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Abstract

Oil recovery projects have become a valuable source in oil industry in the recent years due to market challenges and economic stability. This is a typical practice that have been applied in oil and gas reservoirs to produce the volumes of oil that cannot be obtained by natural energy. Currently there are several methods that have proven to have pros and cons as being used as secondary or tertiary recovery technics. Within the most typical methods applied there are water flooding, chemical injection by the use of polymers and surfactants and thermal recovery methods.

However, traditional technics have faced inconveniences that are exacerbated when producing heavy oil. On one hand waterflooding offers in most of the cases the lowest investment required but at the same time results have shown the lowest recovery value and sweep efficiency. In contrast chemical injection performs in the most effective way, with a stable displacement front and wettability changes that result in highest oil recovery values, but affecting economic budget with high investment that make companies think twice before its application. Additionally, considering the fact that heavy oil reservoirs represent most of the current worldwide reserves, thus high fluid viscosity shall be expected and consequently unfavorable mobility issues due to differences in fluids velocity through the porous media resulting in early water breakthrough.

Hence, emulsion injection has come up as an attractive alternative to obtain higher oil recovery volumes compared to water flooding with a lower investment than the chemical injection. On one hand, when a stable emulsion is injected in the reservoir usually after a secondary recovery with waterflooding, it will tend to flow through the same high permeable water-wet zone previously covered by waterflooding if is an oil-in-water emulsion type (oil droplets dispersed in a continuous water phase). In this process oil droplets get trapped in the pore throats changing the wettability of the rock surface, decreasing the permeability of the invaded zone. As result water injected afterwards is forced to flow through less permeable zones that were not swept previously and the residual possible-to-mobilize oil that were trapped is displaced and produced, thus oil recovery increase.

On the other hand emulsions are typically stabilized by the use of emulsifiers that are usually added in volumes (up to less than 1%wt) that lead to lower project investment compared to any chemical injection recovery project. However emulsion stabilized by solid particles are also an alternative technic that provides stabilization in oil-in-water and water-in-oil emulsions, but this alternative topic has a limited coverage in the literature. Therefore in this thesis three aspects of oil-in-water emulsions stabilized by clay solid particles were analyzed by experimental and mostly empirical studies that are intended to extent the knowledge in this topic.

First, a better understanding of emulsion stability was addressed by a so-called flotation analysis, in which the behavior of the dispersed phase was assessed under different factors and scenarios. Results suggested that emulsion dispersion is affected by the quantities of the fluids and also by the continuous motion energy applied. Nonetheless stability is not compromised when steady conditions, but dispersed phase shows a flotation behavior that also changes according to dispersed phase and solid particles ratio.

Secondly a procedure to determine the appropriate ratio of solid particles per volume of oil was prepared and tested to assure an efficient oil droplet protection by solid particles against coalescence that leads to dispersed phase separation. An simultaneously to reduce material waste that can lead to impact an oil recovery project by emulsion technique, thus an improved emulsion stability can be obtained without using more material than required.

Finally a permeability reduction study was carried out by core flooding experiments to evaluate permeability changes in a porous media when the emulsion is injected. As a result, both a quantitative and qualitative results were obtained, showing a notorious permeability reduction affected by emulsion oil concentration up to 60% from the initial permeability, and also a remarkable emulsion stability was observed avoiding the droplets breaking, since during the emulsion flooding or by following water flooding no oil was produced at breakthrough.

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Nomenclature

%wt	Concentration percentage in weight
Sor	Residual Oil Saturation
η_0	Viscosity of the external phase
\emptyset	Volume concentration of the disperse phase
η_i	Viscosity of the internal phase
N	Packing coordinator number for the spheres
\emptyset_m	Limiting critical volume
WOR	Water Oil Ratio
Bbl	Barrels
m	Meter
cm	Centimeter
Nm	Nano meter
μm	Micro meter
m^2	Square meter
cp	centipois, viscosity unit
min	Minutes
Hr	Hours
S	Seconds
ΔP	Differential Pressure
L	Liter
g	Grams
PV	Pore Volumes, usually expressed in cm^3
TAN	Total Acid Number
TBN	Total Basic Number
DC	Direct Current Electromagnetic Field
AC	Alternating Current Electromagnetic Field
FW	Formation Water (Synthetic in this book)
LSW	Low Salinity Water
STO1	Stock Tank Oil 1, type of oil used in the emulsion
KOH	Potassium Hydroxide

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1. Introduction

Oil recovery techniques offer the possibility to take advantage of the maximum volume of oil possible to be produced. A typical reservoir production life begins with natural energy extraction thus no additional technics are required since reservoir pressure is great enough to make fluids flow to the surface. Sometimes pumping systems are required to be applied in order to supply the needed energy to allow the fluids to flow up to the surface and be produced.

Once the natural production finalizes, the reservoir must undergoes different production techniques addressing to solve the production decreasing, experienced during a typical field operation. These techniques are commonly known as oil recovery techniques and can be categorized into two different stages one after the other.

