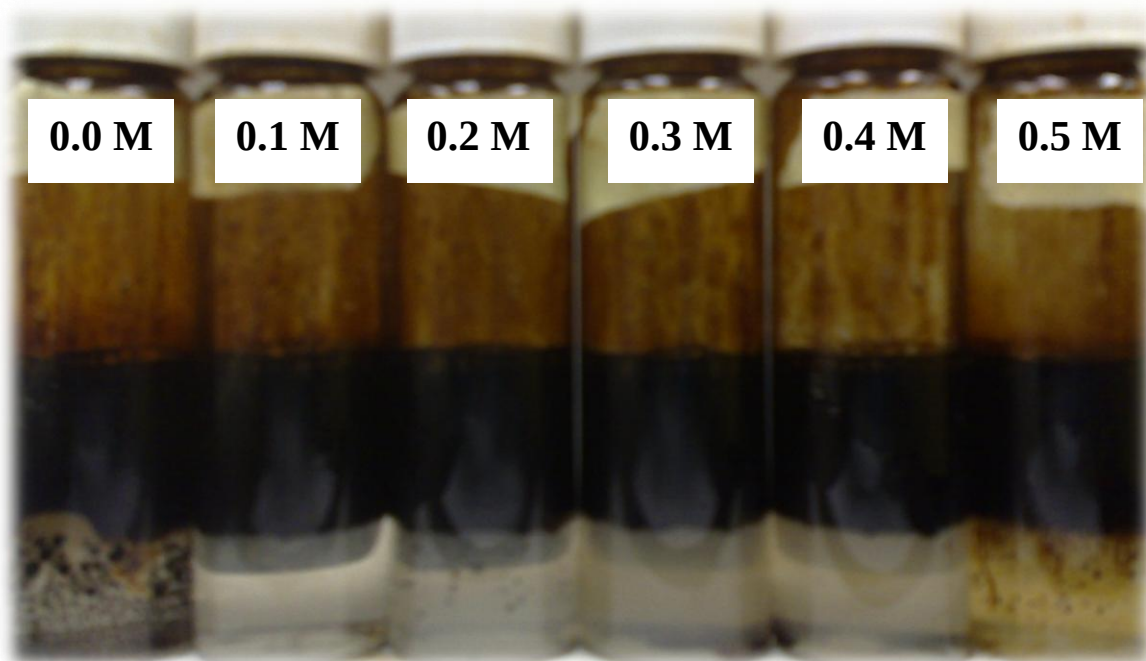


Figure 2-5: Samples of oil/brine (before being heated) with 0.20% ONYXIDE 200, and increasing sodium carbonate concentration.

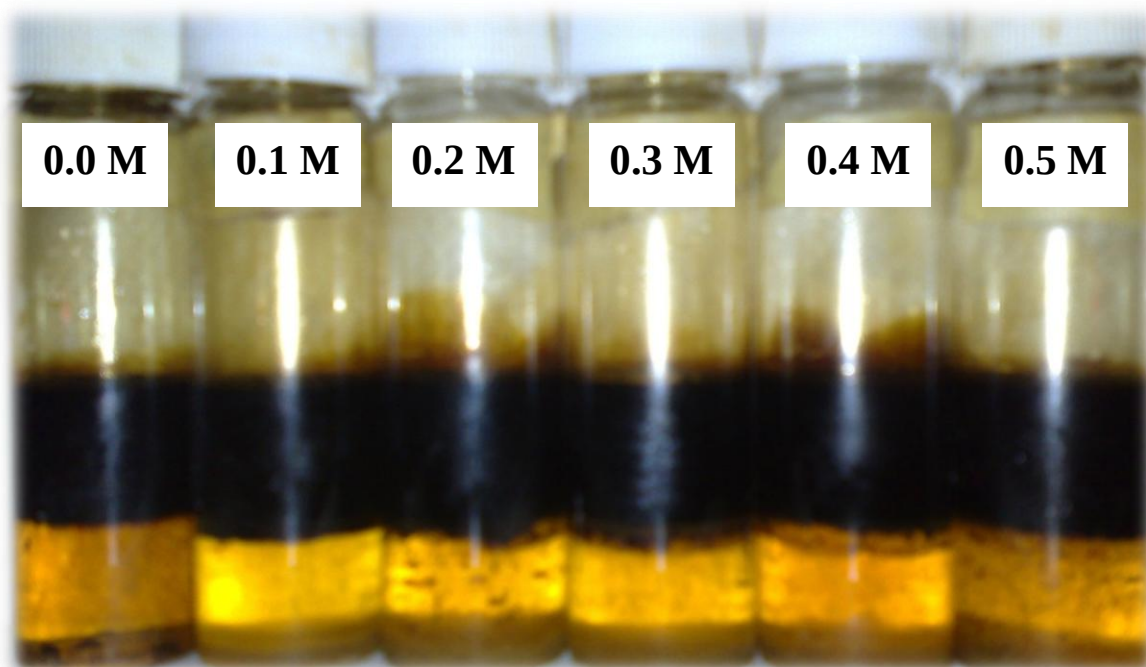


Figure 2-6: Samples of oil/brine (after being heated) with 0.20% ONYXIDE 200, and increasing sodium carbonate concentration.

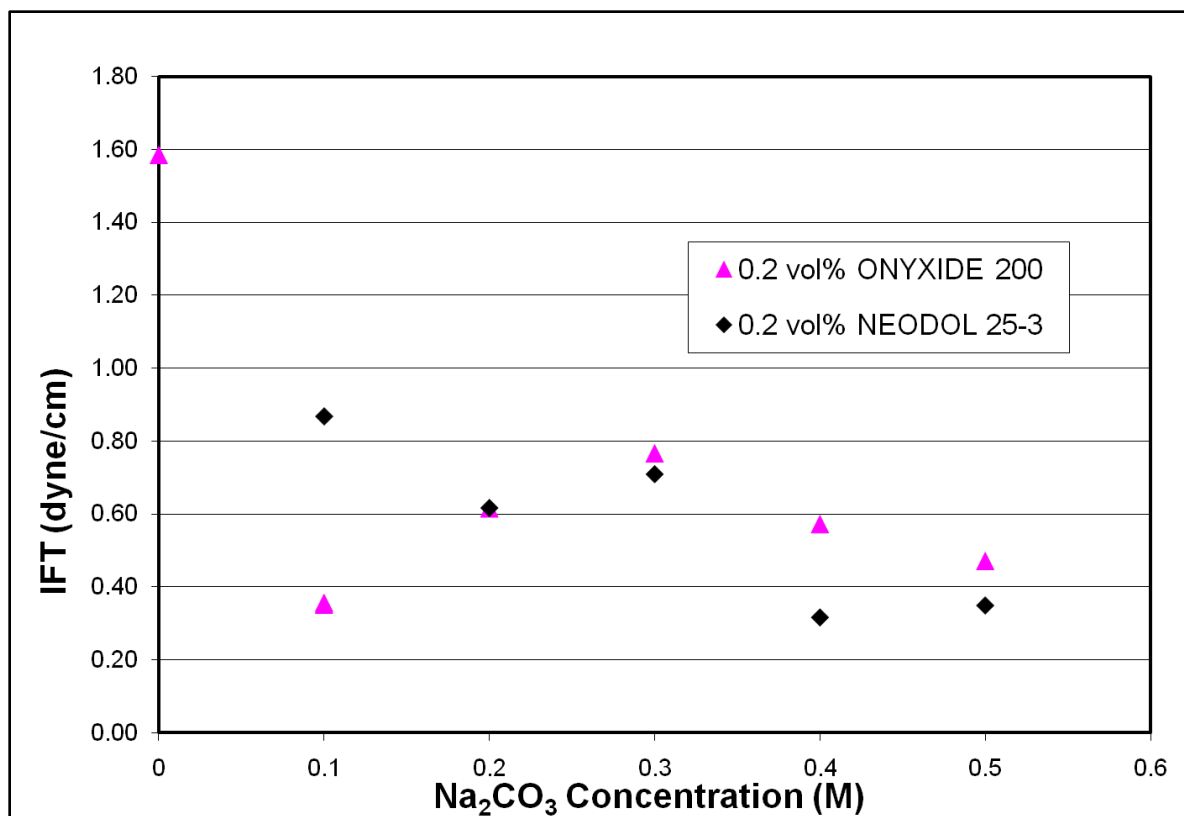


Figure 2-7: IFT reduction due to sodium carbonate concentration with two types of surfactants.

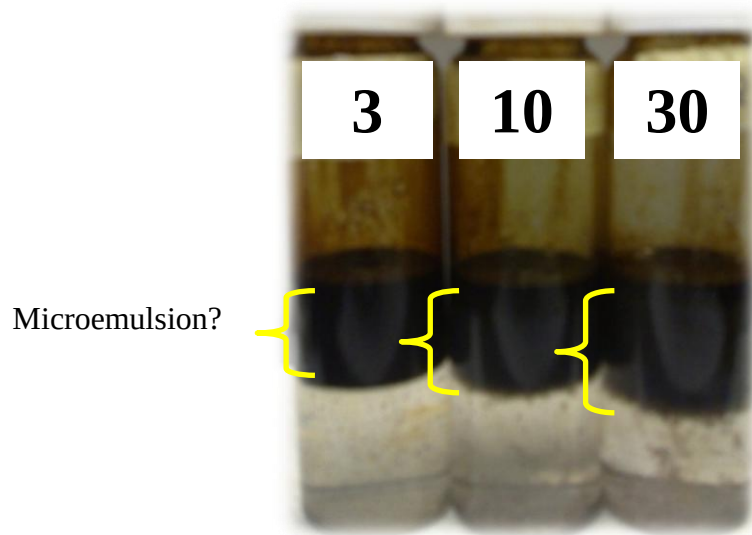


Figure 2-8: Samples of oil/brine, before being heated, with 0.20vol% ONYXIDE 200, 0.20 M of sodium carbonate and increasing WOR.

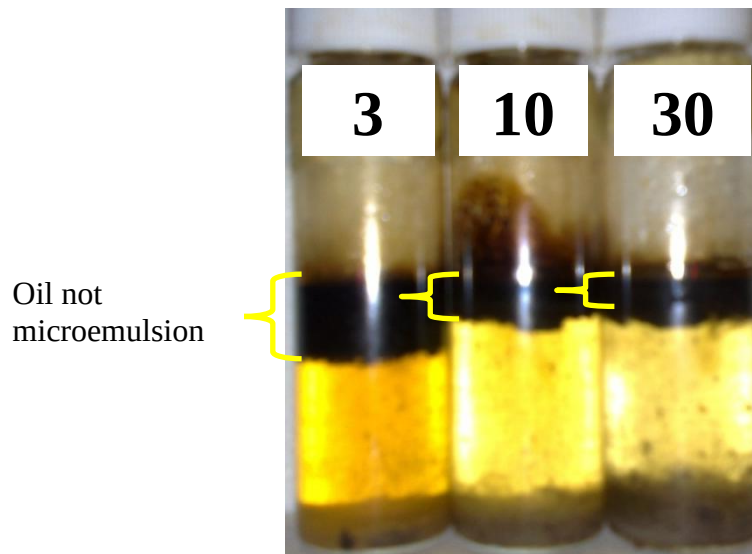


Figure 2-9: Samples of oil/brine, after being heated, with 0.20vol% ONYXIDE 200, 0.20 M of sodium carbonate and increasing WOR.

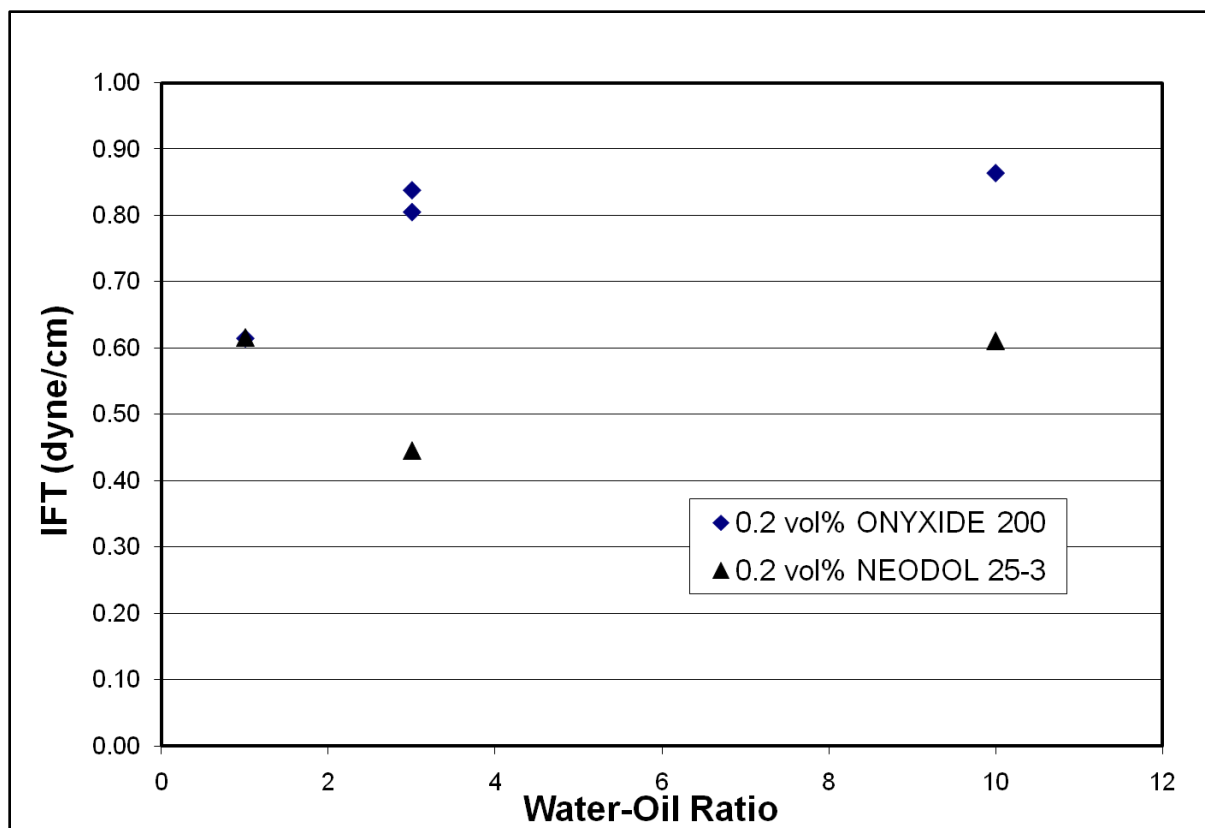


Figure 2-10: Negligible effect of WOR on IFT values.