On one hand as the cumulative production increases the reservoir experiences a pressure depletion process and eventually additional methods shall be applied to restore the reservoir pressure and continuing the extraction. This production stage is commonly known as Secondary Recovery and typically water or gas is injected into the reservoir to drive the remaining oil in the production zone. However, the sweep effectiveness of secondary recovery methods are strongly affected by different factors, including the type of fluid, since as the viscosity increases the mobility of the displacing fluid is faster than the displaced one (oil), resulting in an early breakthrough and poor recoveries are expected. But also other characteristic such as production zone thickness, reservoir depth and rock properties may influenced the application of techniques such as gas flooding.

The secondary recovery finalizes when displacing fluid reaches the breakthrough and starts to be produced. In most of the cases, mobility issues are the responsible for recovery results. However even though macro-efficiency results are considered satisfactory there is still oil trapped (at its S_{or}) in the porous media that can be mobilized. At this point the fluids flow through the reservoir porous media starts to be dominated by other type of forces, mainly ruled by capillary and viscous forces. Under inconvenient conditions these forces may cause the flow to cease and eventually Tertiary Recovery techniques are required to overcome the restrictions.

Typically tertiary recovery techniques include chemical injection addressing to solve oil trapping by a combination of mobility control improvement, wettability changes and/or residual oil saturation reduction. Chemical injection is often useful for improving the sweep in the reservoir. Different issues may be solved by the use of chemicals. On one hand by polymer injection water mobility may be decreased, thus a favorable mobility ratio can be obtained and volumetric sweep efficiency are optimized.

Another chemical injection that is frequently use is the surfactant flooding. This recovery technique reduces the capillary forces that may retain the small oil droplets trapped in reservoir porous media. As result residual oil saturation may be decreased by increasing the oil displacement, thus the oil recovery. Despite chemical flooding may lead to convenient results in oil recovery, these techniques are usually economically contrasted with final earnings, since the use of chemical usually increases the investment exponentially in a field development project.

Additionally another factor that may affect the secondary and tertiary results is the presence of thief zones in which rock higher permeability may result in faster channeling of the injected fluid through these zones. In this case reservoir heterogeneity shall be lowering to avoid low sweep efficiency due to uncovered zones. Several methods have been used to reduce the permeability of high permeable zones. Injection of polymers and gels or cross-linked aldehydes are typical agents that can be injected for the profile modification, however these techniques only affects the closet region

to the wellbore due to fast action of the agents, once in place, gels are immobile. Usually this injection is followed by waterflooding which, in most of the cases, finds a new path between the gels and decreasing the permeability reduction effect in the formation.

Due to the inconveniences presented above and such others with thermal and non-thermal techniques, oil industry has found in the emulsion flooding an attractive technology for increasing the oil recoveries, avoiding the low oil displacements and sweep efficiencies obtained in waterflooding and high investment required in the chemical injection. It also proves to be an excellent agent for profile modification in the reduction of the permeability of high permeable zones. Several labs and in-field experiments have been carried out, and in most of the cases water-in-oil or oil-in-water emulsions have showed improvements in the oil sweep on the tertiary recovery and increases in oil recovery compared to water flooding.

Emulsion flooding as an oil recovery method has been studied by different researchers, however the literature in this topic is still limited. Since despite the remarkable results in oil recovery showed by lab researches, the operational application of this technique has not been widely used. Additionally most of the researches are focused on the traditional emulsion making, typically stabilized by an emulsifier agent and sometimes due to emulsion thermodynamically instability, the oil droplet protection offers by emulsifier agent must be improved.

The use of solid particles as “emulsifier” agent has called the attention of the experts. Solids are attracted to oil-water interface with strong bonds and the emulsion stability can last for months or even years. Moreover the reduction in the use of chemicals decrease the project investment required for a reservoir development. However, as mentioned before, the available literature with regards to the emulsion application as secondary or tertiary method is very limited, and the lack of information is even more exacerbated when other emulsion stabilizing alternatives are considered.

This thesis is intended to contribute to increase the knowledge about the use of oil-in-water emulsions stabilized by clay solid particles and its use in the secondary and tertiary recovery processes. Therefore several lab experiments have been executed, and qualitative and quantitative results are shown in this study.

In this research three main topics were covered, initially a better understanding of emulsion stabilization by solid particles was carried out by a flotation analysis of oil droplets along a synthetic formation water and also how the emulsion-making is affected by the quantity ratio of solid particles and oil and under other parameter such as temperature variances.

Secondly, a method was prepared and tested to determine the suitable quantity of solid particles required per volume of oil, that lead to assure both a proper oil-water interface protection against coalescence and avoid the waste of excessive particles material by a screening analysis of solid particles and oil. The results for this topic were specially focused to reduce project investment by the reuse of production water (or disposal water) and also diminish at most the solid particles material required in an emulsion flooding project.

Finally permeability changes derived from emulsion injection were analyzed by performing a core flooding lab study, in which permeability reduction was assessed to determine the impact of injecting an emulsion in the porous media. It also determines the level of emulsion stability offered by the solid particles when flowing through the tortuous core paths.

Experiments description and suggested procedures are shown in the same order as explained before, covering **Flotation**, **Screening** and **Core Flooding** studies separately. Consequently, experiments results and discussions are presented following this workflow.

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2. Literature Study

This chapter will provide theoretical information found in the literature mainly focused on oil-in-water emulsions that were used in this experimental study. Initially generalities of emulsions will be given including definition, the different types of emulsion, physical aspects about emulsions and how stability is affected and could be improved. The majority of this literature is based on two of the books, Schramm's (1) and Becher's (2), which are considered one of the main source of information regarding emulsions and that have served as reference for numerous papers in the matter. Following by a brief introduction of enhanced oil recovery in order to understand the main purpose of this practice in the oil industry and finally some published studies and theoretical information regarding emulsions used as an oil recovery method and the benefits offered by this practice.

2.1. Emulsion Generalities

Petroleum emulsions have been treated for a long time in the industry, and can be encountered at all stages in the production and processing flow line, including drilling, hydrocarbon production, processing plant and transportation emulsions.

Physical properties of an emulsion depends on the nature of the mixed fluids (water and oil), oils have a wide range of components, consequently hydrocarbons may vary from composition, and thus physical properties such as viscosity and density. Those characteristic may dictated by the physical appearance and properties of the resulting emulsion (1).

2.1.1. Definition and Classification

Schramm (1) defines an emulsion as a special kind of colloidal dispersion, in which a liquid is dispersed in a continuous liquid phase of different composition. Colloidal droplets have at least one dimension between 1 and 1000 nm. Likewise Becher (2) states that an emulsion is a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter, in general, exceed 0.1 μm .

Therefore emulsion is a mixture of immiscible fluids, in which one is in aqueous phase and the other is a hydrocarbon (referred as oil phase). Additionally are observed two types of phases, the dispersed phase is the one that is reduced to the form of droplets and sometimes referred to as the internal phase, and the continuous phase as the external phase. Then two types of emulsions may be formed depending on which liquid forms the continuous phase: oil-in-water (O/W) for oil droplets dispersed in aqueous phase (water) and water-in-oil for water droplets dispersed in oil (1).

Colloidal dispersion has been classified into two different categories: Lyophilic colloids that are formed spontaneous when the two phases interacts this type of dispersion is thermodynamically more stable than the phases separately. And the Lyophobic colloids that they are not formed spontaneously due to its thermodynamic instability; petroleum emulsion are considered lyophobic colloids (1).

Additionally emulsions have basically three components, water, oil and an emulsifying agent. This last is the responsible for both to reduce the interfacial tension increasing the interfacial area with minimum input energy, and to form a protective film at the droplets surface to prevent coalescence with others. This formed film between oil-water interface will be crucial in the emulsion stability. These emulsifying agents may be soluble in both water and oil due to its constituents, on one hand a long hydrocarbon chain is present that is soluble with oil, and a polar group that may be carboxylate, sulfate, ether and alcohol that is soluble in aqueous phase. Additionally emulsifiers may content one

or more of the following: simple inorganic electrolytes, surfactants, macromolecules or finely divided solids (1):

2.1.2. How to Create an Emulsion

As indicated previously an emulsion is a mixture of water, oil and emulsifying agent. In the classical method explained in Schramm (1), the emulsifying agent is dissolved into the phase in which it is most soluble, afterwards the immiscible phase is added and the whole mixture is vigorously agitated.

The level of agitation determines the size of formed droplets, therefore the smaller drop size will be achieved with a strong agitation. Frequently after the first mixing a second one is needed in which a very high applied mechanical shear forces are required. Usually provided by a colloid mill or ultrasound generator, but also by a propeller-style mixer (1).

2.1.3. Physical Characteristics and Characterization

The physical appearance of an emulsion will depend on the droplets sizes and the difference in refractive indices between phases. Consequently the transparency of an emulsion may be observed by a refractive index of each phase is the same and also if the dispersed phase is made up of droplets small enough compared with the wavelength of the illuminating light (1).

There are different physical methods that may be applied to identify the nature of an emulsion:

Texture. Usually emulsion texture indicates physical properties of the external phase. Therefore oily or watery texture may be found upon the viscosity of the continuous phase.

Mixing. Emulsion may be mixed with a miscible fluid regarding the external phase, determining the type of emulsion.

Dyeing. Emulsions are most readily and continuously colored by dyes soluble in the continuous phase.

Conductance. Water conductivity is greater than oil conductivity. Therefore if water is the continuous phase the oil-in-water emulsion will have a high specific conductance.

Inversion. If an emulsion is very concentrated, it will probably invert when diluted with additional internal phase.

Fluoresce. If the oil phase fluoresces, then fluorescence microscopy can be used to determine the emulsion type as long as the droplets sizes are larger than the instrument limit resolution.

2.1.4. Rheology of Emulsions

Becher (2) provides an extensive literature about emulsions properties. Emulsions flow is directly linked to rheology bulk properties such as viscosity, which will dictate, but not limited to, the flow of the emulsion throughout the porous media, this chapter shows some remarks found in the referenced book.

2.1.4.1. Viscous flow

The viscosity coefficient of a Newtonian fluid is defined as the shearing stress (τ) exert across an area when there is unit velocity gradient normal to area, defined by Eq. 2.1

$$\tau = \eta \frac{du}{dy} = \eta D \dots\dots\dots (\text{Eq. 2.1})$$

For flow in the x-direction. If the shear is (σ), then D is the time rate of change of shear and Eq. 2.1 may be written:

$$\tau = \eta \frac{d\sigma}{dt} \dots\dots\dots (\text{Eq. 2.2})$$

In most simple liquids, τ is proportional to $d\sigma/dt$ (or D) as long as the flow is laminar, that is non-turbulent. In other word, the constant η (the viscosity coefficient) is independent of the velocity gradient, and the liquid is Newtonian (2).