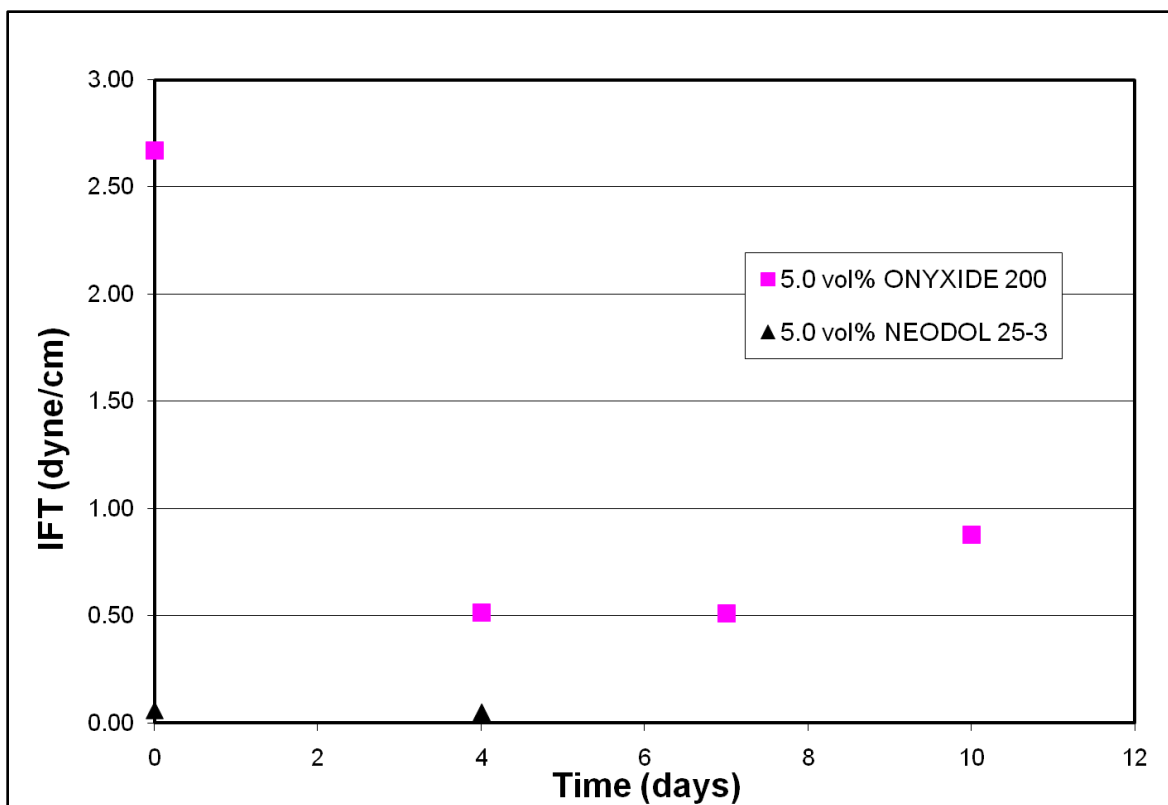


Figure 2-11: Thermal stability of two types of surfactants.

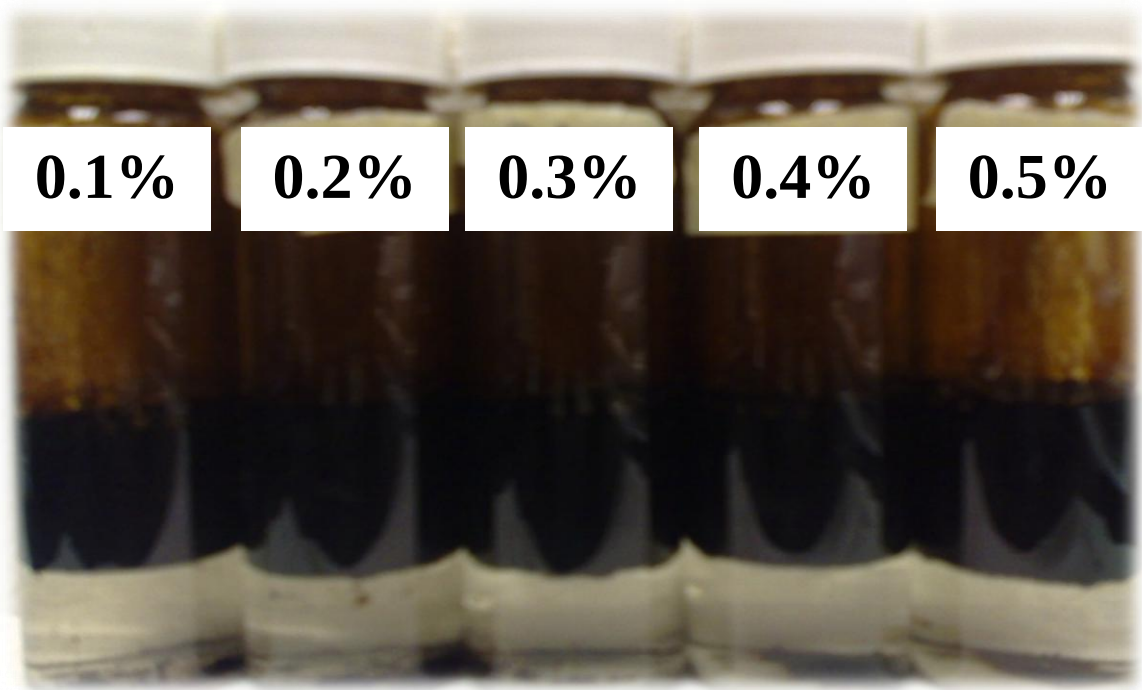


Figure 2-12: Samples of oil/brine, before being heated, with 0.20 M sodium carbonate and increasing surfactant concentration.

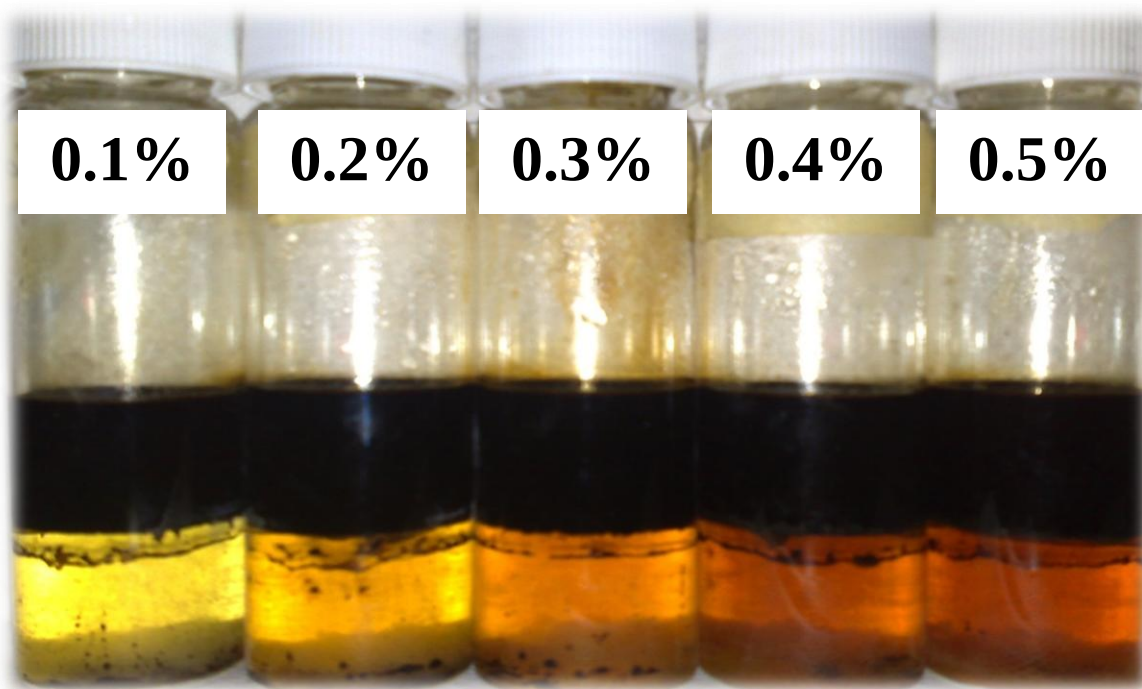


Figure 2-13: Samples of oil/brine, after being heated, with 0.20 M sodium carbonate and increasing surfactant concentration.

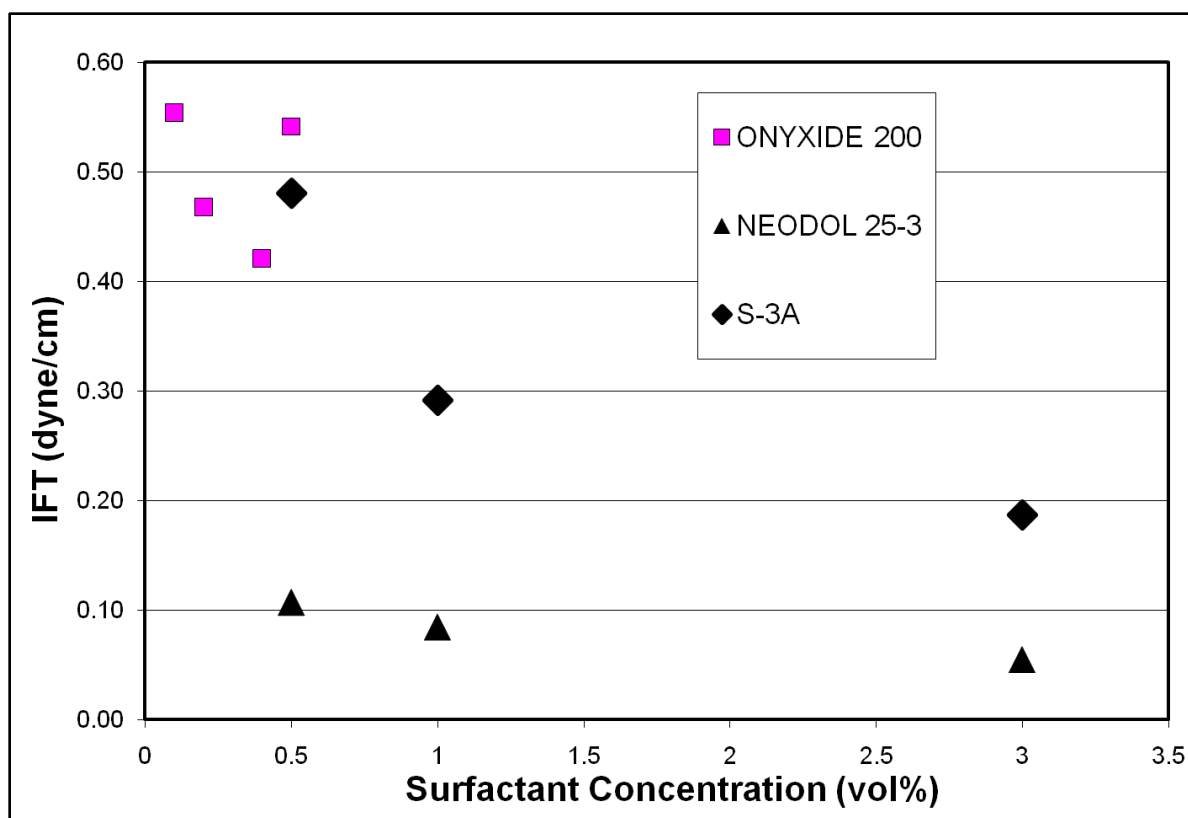


Figure 2-14: IFT reduction due to the increase of surfactant concentration.

Chapter 3

3. Micromodel Experiments

Micromodels are two-dimensional systems in which an etched silicon wafer is bonded to a glass wafer. Because micromodels are only two-dimensional, extrapolating results to 3-dimensional systems has to be done cautiously. Micromodels provide a tool of direct visualization of fluid interactions when conducting an experiment. The following section describes the process of fabricating the micromodels then discusses the micromodel experiments.

3.1. Micromodel Fabrication

The wafers used to make the micromodels are 4" Silicon wafers, K Prime, 4P <100> B S42565. Two pore networks from two masks: mask 1 and mask 2 were used to make the micromodels. Each mask contains a 5X5 cm pore network. Mask 1 contains a pore network similar to a Berea sandstone made from a repeated square pattern shown on Figure 3-1. The pattern is 490 μm by 400 μm and is repeated 102 times across each side of the network. Grain sizes range in length from 30 to 300 μm . Porosity is about 47%. The permeability of mask 1 micromodels was measured by Inwood (2008) and was of the order of 1 Darcy.

Mask 2 is sandstone with a repeated image shown on

Figure 3-2. The repeated image is 0.22X0.64 cm. The porosity is about 54% with grain size ranging from 125 to 250 μm in diameter. The permeability of mask 2 micromodels were measured by injecting distilled water at variable pressures and recording the corresponding flow rates, and at variable flow rates and recording the corresponding pressures as shown on Table 3-1. The permeability of the micromodels came out to be around 3 Darcy.

Most of the steps involved in making the micromodels take place in Stanford Nanofabrication Facility (SNF), shown in details in Appendix A.A, and they are the following (Stanford Nanofabrication Facility 2009):

3.1.1. Dehydration:

The wafers are dehydrated in a dehydrating oven for about 30 minutes. Dehydration is performed at 150°C and involves priming the wafers with hexamethyldisilazane (HMDS). The HMDS improves the photoresist adhesion to the wafers.

3.1.2. Coating:

The silicon wafers are then coated with Shipley 3612 photoresist in one of the svcoat tracks. Shipley 3612 is 1-1.6 μm thick. The following programs are chosen:

- Prime program: off
- Coat program: program # 8
- Prebake program: program # 2

3.1.3. Exposure:

At this step, a mask containing the pore network is needed. A karlsuss aligner is used to expose the wafers to the mask. A soft contact program with 2.6-seconds exposure time and 40- μm gap width was selected.

3.1.4. Developing:

The pore network has been transferred to the wafers at this point and they need to be developed to remove the excessive photoresist. Developing takes place in one of the svgdev tracks. The following programs are chosen:

- Developing program: program # 4
- Oven bake: program # 2

3.1.5. Etching:

After developing the wafers, the wafers are taken out from the photolithography area. They are etched in the stetch which is an inductive charged plasma etcher. For our case, we use a deep etching recipe. The input etching time depends on the desired etching depth. The wafer is etched for a specific time (say 5 minutes). Then, the etched depth is measured using a microscope, the P2, or the zygo. The etching rate is calculated and then etching time is chosen. One thing to note about the etcher is that it does not etch uniformly. It etches the most at the edges. In the micromodels used in this work, the etching depth is about 30 μm at the middle and 40 μm at the edges.

3.1.6. Anodic Bonding:

After etching the wafers, four ports are drilled at the corners of the network in the Stanford crystal shop. They are then cleaned in the wbsilicide wet bench in the SNF along with 4" Pyrex glass wafers in a hot bath (120°F) of 9:1 sulfuric acid:hydrogen peroxide. The silicon wafers are anodically bonded with the glass wafers under 1200 volts. The bonding apparatus consists of a hot plate, a voltage source, and a voltage plate. The hot plate is connected to the positive voltage source and the voltage plate is grounded. The etched silicon wafer is heated by itself for 45 minutes on the hot plate at a temperature of 350°C. the wafer is then dusted to ensure that no particles reside on it. After that, a clean glass wafer is placed on top of the silicon wafer for two minutes. The

temperature is then reduced to 300°C and the voltage plate is placed on top of the glass wafer as shown on Figure 3-3. It is recommended to apply evenly distributed weight on the voltage plate. After that, the voltage source is turned on for 50 minutes to have a complete bonding (Hornbrook 1991). Figure 3-4 shows a micromodel with the four ports (surrounded by the red circles), two fractures (shown by the solid green lines), and the 5X5 cm pore network.

3.2. Experimental Setup

Figure 3-5 shows the schematic of the main components in the experiments. The injection part is made of a syringe pump that is filled with distilled water. The pump is connected by plastic tubes to bombs filled with the injectants. The tubes are connected to the bottom of the bombs if they carry the heavier fluid and to the top if they carry the lighter fluid. The data gathering part consists of a microscope and a camera. The microscope is Nikon Eclipse ME 600 (reflected light) with 40X, 100X, and 200X magnifications. The camera is a Nikon Coolpix P5100. The micromodel along with its holder is shown on Figure 3-6. It has to be noted that the injected fluid has to go through the injection port and the o-ring dead volume. Each port accounts for 0.1 ml in terms of volume which is more than twice the micromodel pore volume (0.041 ml for Mask I micromodels and 0.047 ml for Mask II micromodels). This eventually increases the uncertainty in volumetric analysis and thus image analysis is the only technique used to quantify recovery.

3.3. Experimental Procedure

Several micromodel experiments were conducted. The microscopic images are collected as shown on Figure 3-7. The micromodel area is divided into 25 squares. One image is taken in each square with 100X and 200X magnification. In the results, a representative image after each process is displayed.

In each micromodel experiment, CO₂ is first injected to displace air if the micromodel is new. After that, distilled water is injected, then brine, then oil to obtain initial oil saturation. If the micromodel is used, it is cleaned with toluene to dissolve/remove residing fluids. Iso-propanol is then injected to push the toluene out followed by distilled water, brine, and then oil. Injection rates for a water flood or a surfactant flood was held at a constant rate to achieve a Darcy velocity of 1 m/day. Before stating the experiment procedures, the image analysis method has to be described.

3.3.1. Image Analysis

Matlab image analysis tools were utilized to quantify the remaining oil after each flooding stage in the experiment. The code, shown on Appendix A.B, was initially constructed by Buchgraber (2008) and then modified to enhance its speed. The main principle of the code is to convert the Red Green Blue (RGB) image to a binary image (black and white). The RGB cutoff values for oil is determined and then inputted into the code. The code replaces pixels' values above the cutoffs to one (white) and below the

cutoffs to zero (black). The number of zeros indicates how much “black” is in the image. It has to be noted that the grain edges and sometimes parts of the etched surface of the micromodel have the same RGB values as the oil. Hence, blackness due to the edge effect (and etched surface) has to be subtracted from the “black” number. The edge effect is determined by running the image analysis on a waterflooded micromodel. The average “black” number in this case is used as the edge effect. For mask 1 micromodels, the edge effect is about $32.6 \pm 4\%$ while it is about $17.7 \pm 3\%$ for mask 2 micromodels. After subtracting the edge effect, the new “black” number is divided by the porosity (ϕ) of the micromodel to obtain oil saturation (S_o) as the following:

$$S_o = \frac{\text{Black} - \text{Edge Effect}}{\phi} \quad (3-1)$$

Results from the various experiments are now discussed.

3.3.2. Experiment I

This is an early experiment where S-3A was injected in a secondary recovery mode. The pore network is obtained from mask 1. Figure 3-8 shows a micromodel image after an oil flood. Right after the oil flood, a 5% filtered S-3A solution with 0.2M Na_2CO_3 was injected (Figure 3-9). The solution was filtered because it had a lot of suspended particles that might cause blockage in the micromodel. Heating the sample did not dissolve these particles. It can be seen in Figure 3-9 that some of the oil was not recovered (29% remained) and that irreducible water occupied the small pores and throats of the micromodel indicating that the model is water wet. Thus, 2% unfiltered S-3A was injected and it did recover most of the oil where only 10% remained (Figure 3-10).

3.3.3. Experiment II

NEODOL 25-3 was used in a tertiary recovery mode. The pore network in this micromodel is from mask 2. Figure 3-11 shows the microscopic image after an oil flood (59% initial oil saturation). After that, about 1 pore volume brine was injected to recover some of the oil as seen in Figure 3-12 (15% of oil remained). Then, 1% NEODOL 25-3 with 0.2 M Na_2CO_3 was injected. All the oil was recovered with the NEODOL as in Figure 3-13 (5% of oil remained). However, a second phase was observed at this stage. This phase is more likely to a surfactant or a microemulsion phase.

3.3.4. Experiment III

In this set of experiments, spontaneous imbibition is investigated. NEODOL 25-3 is injected in a secondary mode at one end of a channel of the micromodel (injection port) while keeping all the other ports open including the port at the other end of the injection channel. NEODOL 25-3 flows through the channel and imbibes into the strongly water wet micromodel. Spontaneous imbibition was performed for one day followed by a forced imbibition for another day by closing the port at the other end of the channel. Two

experiments were conducted in this set: one held horizontally and the other held vertically.

3.3.4.1. Horizontal Set-up

The purpose of this experiment is to have it as a frame of reference for the vertical experiment. Image analysis indicates that the micromodel was 54% saturated with oil after the oil flood (Figure 3-14). About 33% of oil remained after the spontaneous imbibition (Figure 3-15). Forced imbibition recovered more oil and only 14% oil remained in the micromodel (Figure 3-16).

3.3.4.2. Vertical Set-up

While all the previous experiments were conducted horizontally, the micromodel was held vertically during surfactant injection in this experiment to include gravity effect at low IFT values. Table 3-2 shows the Bond number calculations for this experiment. At 1 vol% of NEODOL 25-3, the pore size has to be at least about 900 microns to achieve a Bond number of 10 as shown by Part A of the table. For an average pore size of 141 microns however, the Bond number is 0.25. Thus, an assumption was made that the pore size (d) in the Bond number can be used as the oil drop vertical diameter. In the horizontal experiment, the Bond number is about 0.015, using the etching depth of 35 μ m as d , that shows that gravity effects are negligible in a horizontal set-up.

The experiment started with 54% of oil saturating the micromodel (Figure 3-17). The spontaneous imbibition recovers some of the oil and 32% remained which is a 1% marginal improvement compared to the horizontal set-up (Figure 3-18). The 1% however, falls in the uncertainty range of the edge effect and a solid conclusion cannot be drawn from this number. The forced imbibition recovers most of the oil and only 6% remains at the end of the experiment (Figure 3-19). This shows an 8% marginal improvement over the horizontal set-up indicating that buoyancy assisted in recovering more oil. The remaining oil drops have very small diameters leading to very small Bond numbers. Hence, gravity is not sufficient to displace the remaining oil out of the micromodel.

3.3.5. Experiment IV

The purpose of this experiment is to mimic current conditions of waterflooded reservoirs. In this experiment, the micromodel was waterflooded after an initial oil saturation of 48% (Figure 3-20). Oil remaining after the waterflood is about 34% (Figure 3-21). A solution of NEODOL 25-3 was injected at a tenth of the regular injection rate to replace the water contacting the oil. The idea is to leave the surfactants contacting the oil to lower the IFT. The micromodel is held vertically for four days and 24% of oil remained (Figure 3-22). The injection rate was increased to the regular injection rate for 5 days and only 9% of the oil remained (Figure 3-23). Bond numbers for the remaining oil drops are much smaller than the cutoff and thus gravity effect is not strong enough to displace them.

Table 3-1: Permeability calculations of mask 2 micromodels.

viscosity (cp / Pa.s)		1	0.001	
Length (cm / m)		5	0.05	
Area (cm*micro m / m²)		175	1.75E-06	
P (psi)	P (Pa)	Q (ml/min)	Q (m³/s)	k (m²)
15	103421.35	0.94	1.57E-08	4.33E-12
20	137895.14	1.35	2.25E-08	4.66E-12
10	68947.57	0.56	9.33E-09	3.87E-12
4	27579.03	0.1	1.67E-09	1.73E-12
2	13789.51	0.01	1.67E-10	3.45E-13
15	103421.36	1	1.67E-08	4.60E-12
Average			3.26E-12	3.26 Darcy

Table 3-2: Bond number calculations for the vertical experiment.

A: Minimum pore size for 1% NEODOL 25-3 to achieve a Bond number of 10		B: Bond number for the average pore size of 141 microns	
Water density (g/cc)	1	Water density (g/cc)	1
Oil density (g/cc)	0.893	Oil density (g/cc)	0.893
gravity acceleration (m/s ²)	9.81	gravity acceleration (m/s ²)	9.81
pore size (m)	8.97E-04	pore size (m)	1.41E-04
IFT (N/m)	8.46E-05	IFT (N/m)	8.46E-05
Bond Number		Bond Number	
10.00		0.25	

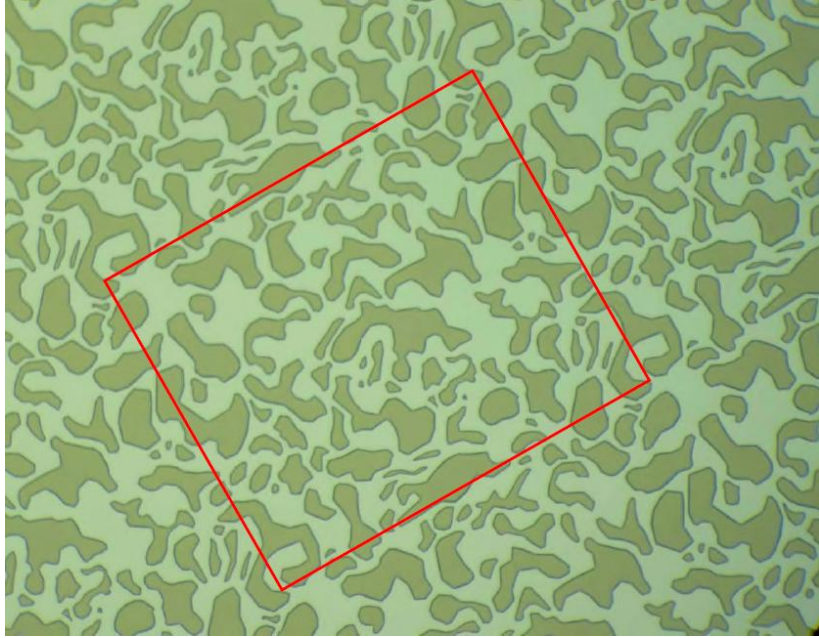


Figure 3-1: Repeated square pattern in mask 1 (Inwood 2008).