For most emulsions, however, Newtonian flow is the exception rather than the rule, and the viscosity η is a function of the rate of the shear. Figure 2.1, in which the stress τ is plotted against the shear rate $d\sigma/dt$, illustrates the four general types of flow behavior characteristic of fluids: Newtonian, Bingham plastic, shear-thickening (pseudoplastic) and shear-thinning (dilatant) (2).

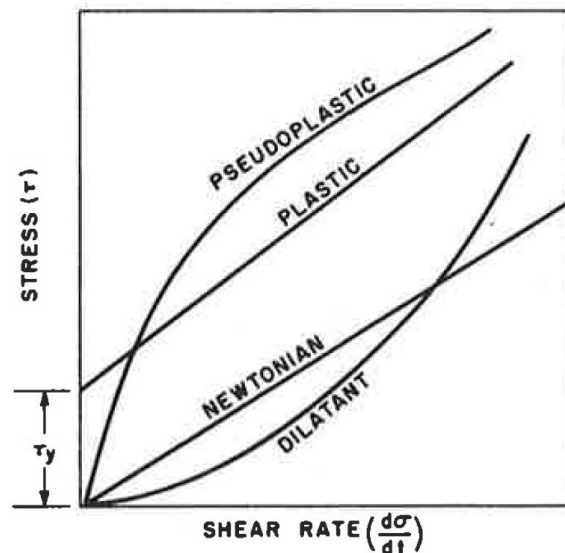


Figure 2.1 - The four types of flow that may be exhibit by fluids: Newtonian, Plastic, Pseudoplastic and dilatant. Ref (2).

In the case of Bingham plastics the fluids has some inherent structure which totally resist sharing up to some magnitude τ_y , the so-called yield strength or yield value. For a Bingham plastic this is defined by the intercept of the flow curve with the shear stress axis, as Figure 2.1 when the yield strength is reached the structure breaks down, and (after a short curve region) a straight-line relationship ensues. The slope of this line is defined as the coefficient of rigidity. Drilling muds, in the field emulsions are examples of liquids with theses flow properties (2).

Shear-thinning flow, is the opposite of shear-thickening flow; the viscosity coefficient decrease with the rate of shear. This type of flow is apparently rare in emulsions. In shear-thickening flow, no yield value is exhibited, but the value of the viscosity coefficient is clearly dependent on the shear rate. In such liquids, some sort of intermolecular structure is apparently build up under the influence of the shear force (2).

In addition to the above readily defined types of flow there exist the so called thixotropic and rheopectic systems. In these, the flow properties depend not only on the shear rate, but also on the length of the time the shearing stress is applied. In thixotropic flow, viscosity decrease with the time, and vice versa or rheopectic (2).

In non-Newtonian systems, viscosity is a function of the rate of stress. Thus, a series of different viscosity value may be obtained by measurements on the same liquids. It is inaccurate to refer to these results as the “viscosity” of the liquids; the designation of “apparent viscosity” is preferred. Hence, if the shear rate is stated in reporting such data, the quantity is unequivocally defined and is useful, for example, in quality control. On the other hand, such apparent viscosities are of questionable value in theoretical investigations. Unfortunately, in the past it has not always been made clear that measurements were made under Newtonian conditions, or at least, on the linear portion of the stress-shear-rate curve (2).

Factor that may affect the rheological properties of an emulsion are listed below and explained ahead:

- Viscosity of the external phase (η_0)
- Volume concentration of the dispersed phase (ϕ)
- Viscosity of the internal phase (η_i)
- Nature of the emulsifying agent and the interfacial film
- Particles-size distribution
- Electroviscous effect

2.1.4.2. Viscosity of External Phase

Virtually all theoretical or empirical treatments of emulsions viscosity consider the viscosity of the continuous or external phase η_0 to be the principal factor in defining the viscosity of the final emulsion. Most equations assume a direct proportionality between the viscosity of the emulsion and the viscosity of the external phase, and most of the published equations may be put in the form of (2):

$$\eta = \eta_0(x) \dots \dots \dots (\text{Eq. 2.3})$$

Where x represents the summation of all the other properties which may affect the viscosity. In many emulsions, the emulsifying agent is at least partly dissolved in the external phase. Hence η_0 is the viscosity of the solution, rather than of the pure liquid. This may be especially important when colloidal stabilizing agent are employed, because they have a marked effect on the viscosity.

2.1.4.3. Concentration of the Disperse Phase

The convenient theoretical concentration term is volume percent or volume fraction. The symbol ϕ is usually taken to mean the latter, although some workers prefer the percentage form of expression (2).

The classic equation relating the viscosity of a suspension with that of the suspending liquid is due to Einstein (3):

$$\eta = \eta_0(1 + 2.5\phi) \dots \dots \dots (\text{Eq 2.4})$$

It should be pointed out that equation Eq 2.4 is usually held to be valid only for volume fractions $\phi < 0.02$ of suspensions of particles which may be approximated by hard spheres. However, it has been successfully applied, on occasion, up to $\phi \approx 0.1$.