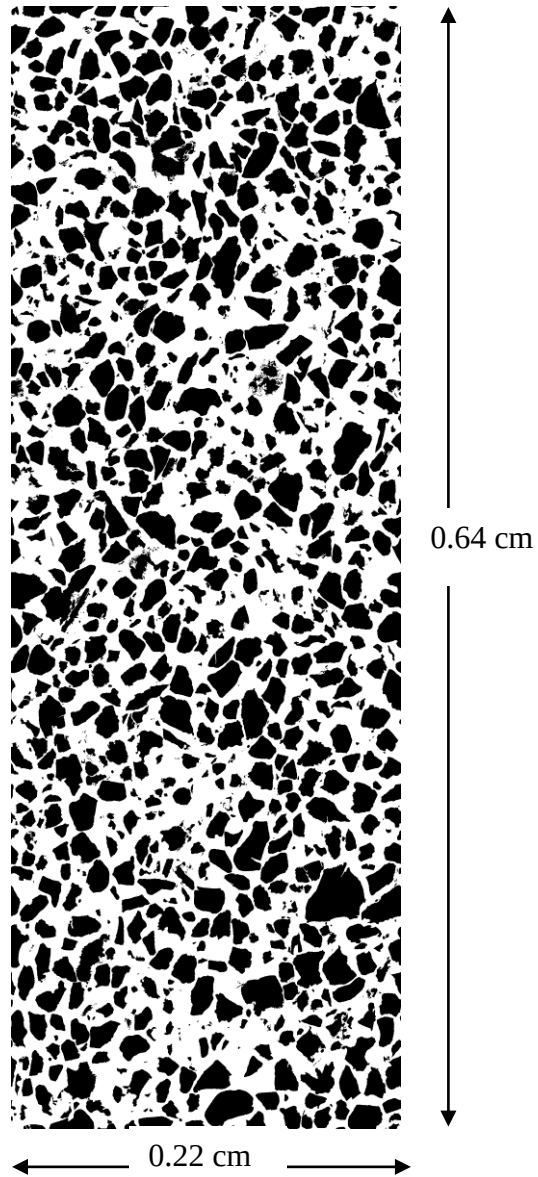


Figure 3-2: Repeated pattern in mask 2.

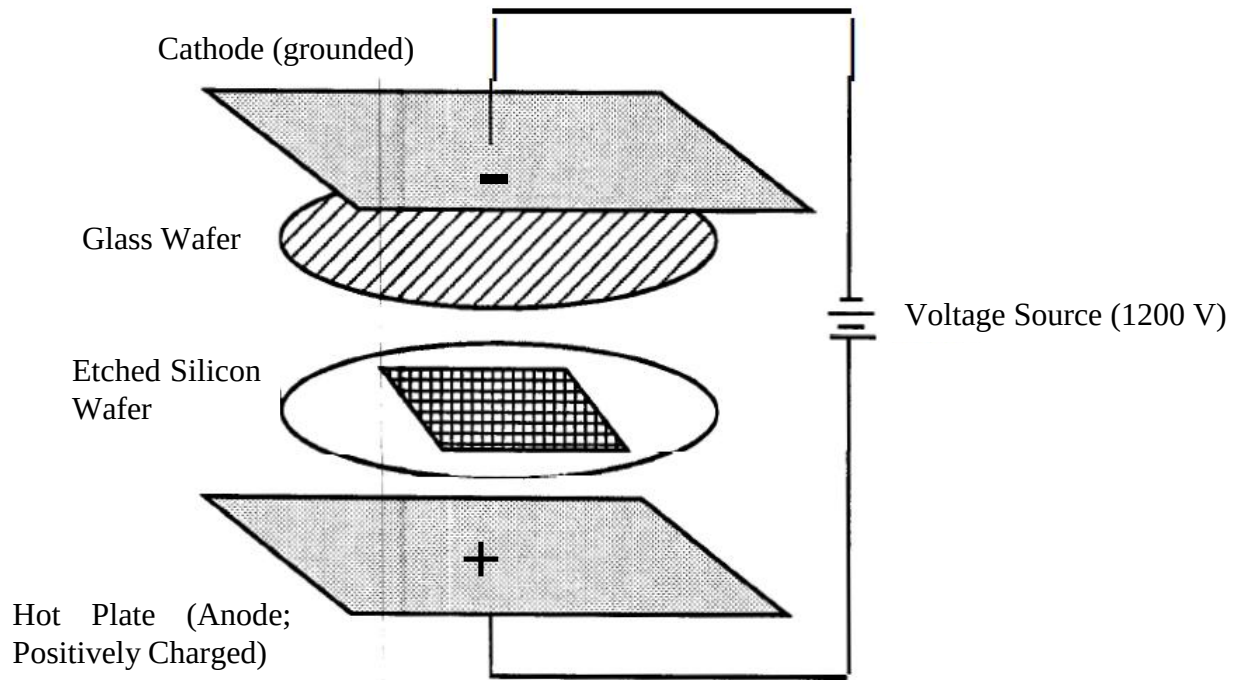


Figure 3-3: Bonding apparatus (Hornbrook 1991).

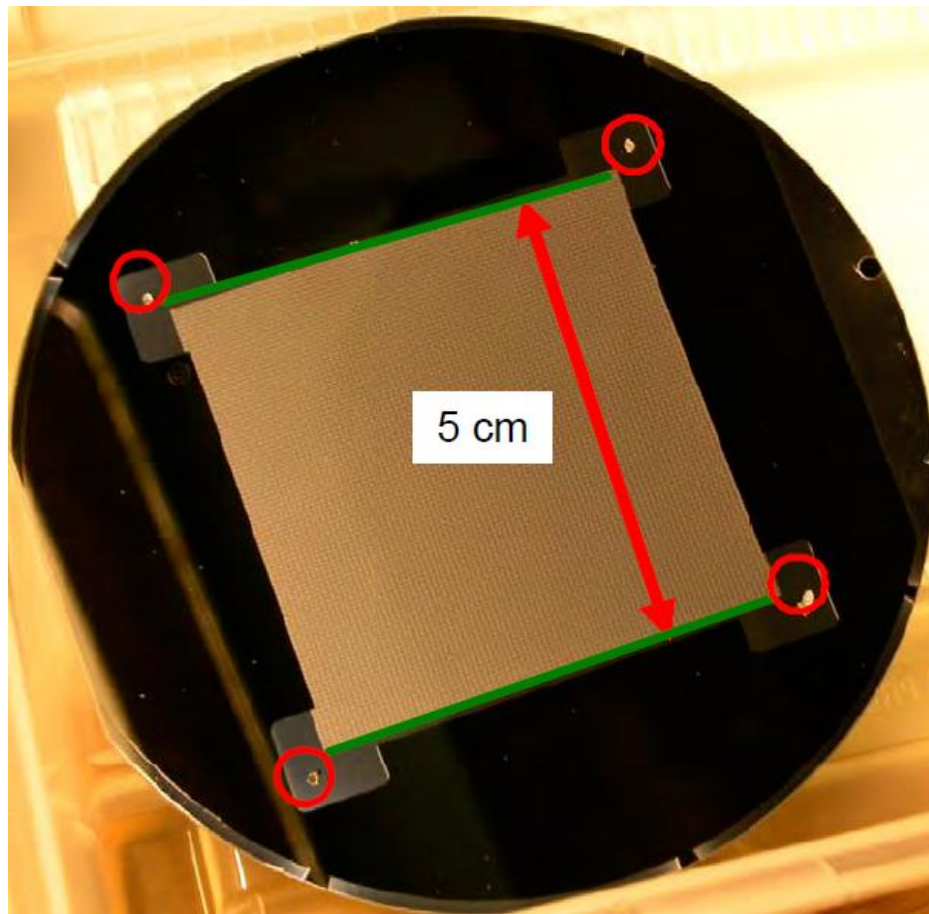


Figure 3-4: A typical micromodel (Inwood 2008).

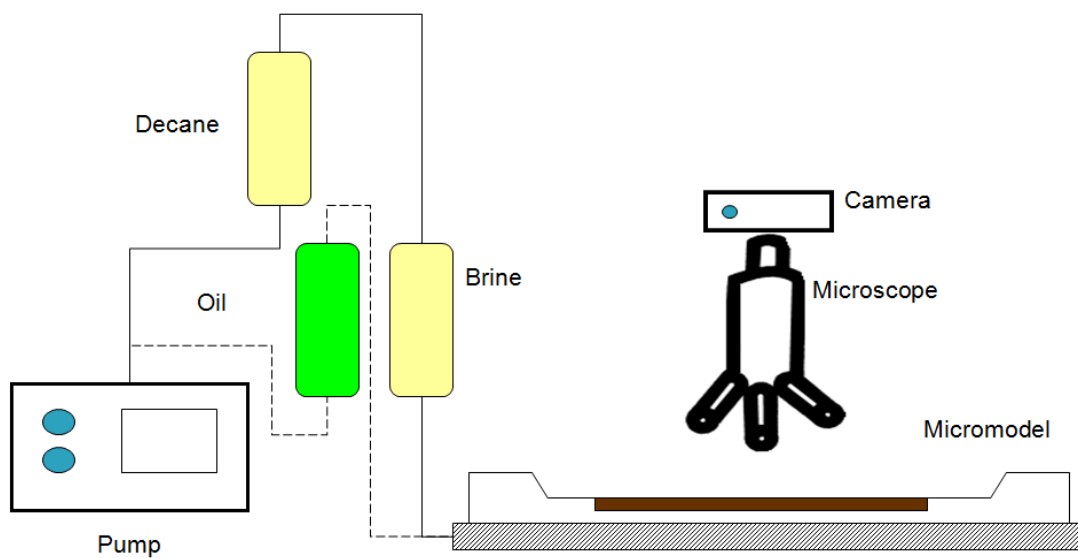
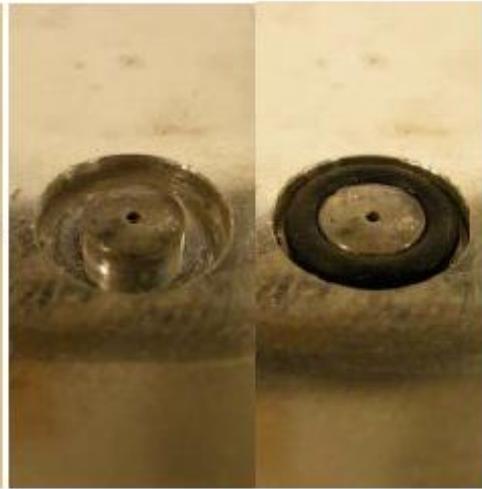


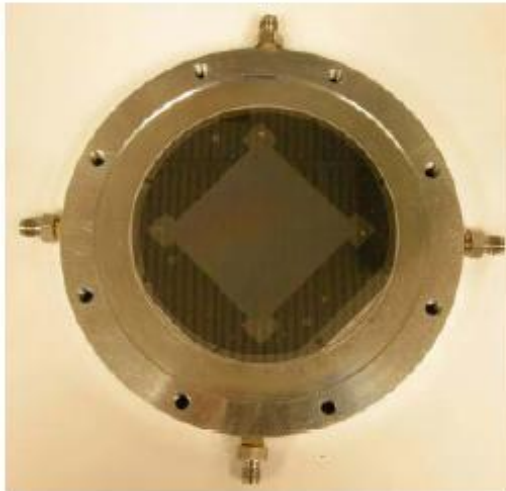
Figure 3-5: Schematic of apparatus.



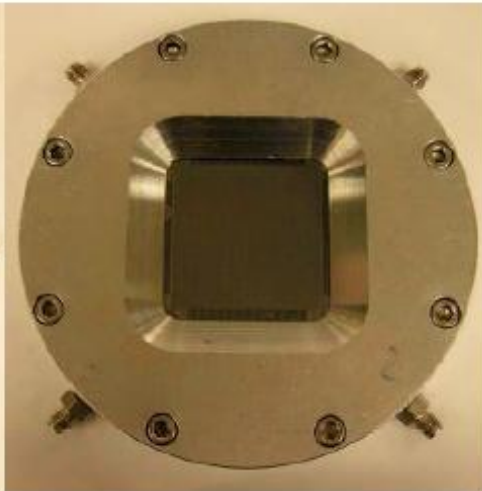
(a)



(b)

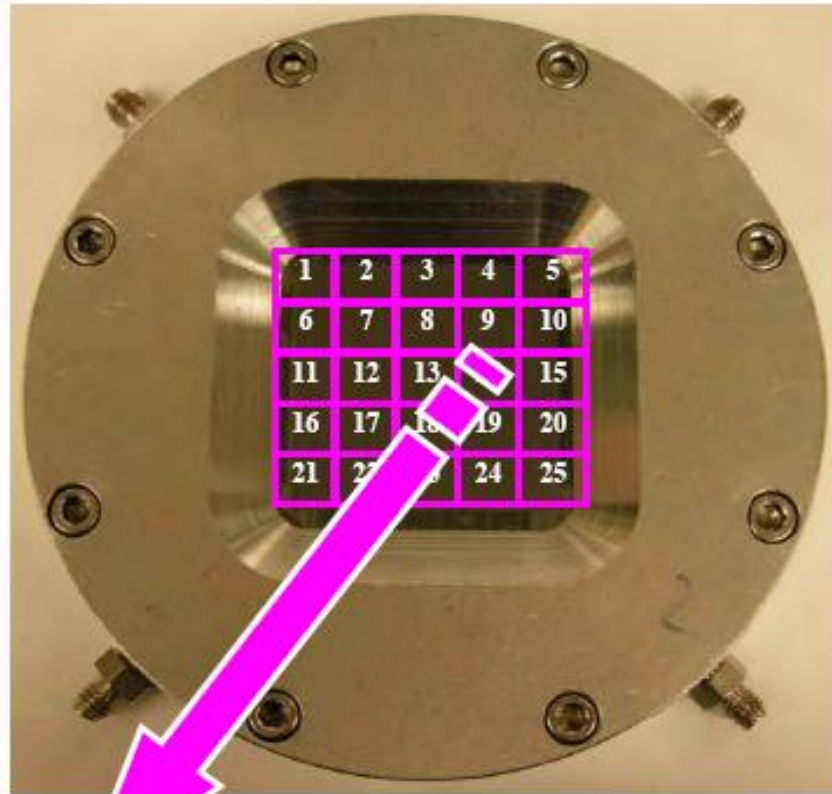


(c)



(d)

Figure 3-6: The micromodel holder (Inwood 2008).



(a)

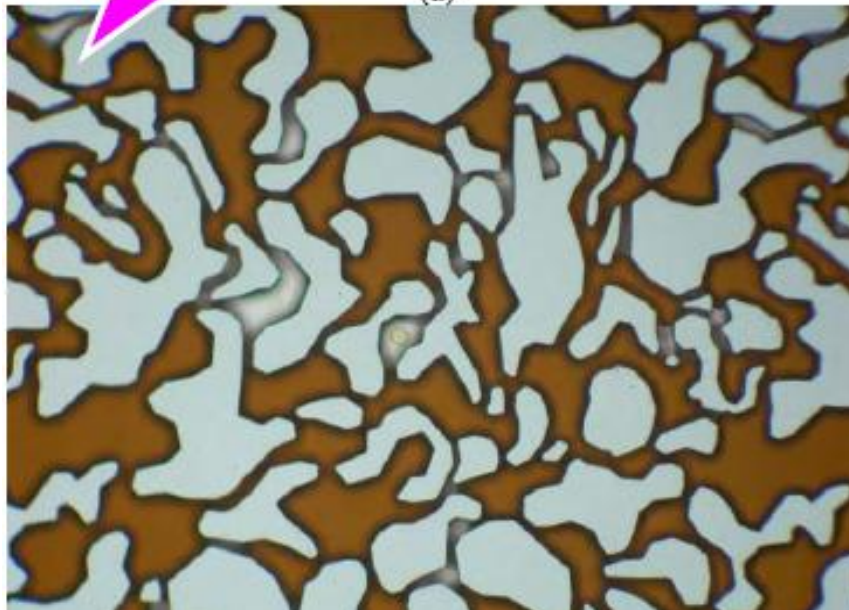


Figure 3-7: 25 microscopic images are obtained (Inwood 2008).

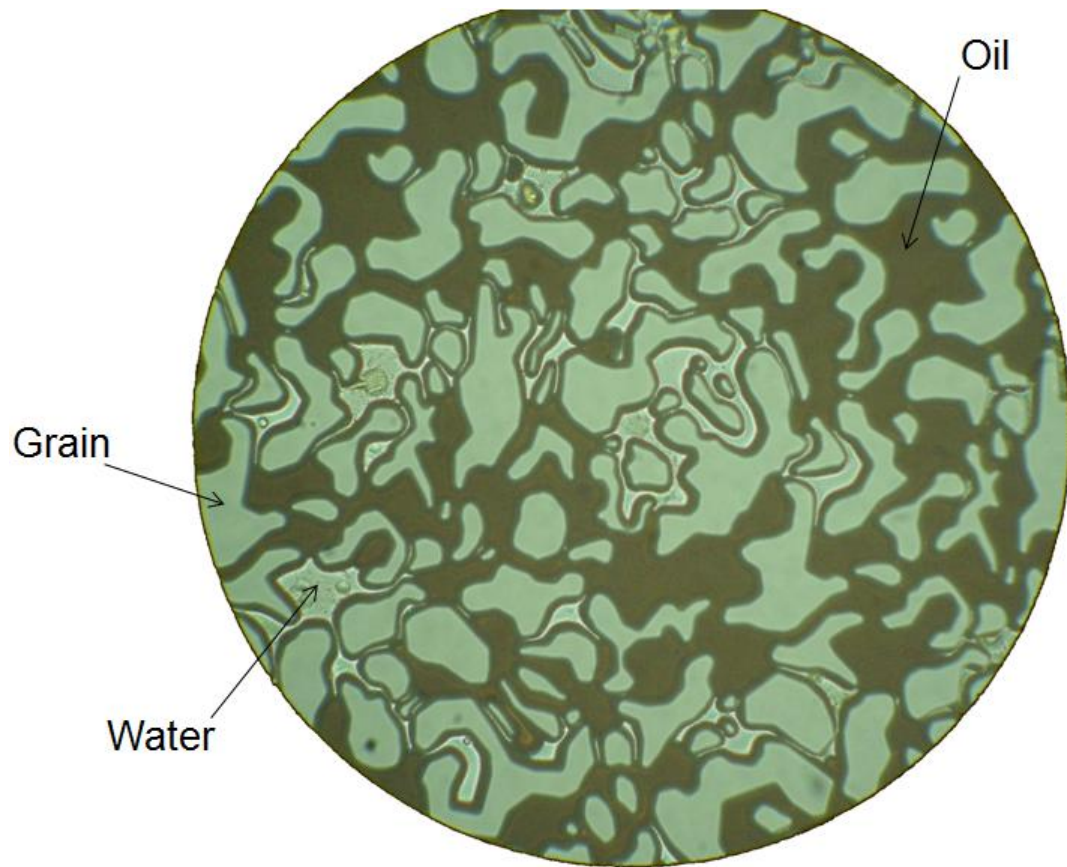


Figure 3-8: 200X microscopic image after the oil flood.

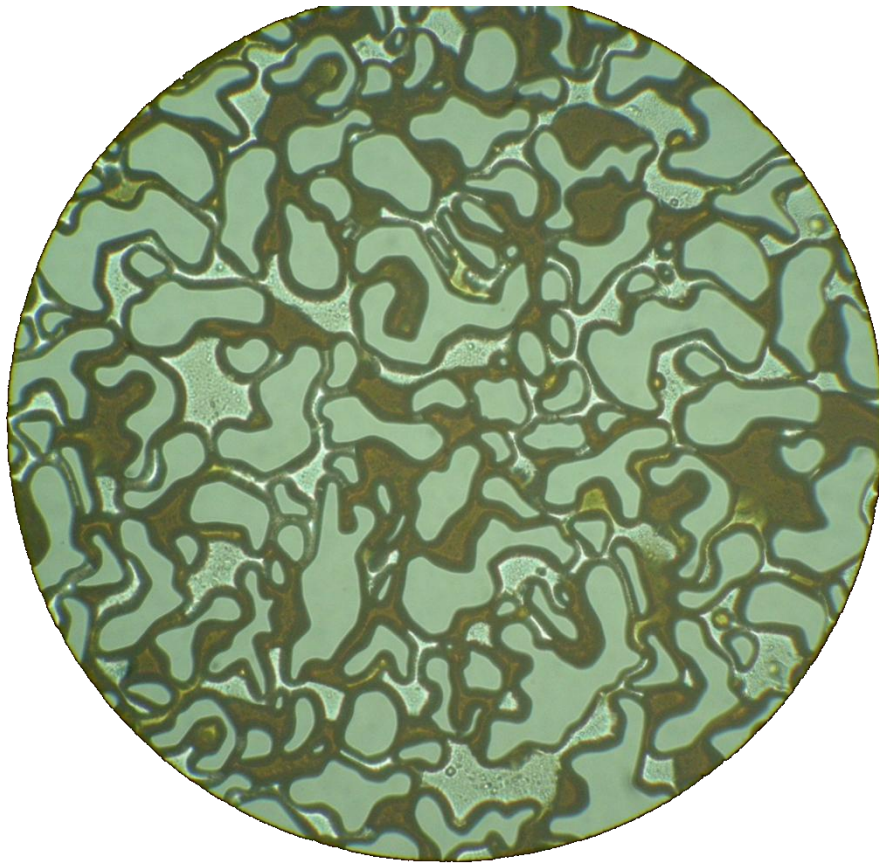


Figure 3-9: 200X microscopic image after the 5% filtered S-3A flood.

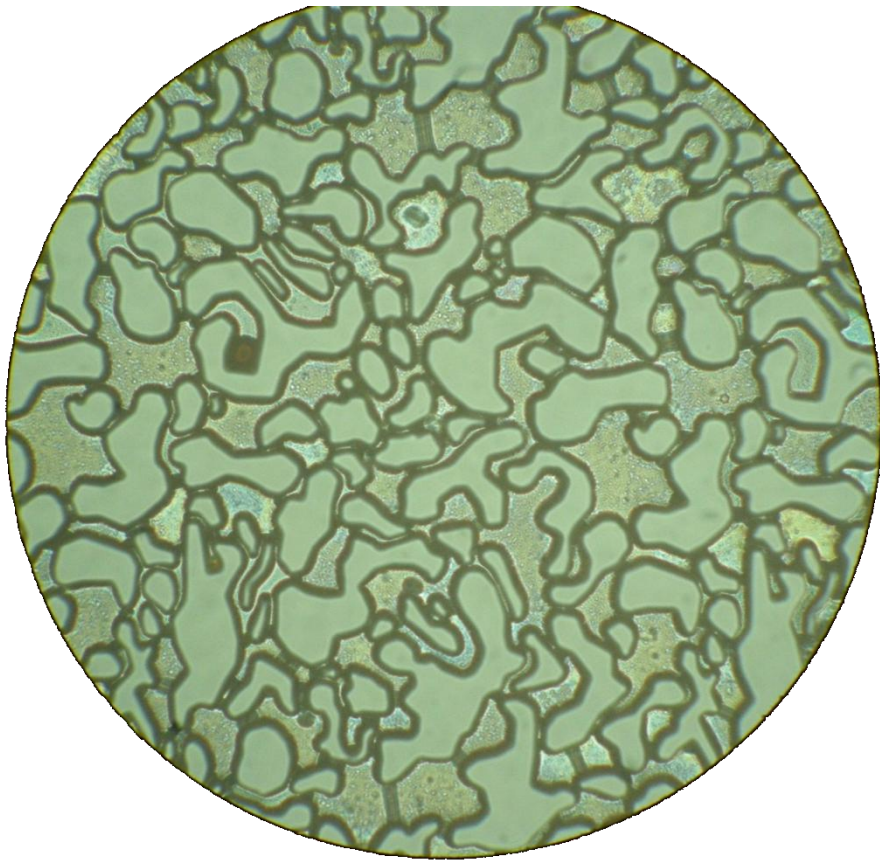


Figure 3-10: 200X microscopic image after the 2% unfiltered S-3A flood.

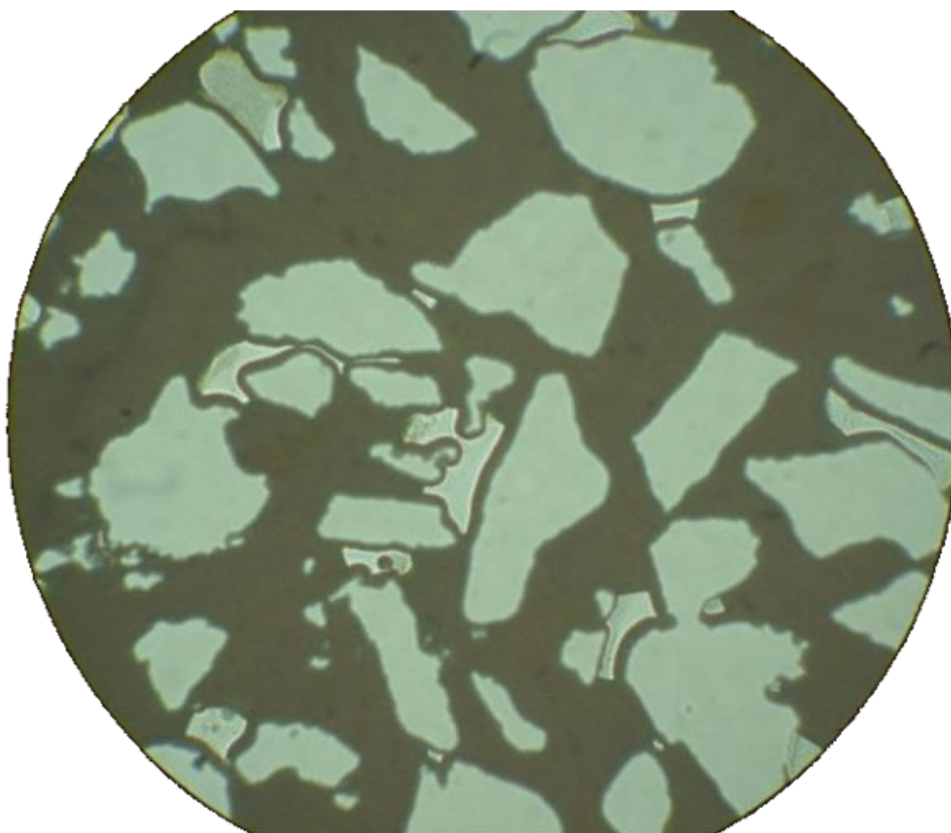


Figure 3-11: 200X microscopic image of the micromodel after the oil flood.