The quantities relative viscosity and specific viscosity may be defined by writing Eq 2.4 in different ways.

Relative viscosity:

$$\eta_r = \eta/\eta_o = 1 + 2.5\theta \dots \dots \dots (\text{Eq. 2.5})$$

Specific viscosity:

$$\eta_{sp} = \eta_r - 1 = 2.5\theta \dots \dots \dots (\text{Eq. 2.6})$$

The concentration limitation on Eq. 2.4 can be surmounted by extrapolating η_{sp} to zero concentration of the dispersed phase

$$\left[\frac{(\eta/\eta_o) - 1}{\theta} \right]_{\theta \rightarrow 0} = \left[\frac{\eta_{sp}}{\theta} \right]_{\theta \rightarrow 0} = 2.5 \dots \dots \dots (\text{Eq. 2.7})$$

In the literature Eq 2.7 is modified by different mentioned authors proved by correlations (2). Additionally other equations have been suggested for the case of emulsions. For example, Richardson (4) has suggested, on theoretical grounds, that at any particular shear rate, the relation between emulsion viscosity and volume concentration is exponential, that is,

$$\eta = \eta_o e^{k\theta} \text{ or } \ln(\eta/\eta_o) = k\theta \dots \dots \dots (\text{Eq. 2.8})$$

Generally speaking emulsions containing more than 50% of dispersed phase show considerable non-Newtonian behavior. For such systems, Eq. 2.9 is derived:

$$\eta = \eta_o \left[\frac{1}{1 - \theta^{1/3}} \right] \dots \dots \dots (\text{Eq. 2.9})$$

This equation is commonly cited as being appropriate for emulsions, but it must be used with caution. It is pointed out that it only applies in the linear portion of the shear- flow curves, but it has also been used in concentration ranges for which there is no theoretical justification (however it has been found to fit the data reasonably well in a number of cases) (2).

2.1.4.4. Concentrated Emulsions

Many of the cases above cited equations are found to be applicable only at low or moderate phase concentrations, for example, of the order of $\phi \leq 0.3$ or 0.52 in some cases. Some considerations have been given to emulsions containing greater values of the internal phase. These equations usually involve an experimentally defined value of the phase volume ϕ (2).

Concentrated emulsions (those with high internal phase concentration), not surprisingly, have a high viscosity. In fact, they exhibit a gel-like appearance and texture, and thus are often referred to a gel emulsions. Emulsions of this sort have been the subject of study in recent years, especially with respect to their rheology. Eq. 2.10 has been derived for high concentrations of spheres (approaching close packing) (2).

$$\eta_r = \frac{N\phi_m}{8} \left(\frac{(\phi/\phi_m)^{1/3}}{1 - (\phi/\phi_m)^{1/3}} \right) \dots \dots \dots (\text{Eq. 2.10})$$

Where N is the packing coordinator number for the spheres (2), and ϕ_m is the limiting critical volume fraction that is the phase volume at which inversion occurs. For simple cubic packing, $N=6$ and $\phi_m=\pi/6$, so that $N \phi_m/8 \approx \pi/8$. For cubic or hexagonal close packing, $N=12$, $\phi_m=0.75$ and $N \phi_m/8 \approx 9/8$. In the referenced book may be observed several correlations based on Eq. 2.10 established by other authors.

2.1.4.5. Viscosity of Internal Phase

It will have been noted by Becher (2) that a large number of investigations of the effect of the concentration of the internal phase on concentration have involved model systems, for example, suspensions of glass spheres. In such cases, the viscosity of the internal phase may be regarded as infinite; this does not apply however to emulsions, where the internal phase viscosity may play a more-or-less significant role.

In fact, no great amount of consideration has been given to this factor since the early work of Taylor (5) who extended the hydrodynamic considerations of Einstein in Eq. 2.4 by assuming that any interfacial film that existed merely transmitted tangential stress from one phase to the other, thus arriving at the relation:

$$\eta = \eta_o \left[1 + 2.5\phi \left(\frac{\eta_i^2 \eta_o}{\eta_i + \eta_o} \right) \right] \dots \dots \dots (\text{Eq. 2.11})$$

Where η_i is the viscosity of the internal phase. It should be noted that the coefficient of the term in the phase concentration (which is equivalent to $\eta = \eta_o (1 + a_0\phi + a_1\phi^2 + a_2\phi^3 + \dots)$, where a_0, a_1, a_2, \dots are constants, and where a_0 is usually taken to have the value 2.5.) may be written:

$$\frac{\frac{5}{2}p+1}{p+1} \dots \dots \dots (\text{Eq. 2.12})$$

Where $p = \eta_i / \eta_o$. According to Taylor's equation, then a_0 varies from unity to 5/2 (Einstein value) for the p between zero and infinity.

The type of circulation patterns to be expected inside the droplet, on the basis of Taylor's theory, is shown in Figure 2.2 in the left figure p is taken to be unity and in the right figure $p = 1/4$. Some authors have shown that in certain emulsions, where such circulation occurs the Taylor's equation applies exactly. In other cases where the agreement is less satisfactory, they propose that the presence of a more-or-less rigid interfacial film inhibit the internal circulation, and that the case in most practical emulsions, stabilized by a substantial concentration of surface-active agent. Also it is pointed out that Taylor's theory assumes that the droplets remain spherical under shear, however this condition cannot be satisfied under high shear rates and it would be expected that deviations from Eq. 2.11 would be found under such conditions (2).