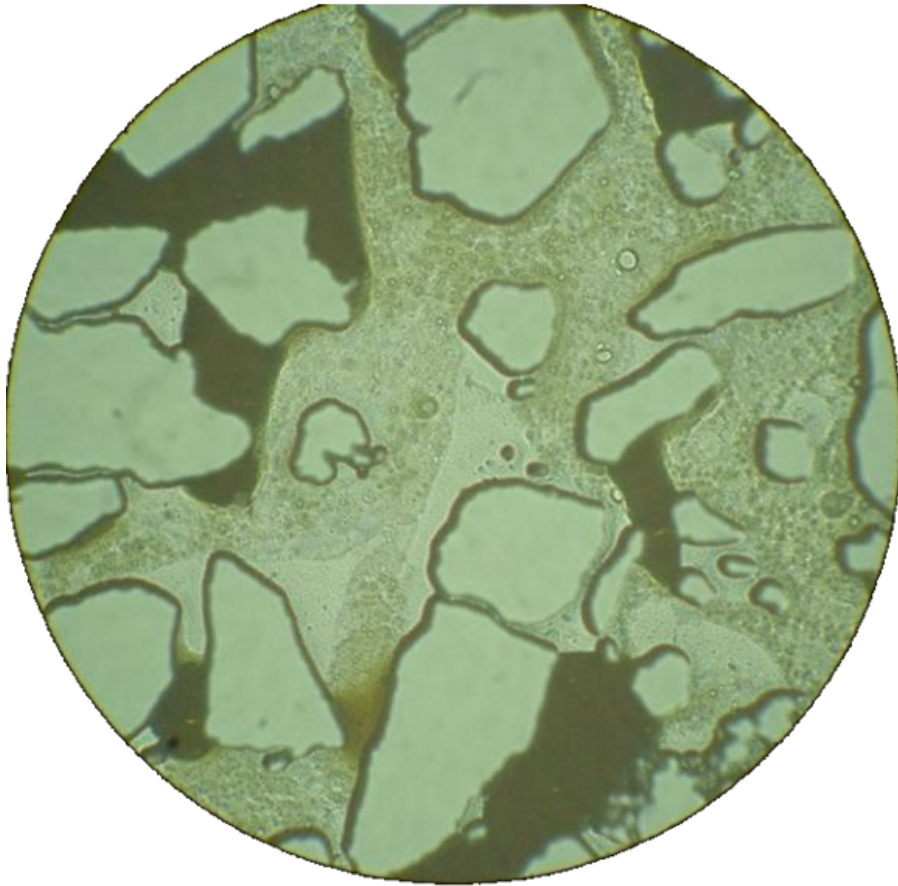


Figure 3-12: 200X microscopic image after the waterflood.

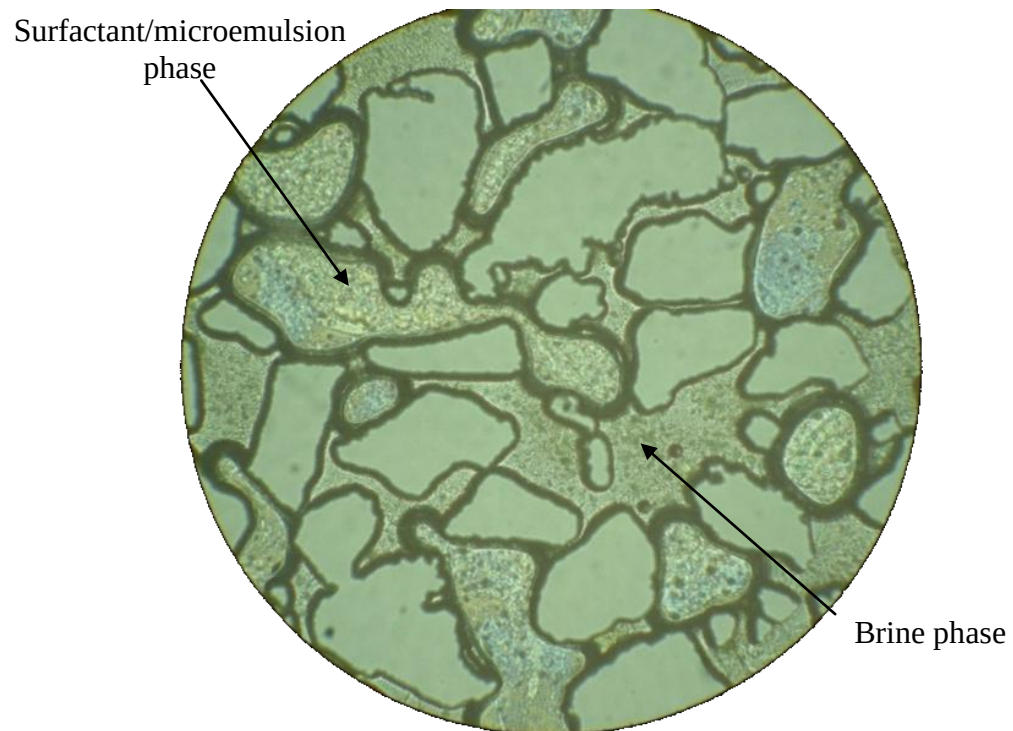


Figure 3-13: 200X microscopic image after the NEODOL 25-3 flood.

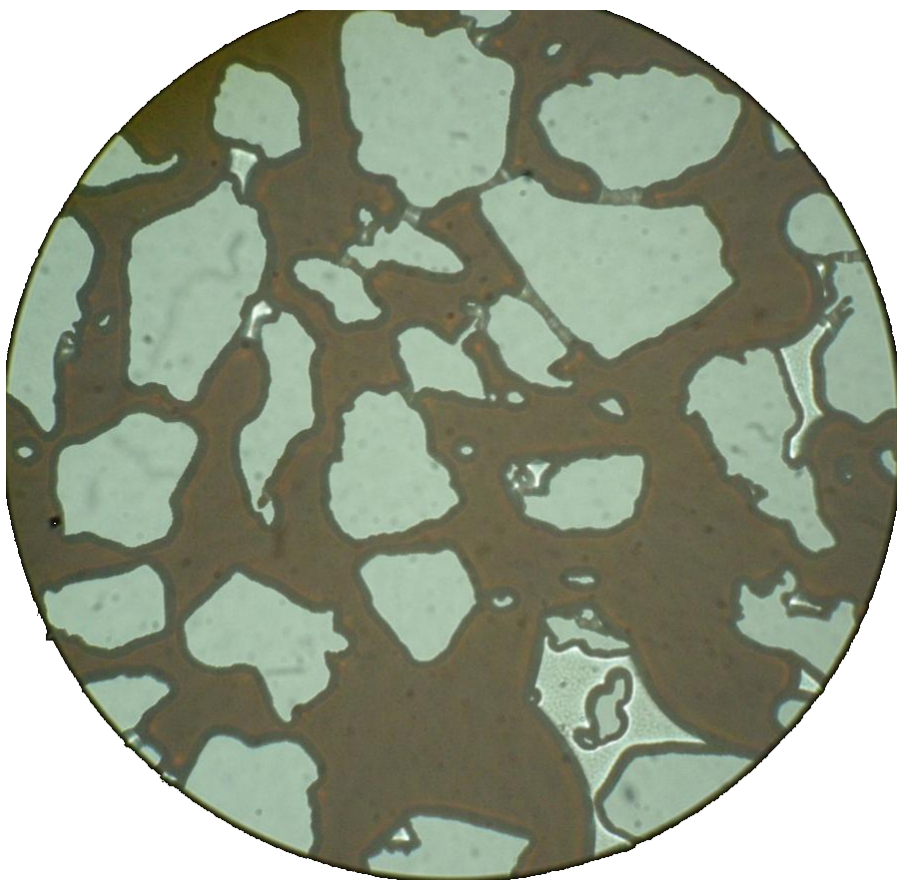


Figure 3-14: 200X microscopic image after the oil flood (horizontal set-up).

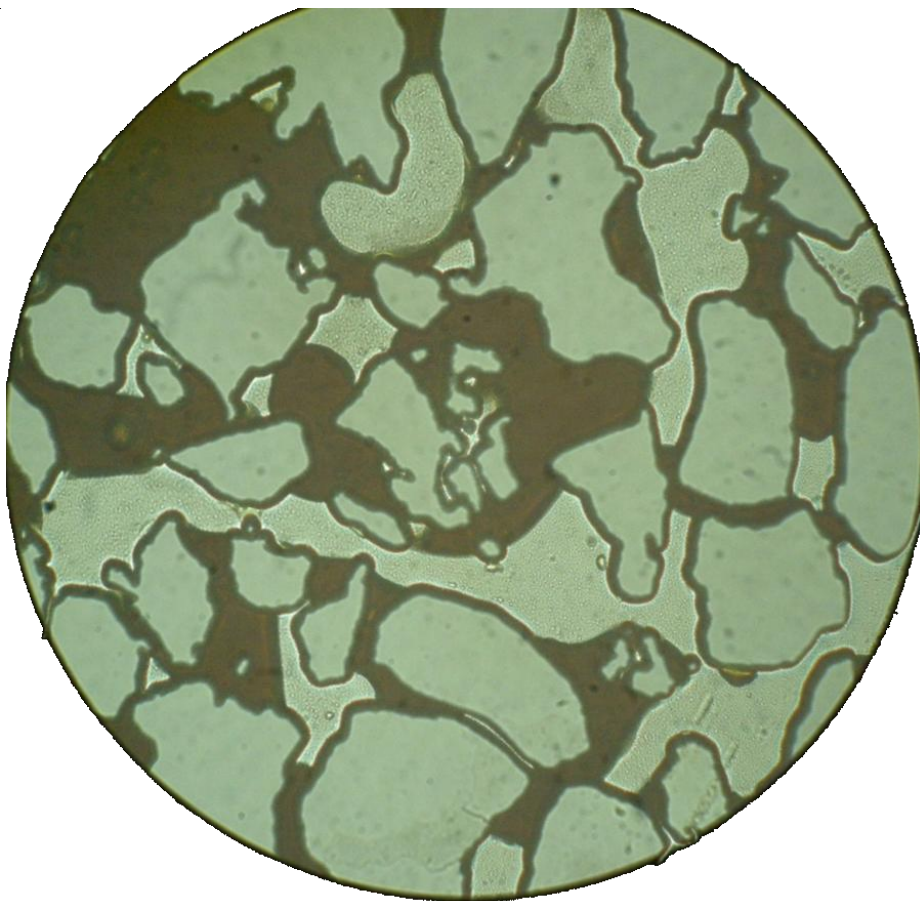


Figure 3-15: 200X microscopic image after the NEODOL 25-3 flood (horizontal set-up, spontaneous imbibition)

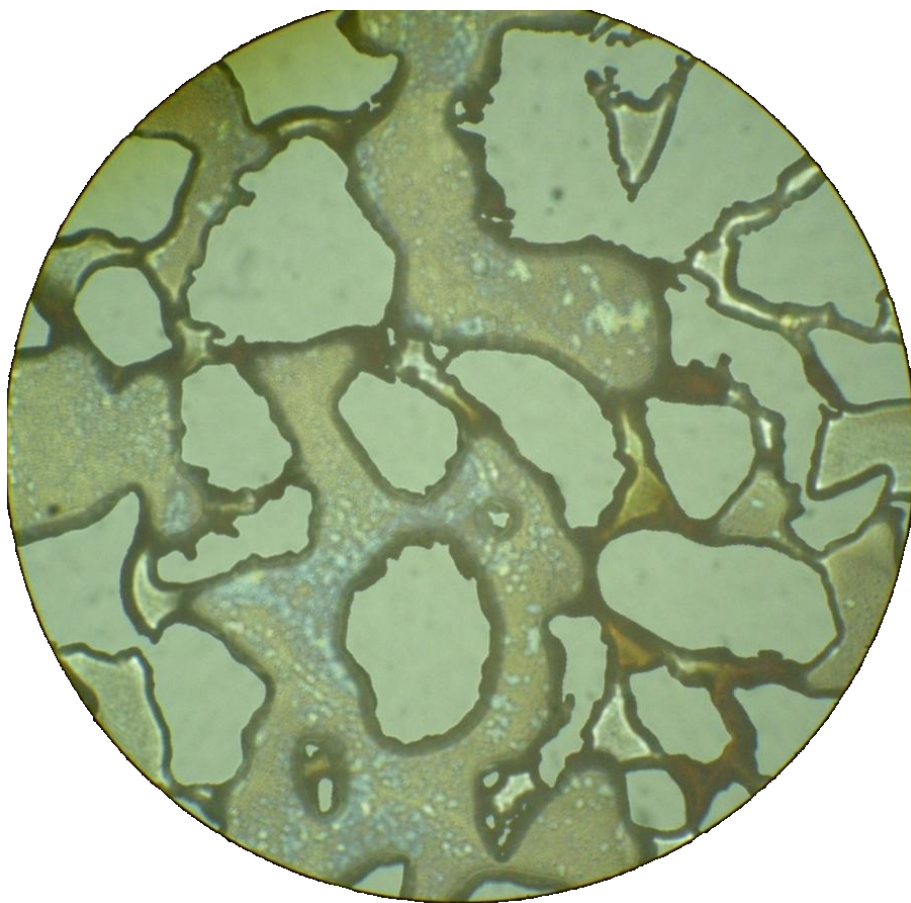


Figure 3-16: 200X microscopic image after the NEODOL 25-3 flood (horizontal set-up, forced imbibition)

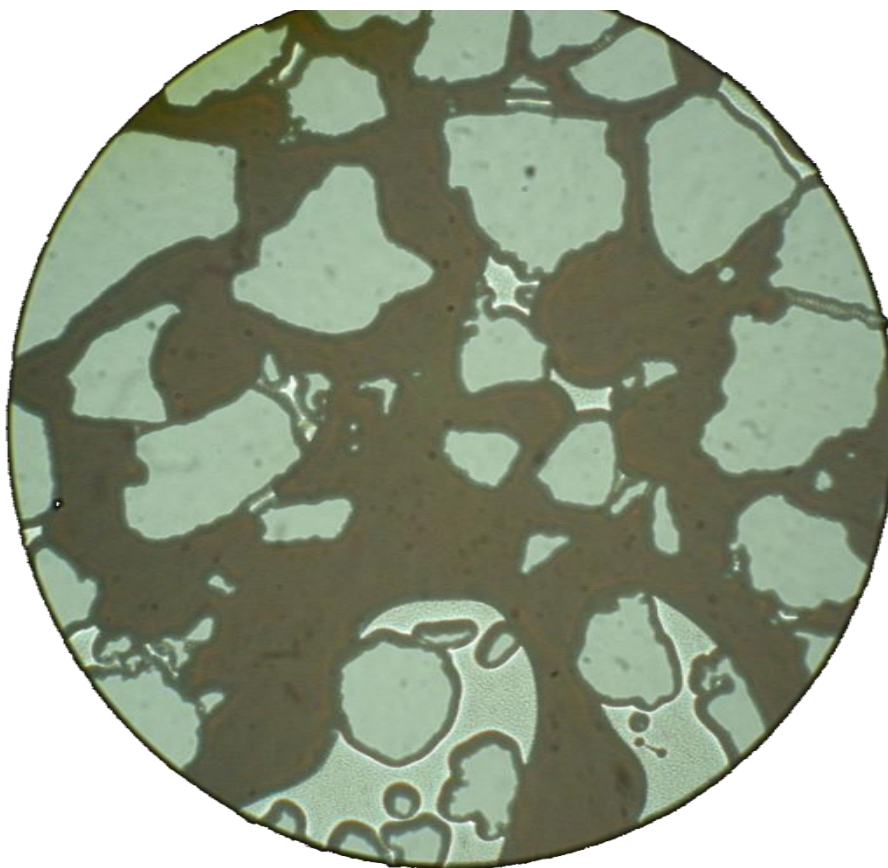


Figure 3-17: 200X microscopic image after the oil flood (vertical set-up)

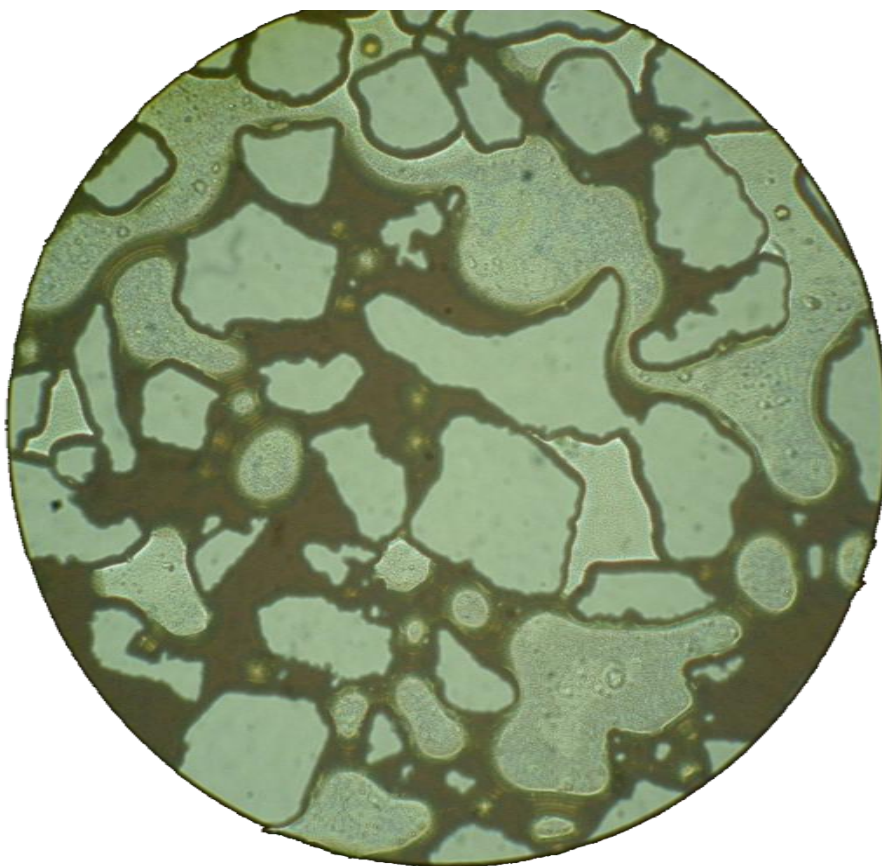


Figure 3-18: 200X microscopic image after the oil flood (vertical set-up, spontaneous imbibition)

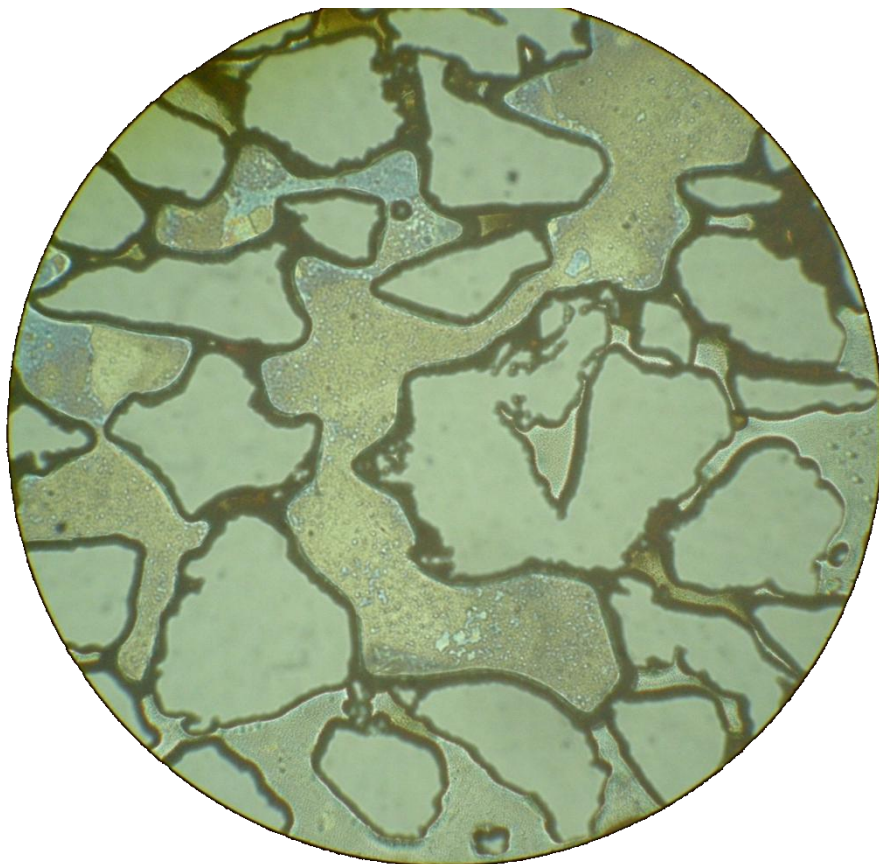


Figure 3-19: 200X microscopic image after the oil flood (vertical set-up, forced imbibition)

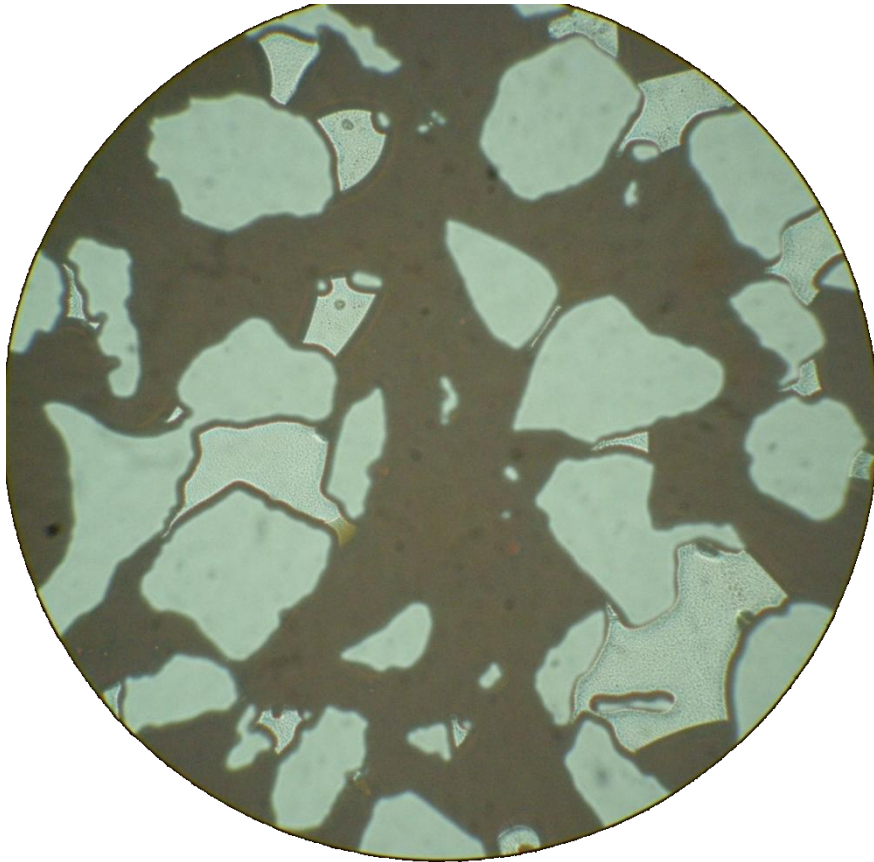


Figure 3-20: 200X microscopic image after the oil flood (Experiment IV)

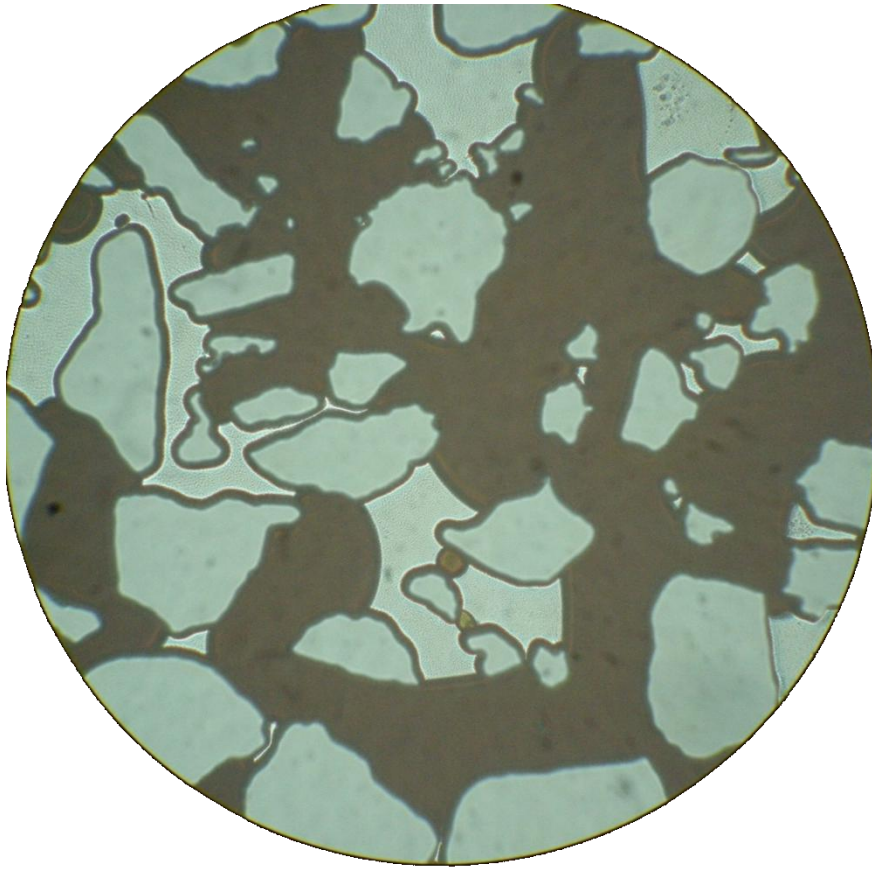


Figure 3-21: 200X microscopic image after the waterflood (Experiment IV)

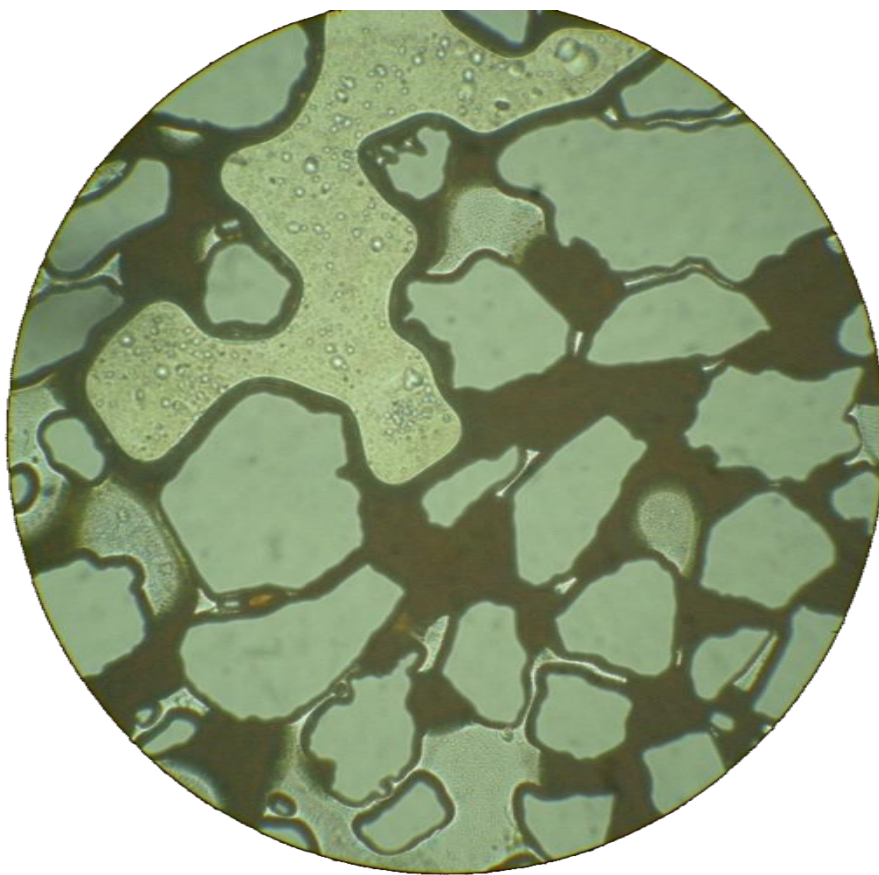


Figure 3-22: 200X microscopic image after the NEODOL 25-3 flood at a low rate (Experiment IV)