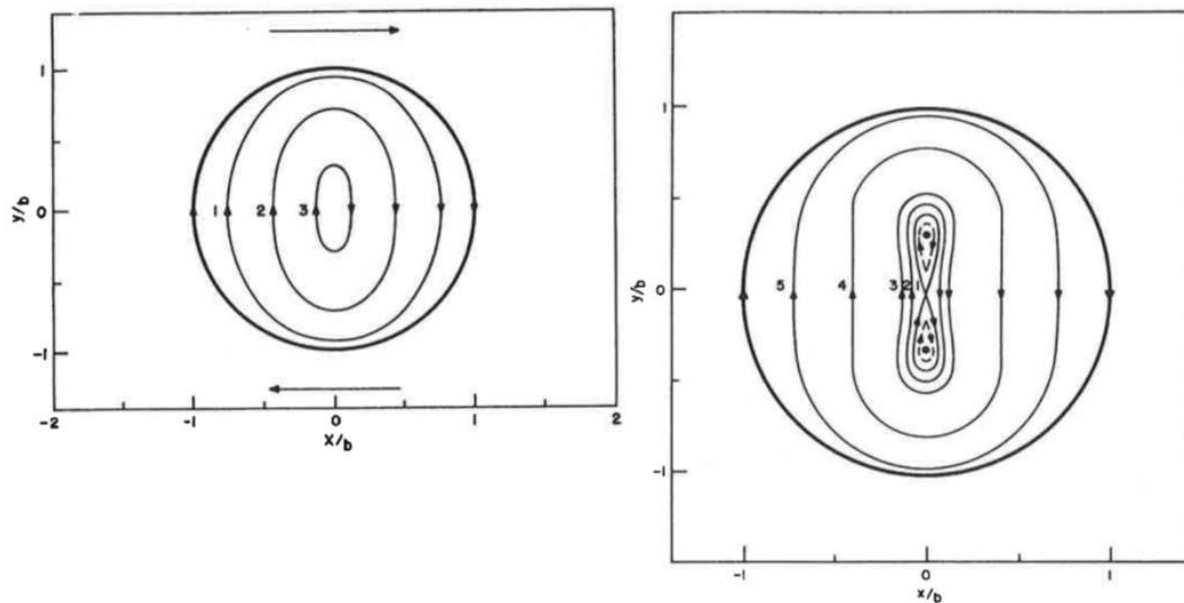


Figure 2.2 – Circulation inside a fluid sphere for $p=1$ (left) and $P=1/4$ (right). Ref (2).

Summing up, hydrodynamic theory appears to indicate that the viscosity of the internal phase can be significant if the droplets behave as liquids. If, on the other hand, the conditions are such that the droplets behave as rigid spheres, the chemical nature of the dispersed phase is likely to have a greater effect. This is, in a sense, fortunate, because a great deal has been learned about the flow of suspensions in general, and emulsions in particular, through studies on model systems consisting of suspensions of rigid spheres.

2.1.4.6. Interfacial Film and Emulsifying Agent

It has been suggested above that the presence of an interfacial film may affect emulsion viscosity by reason of its effect on the internal circulation of the droplet. The interfacial film (and the properties exhibited by the film) results from the presence of the emulsifying agent itself. More than 50 years ago Toms (6) carried out an extensive investigation of a series of oil-in-water emulsions of n-hexane, cyclohexane, xylene, toluene, decalin, benzene, tetralin, aniline, chlorobenzene, nitrobenzene and chloroform, stabilized by sodium laurate and oleate, and potassium laurate, myristate, and oleate.

According to Toms (6) (on the basis of the mutual solubility of the organic liquids, soaps and water), the variations in viscosity may be due to three causes:

1. Part of the soap stabilizer may enter dispersed phase globules and form a gel of solvated surface-active agent; this would bring about a change in the rigidity of the interfacial film and alter the deformability of the droplets (under shear).
2. The soap at the interface may alter the degree of mutual dispersion of the two liquids, and thus effectively change the volume ratio.
3. A transfer of organic liquid across the interface might lead to peptization of the soap micelles in the aqueous phase, thus changing the viscosity of the external phase η_0 .

Additionally studies was carried out in the matter by several authors mentioned in the referenced literature, some conclusion (2):

- The viscosity of emulsions depends on the nature of the emulsifier used.
- The common view that an increase of viscosity increase stability by hindering coalescence of drops cannot be justified.

- The variation of viscosity with the nature of the emulsifier is explained by the assumption that the nature of the interfacial film, which stabilizes the emulsion plays a vital part in determining the viscosity.

2.2. Stability of Emulsions

As stated before emulsion stability is a function of interfacial film between immiscible fluids and the size of the droplets. In such a way that the dispersed phase remains, droplets do not settle out or float rapidly and coalescence is carried out slowly.