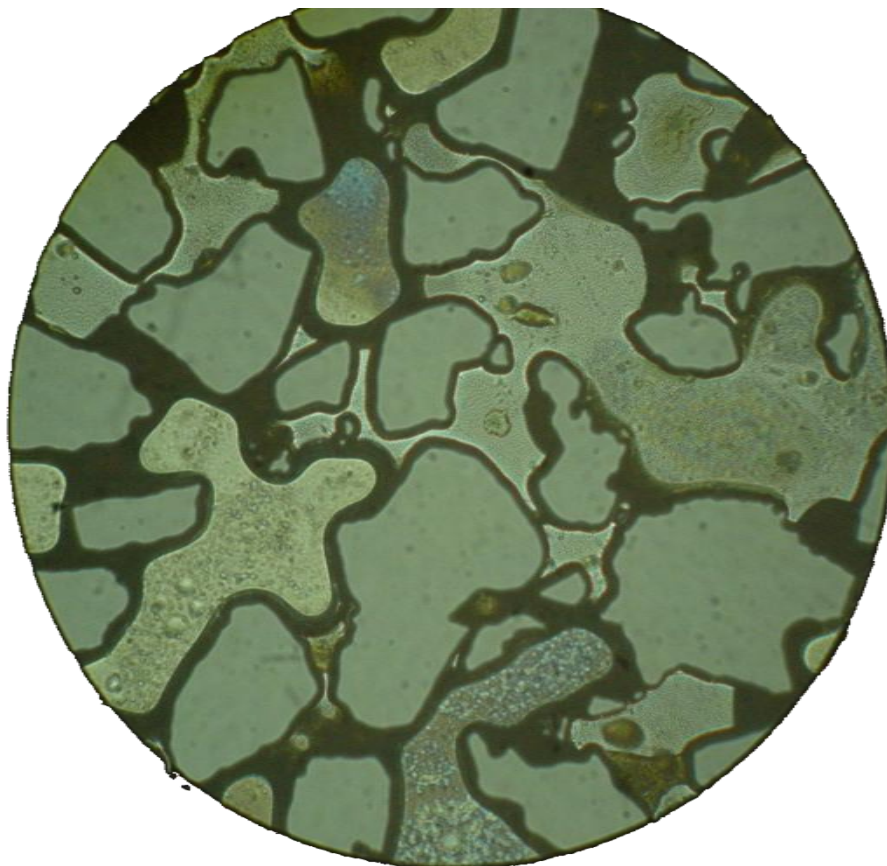


Figure 3-23: 200X microscopic image after the NEODOL 25-3 flood at the regular flow rate (Experiment IV)

Chapter 4

4. Discussion and Conclusion

This work consisted of two phases: a fluid characterization phase and a micromodel experiment phase. The fluid characterization phase identified brine composition, the appropriate surfactant to use, surfactant concentration, and sodium carbonate concentration.

Hard water, containing calcium, is not recommended to be used when sodium carbonates are used as alkaline. Precipitates, which might block pores/throats, form when sodium carbonate was added to the brine. A decision was made to eliminate calcium chloride from the brine composition. Another option is to add sodium metaborate as suggested by Flaaten et al (2008) that prevents precipitations.

Dilute anionic surfactants with sodium carbonate reduce IFT to low values reducing capillary forces that trap oil. Such reduction in IFT frees retained oil to the matrix and eases its flow out of the micromodel. The surfactant screening indicates that NEODOL 25-3 is the most promising surfactant in terms of IFT reduction.

Thermal stability of surfactants was examined. This was performed by heating samples of surfactant solutions for increasing intervals of time. Measurements of IFT are taken to see if there is any significant change in the values that would indicate surfactant instability at high temperatures. The study shows that the tested surfactants were thermally stable and compatible for the given reservoir temperature (210°F).

By conducting the micromodel experiments, it was visible that injection of dilute surfactant solutions with sodium carbonate recovered most of the oil. This was concluded by image analysis that shows that only 6-14% of oil remained after the surfactant flood compared to 15-34% after a waterflood.

Bond number calculation indicates that for a 1 vol% NEODOL 25-3, the oil drop vertical diameter has to be at least 900 μm for gravitational forces to become dominant. It was shown that experiments conducted vertically lead to higher oil recovery than horizontal experiments. This result was also enforced by the calculation of the Bond number for the horizontal case. It was found to be 0.015 which is much less than the cutoff indicating a negligible effect of gravity in a horizontal set-up. In other words, under similar magnitudes of viscous and capillary forces, buoyancy is the additional recovery mechanism in the vertical set up.

Spontaneous imbibition was achieved and significantly recovered retained oil. The marginal improvement of remaining oil in the vertical set-up is 1% compared to the

horizontal set-up. This number however, is within the uncertainty range of the edge effect and no solid conclusion can be drawn from this number.

For future work, it is recommended to include more surfactants in the study. The screening criteria can also include wettability alteration and surfactant adsorption. A possible next step is to vertically conduct core flooding experiments and use a CT scanner to monitor front movements and saturation profiles. A 360° spontaneous imbibition can be investigated by injecting the dilute surfactants in fractures that fully surround the core.

Nomenclature

IFT: Interfacial tension
Bo: Bond number
Ca: Capillary number
d: Pore size diameter
f: angular velocity, msec/shaft rev
g: Gravity acceleration
 k_{rw} : Water relative permeability
 k_{ro} : Oil relative permeability
l: Liters
m: Meters
ml: Milliliters
M: Molar concentration
M: Mobility ratio
r: Elongated oil drop radius, meters
RGB: Red Green Blue
SNF: Stanford Nanofabrication Facility
 S_o : Oil saturation
 u_i : Injectant Darcy velocity
WAG: Water-Alternating Gas
WOR: Water-Oil Ratio
 μ_i : Injectant viscosity
 μ_w : Water viscosity
 μ_o : Oil viscosity
 μm : Micrometers
 ω : Spinning velocity
 ϕ : porosity
 ρ : Fluid density
 σ : Interfacial tension

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Appendix A

A. Wafer Run Procedure

RUNNING PROCEDURES FOR
MICROMODEL FABRICATION

QING CHEN
SUPRI-A, STANFORD PETROLEUM
DEPARTMENT
FIRST WORK ON 8/2/04
VERSION 1.1, LAST UPDATED 10/26/06
REVISED BY: AMAR J ALSHEHRI AND
BOLIVIA VEGA ON JUNE 2008

4.1. General Description

Micromodel is a network of porous structures and channels, which is widely used for experimental studies of 2-D fluid flow through porous media. Stanford Micromodel is designed and fabricated by anodically bonding a Si wafer with etched pattern to a transparent glass plate, providing optical access for flow visualization. This document describes in details the micromodel fabrication procedures developed at Stanford Petroleum Department over the past 30 years.

4.2. Process Overview

Materials:

- 4” Si wafer, K Prime, 4P <100> B S42565 (WaferNet, Inc.)
- Borofloat 4” diameter X 0.043” thick, standard transparent finish 80/50 – 60/40 scratch/dig, flat to 3-4 waves/inch

The processes to fabricate Stanford Micromodel in order are:

- Wafer precleaning
- Photolithography
 - Coating
 - Exposing
 - Developing
- Deep etching
- Resist removing and cleaning
- Anodic bonding
- Dicing (if necessary)

Note that the procedures described in details below are only compatible with the facilities at CIS, Stanford University.

4.3. Photolithography

4.3.1. Photoresist Coating

Equipment: SVG photoresist spin coater (svgcoat)

Person to contact: Uli Thumser (uthumser@stanford.edu)

Operating Procedures/parameters:

1. YES Oven for 30 minutes (HMDS vapor prime)
2. Prime program: off
3. Coat program #8: 1-1.6.0 μm (this is the amount for a 25 $\square$ m deep RIE)
4. Prebake program #2

4.3.2. Exposure

Equipment: Karl Suss MA-6 contact mask aligner (karlsuss)

Person to contact: Mahnaz Mansourpour (mahnaz@stanford.edu)

Uli Thumser (uthumser@stanford.edu)

frontside align, from 5" mask to 4" wafer

Operating Procedures/parameters:

1. Initiate the system
2. Select program. For our case, soft contact mode is a good option. The other modes are vacuum, vacuum hard, and hard contact
3. Edit parameters for current program.
 - 3.1. time = 2.6 sec
 - 3.2. gap width = 40 μm
4. Change mask
5. Load wafer
6. Focus mask
7. Expose
8. Unload/change wafer
9. Unload/change mask

4.3.3. Developing

Equipment: SVG developer (svgdev)

Person to contact: Uli Thumser (uthumser@stanford.edu)

Operating Procedures/parameters:

1. Develop Program #4:
2. Post Bake?

3. Oven bake #2

4.4. Deep Etching

Equipment: STS multiplex ICP Deep Reactive Ion etcher (stsetch)

Person to contact: Nancy Latta (nlatta@stanford.edu)

Operating Procedures/Parameters

Etch recipe: DEEP

- Select a desired recipe and set it as current by clicking recipe field
- Pre check: 400 Hz.
 - During process: P about 10 Q about 3 and not fluctuating wildly.
- Check and modify settings of the current recipe. Press RECIPE button in the window of Press control–ICP. In the popped-out recipe window, check the settings with the parameters from the STSetch logbook. For those standard recipes, like DEEP, the only parameter that can be changed is the etching time. With assumption that etching rate is constant, the desired etching time can be easily determined from the desired etching depth. Remember to save recipe before exiting the recipe menu if any setting is changed.
- Unload wafer if necessary.
- Load new wafer
- Start etching process by pressing PROCESS button
- Read parameters of machine conditions and write them down on the logbook. Those parameters include
 - He pressure and flow which can be read from the low small window on the left side of the machine
 - Chamber pressure (passivation and etch) which can be read from the right lower part of the machine view window.
- Unload wafer when etching is done.

4.5. Post-check

Check etching depth:

4.5.1. *Using a microscope:*

The depth between white and color is measured as the etching depth – photoresist thickness (about 2 μm) (contact Nancy Latta for help)

4.5.2. *Using Tencor P2 Profilometer:*

The P2 has a stylus that physically touches the etched and the non-etched surface and calculates the difference (contact Uli Thumser for help).

4.5.3. *Using Zygo 3D Surface Profiler:*

The Zygo relies on the reflectivity of different elevated surfaces (contact Uli Thumser for help).

4.6. Resist Removal and Cleaning

Equipment: Nonmetal Wet Bench (wbnonmetal)

Person to contact: Uli Thumser (uthumser@stanford.edu)

Matrix (O2 asher), wbnonmetal (sulfuric acid)

4.7. Anodic Bonding

Equipment: Power supply, Thermolyne hotplate, and Wet chemical cleaning stations

Operation Procedure:

- Clean the materials that will be bonded. The standard clean is as follows:
 - *Silicon wafers:* 20 min Sulfuric/Peroxide Piranha (9:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) clean at 120 °C, followed by 6-cycle deionized water rinse and spinning dry. This cleaning process can be done with wbsilicide (gold-contaminated bath) at SNF Lab.
 - *Glass wafers:* cleaned in Sulfuric/Peroxide Piranha (9:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) for about 10 minutes, rinsed by deionized water thoroughly, and then air dried. This cleaning process can be done with wbsilicide (gold-contaminated bath) at SNF Lab.
- Anodic bonding
 - Place a cleaned wafer on a hotplate preheated to 350°C, with its etched side facing up. The wafer is left on the plate for around 45 minutes, by which a very thin SiO_2 film is formed on the wafer surface and the wafer, initially non-wetting, becomes water wetting.
 - Reduce the hotplate temperature down to 300°C and wait for the temperature to be stabilized. Inspect the wafer surface for any dust that might deposit during preheating period. Blow off any visible dust from the surface with compressed clean air if necessary.
 - Place a cleaned glass wafer right on the top of the wafer, and align as desired. Allow the wafers to heat for at least 1 minute.
 - Preset the voltage of the power supply between 900 and 1200 volts. Turn the power supply to standby mode, and allow it to warm up for 2 minutes. The anode of the power supply is connected to the hotplate and the other electrode (cathode) is connected to an aluminum plate wrapped by a copper mesh. Place the aluminum plate on the top of the glass wafer gently and then turn on the power supply to apply a high voltage.
 - After 50 minutes, bonding should be achieved.

- Turn off the electricity, remove the new micromodel from the hotplate using tweezers, and allow it to cool to room temperature. Don't leave the micromodel on the hotplate for cooling. There are two reasons for not doing that: it takes longer to cool the model; it was occasionally found that the glass got cracked during cooling on the hotplate.

B. Image Analysis Code

```
function average=oilperc(dirname)
% Initilize white and black values
sumwhite=0;
sumblack=0;
% Obtain images
cd(dirname)
names=dir('*.JPG');
nnames=length(names);
oil=zeros(nnames,1);
% Define crop dimensions
i1=1000; j1=300;
width=1800; height=2050;
pixels = width * height / 100;
% Define RGB cutoffs for oil
R=110; G=115; B=90;
for i=1:nnames
    fname=names(i).name
    X =imread(fname);
    X=imcrop(X,[i1 j1 width height]);
    Y = (X(:, :,1)>R) + (X(:, :,2)>G) + (X(:, :,3)>B);
    Y = floor(Y./3);

    datei=['blackwhite' fname ];
    imwrite(Y,datei,'jpg');
    white=sum(sum(Y))/pixels
    black=100-white

    sumblack=sumblack+black;
    sumwhite=sumwhite+white;
    oil(i)=black;
    black=0;
    white=0;
end

averagewhite = sumwhite/nnames
averageblack = sumblack/nnames
oil
average = [averagewhite, averageblack]
```