Emulsions stability is affected by three different factors (1): Creaming, that is a result of density difference between immiscible phases. Aggregation, droplets get together with no change in total surface area, however they lose their kinetic independence because the grouped droplets move as a single unit. Coalescence, droplets get together and form a single larger unit with a reduced total surface area, the original species lose their identity and become part of a new species.

Aggregation (1) may lead to coalescence and thus formation of larger droplets until separates the phase. Emulsion can be kinetically stable to some or all three different factor, therefore an emulsion may be thermodynamically unstable but kinetically stable at the same time.

Emulsions used in the oil industry are thermodynamically unstable but can be kinetically stabilized. The way droplets interacts will dictate the level of stability, thus creaming, aggregation and coalescence will have place in this encountering process. Particles are charged in the surface, then repulsion and attraction forces address to interaction behavior of the colloids in the emulsion. Repulsive forces is the results of same charge interaction and attraction forces are Van der Waals forces between particles with opposite charge.

Schramm (1) gives a model in which based on the charge of colloids a certain electrostatic behavior starts to form around particles. Thus ions with opposite charge, called counter-ions, are attracted to the surface, and like charge particles, called co-ions, are repelled. Additionally a diffusion layer exists (electric double layer) as a result of mixing caused by thermal motion. In petroleum emulsions the degree of charge interaction is very complicated.

Becher (2) explains that emulsion may be classified according to their stabilization process: Oil hydrosols, unstabilized emulsions that are usually water external less than 1% of oil phase; Emulsions stabilized by electrolytes: where electrolytes in low concentrations stabilize water- in-oil emulsions; Emulsions stabilized by emulsifying agent: include emulsions stabilized by colloids or solid particles. According to Becher (2) King (7) introduced the concept that the most important factor favoring stability are the strength and compactness of the interfacial film, Additionally it is indicated that interfacial tension is not a critical factor instead the interfacial adsorption of the emulsifying agent is vital for emulsions stability.

However, despite the thermodynamically instability of the emulsion, most of them are stable over a period of time, Kokal (8) stated that oilfields emulsions can be classified on the bases of the degree of kinetic stability:

- Loose Emulsions: that separates in a few minutes.
- Medium Emulsion: will separate in ten minutes or more.
- Tight Emulsions: will separate in hours or even days.

2.2.1. Factors affecting Emulsion Stability

The following factors affect the emulsion stability (8):

2.2.1.1. Heavy Fraction in Crude oil

There are some natural occurring emulsifiers that are concentrated in the polar fraction of the crude oil, with a higher boiling point than the rest of the compounds. These include asphaltenes, resins, and oil-soluble organic acids (e.g. naphthenic and carboxylic acids) and bases. An oil with sufficient natural emulsifier constituents may lead to give stability to the emulsion by the formation of an interfacial films around the droplets of the dispersed phase (8).

2.2.1.2. Droplet size

Emulsions droplets size may be an indication of stability, usually range of sizes are between 0.2 μm and 50 μm (8) but other authors as Schramm (1) talks about 0.001 μm to 0.01 μm . However the size distribution is what leads to a clear indication of stability. More stable emulsions may have a size distribution shift to smaller sizes, and this distribution may be maintained throughout the time.

Droplets sizes are also linked to emulsion viscosity. In Schramm (1), it is stated that the viscosity is higher when droplet sizes are relatively homogeneous, thus when droplet size distribution is narrow rather than wide.

2.2.1.3. Solids

Solid particles can stabilize an emulsion. The effectiveness rely on factors such as particles size, particles interactions and wettability of the solids. Solid particles stabilize an emulsion by diffusing to oil/water interface where they form structures as films that can inhibit coalescence of droplets, and they also can be charged which also may enhance the stability. These particles are suggested a typical size smaller than 1 μm to several microns in size and they must be smaller than the size of emulsion droplets (8).

2.2.1.4. Temperature

Kokal (8) mentioned the effect of temperature in the emulsion stability by affecting the physical properties of the fluids that lead to variation in interfacial film between immiscible fluids, and solubility of the oil in the continuous phase. However temperature effects in oil viscosity is the one of the main factor of emulsion instability, oil viscosity decrease when temperature increases. Temperature also increases the thermal energy of the droplets, thus dynamical interaction is more active between droplets and collision frequency increase, and as explained before collision contributes to phase separation due to droplets merging.

2.2.1.5. pH

The stabilizing films contains acids and bases, asphaltenes, and solids. The presence of acids and bases influences their ionization in the interfacial film and may change the physical properties of the film. Additionally it is indicated that pH also influences the type of emulsion formed. At low pH (acidic) water-in-oil emulsions are formed, on the contrary at high pH (basic) oil-in-water emulsions are generally generated (8).

2.2.2. Mechanism of Improving Stability

2.2.2.1. Solid stabilization

Bragg (9) published a method for stabilizing an oil-in-water emulsion by the addition of solids comprising particles as part of the emulsion. Preferably those particles may have a hydrophilic character for making a water external emulsion and an average particle size about 2 microns or less. Carbon dioxide or another gas can be added to the emulsion to decrease the emulsion viscosity; however, as mentioned before, emulsions tend to have the viscosity of the continuous phase, thus an oil-in-water emulsion usually has viscosities closer to water.

As described by Bragg (9) (10) solid particles may vary widely due to existence of different chemical composition, sizes and shapes. However they should have a certain physical and chemical properties:

First, the solid particles should have at least some hydrophilic character for making an external emulsion because particles must be wetted by the external phase. Solid particles may include clay, quarts, feldspar, gypsum, metal sulfides, metal sulfates, metal oxides, coal dust, asphaltenes or polymers, however the wettability nature may be considered for the desired emulsion.

Second, the solid particles must remain undissolved in the water phase under formation conditions, and have appropriate charge distribution for stabilizing an interfacial film between the internal droplet and the continuous phase.

Third, the particle size should be sufficiently small to provide adequate surface area coverage of the internal phase, particle size can be measured by different techniques including laser light scattering, mesh screen classification, coulter counting method, and settling velocity. Nonetheless particles are often irregular and non-uniform in shape.

The oil used for emulsion making should be preferably produced from the reservoir where the emulsion is intended to be injected. Additionally it should contain the sufficient amount of asphaltenes, polar hydrocarbons or polar resins to help stabilize the interface between solids and oil, otherwise these substances shall be added to a required concentration to stabilize the emulsion, if not then oil droplets will aggregate and coalesce and finally separate from the continuous phase (9).

Chemical reaction could lead to precipitation when an incompatible water-external emulsion is injected and it mixes with formation water due to insufficient ion concentration. Thus, to ensure stability under formation conditions formation, water should be used as continuous phase. Nevertheless, fresh water can be used when ion concentration has been adjusted to assure stability (9).

Some additional factor were mentioned before and should be consider when preparing an emulsions: the order in which the fluids are combined, the mixing energy to create a desired droplet size and achieve a proper mixing and wetting properties of the added solids (10).

2.2.2.1.1. Preparation of an oil-in-water emulsion with solids

Solids used to create a water external emulsion should have a hydrophilic wettability, and preferably should not have been exposed to hydrocarbons before their use. The procedure explained by Bragg (9) (10) is described as follow:

“First disperse the solid in the water, then add oil to the mixture with sufficient continuous shearing/mixing energy to produce oil droplets dispersed and stabilized in the water phase, if necessary to prevent oil-external emulsion, oil can be added to the water in small portions with continuous shearing. This process can produce oil droplets having a averaged size diameter from submicron to 30 microns, this varies depending upon the type and amount of mixing energy, the sizes of added particles, the viscosity of the oil, the composition of polar and asphaltenes hydrocarbons and the ionic composition of the water.”

Solids added to the emulsion act in the same way as an emulsifying agent, since solids are distributed in a certain way as a protection layer all along the oil/water interface to prevent coalescence. As a result emulsions prepared with solid particles may not be thermodynamically stable, but can have a metastable state for months or years, when used in the industry (9).

Once injected emulsions are intended to be trapped in the porous throats due to both pressure difference and greater diameter to produce constriction this is also applicable to emulsion stabilized by emulsifier agents. Formation permeability evaluation must be executed to know the adequate emulsion droplet size that should be injected. This procedure and entrapment mechanisms will be covered further in the next chapter. However Bragg (9) suggests that besides the permeability determination an additional comparative core flood test using an alternative solids type should be executed, using more or less hydrophilic-wettability surface solids than the original that are intended to be used. To determine if increased stability during flow can be achieved. Therefore and optimal solid type, wettability and concentration of solids can be determined.

2.2.2.1.2. Selection of Candidate Solids

Bragg (9) indicates that emulsion stability is achieved if solids used have high surface area/volume ratio, small mass and average size particle size of two microns or less, and have surface that is either attracted to oil phase by polar or asphaltenes hydrocarbons and surface partially or substantially hydrophilic to form an oil-in-water emulsion. Some solids used include, clays such as kaolinites or bentonites, or fumed silica. It is important to point out that surface wettability of the solids may be modified from a natural hydrophilic to oleophilic, thus solids may be used to create either oil-external or water-external emulsions.

Some hydrophilic fumed silicas such as Aerosil® 200 or Aerosil® 90 offered by Evonik Industries AG (11), are just examples of the complete list that is showed in Table 2.1. These are small particles that are naturally hydrophilic (untreated) that form stable structures even under high temperatures (200°C), with specific surface area that can varies from 35 to 410 m²/g , a mean primary particle diameter of 5-50 nm. According to the fabricant fumed silicas have different properties, first property is a preferential aggregate size of approximately one hundred to several hundred nanometers. The second is a surface chemistry that allows the aggregates to build network structures via hydrogen bonds or van der Waals forces – either with one another or with other filler materials such as pigments, additives, resins, solvents, etc. According to Bragg (9) with oil external emulsions concentrations of these silicas (other not referenced here) have been found effective from ≥0.5 g/L to ≤20 g/L, however concentrations for water external emulsions are not published, nonetheless suggested experiment was described above for suitable concentration determination.

Other solid particles are the natural clays such as kaolinite with an effective particles size of 1.0 microns or less, with a high surface area of 10-20 m²/g, this clay normally have hydrophilic surfaces. Other clays are the Bentonites clays, this consists of aggregates that can be broken up in particles with an average size diameter of 2 microns or less (9).

Table 2.1 – Aerosil® Hydrophilic fumed silica. Ref (11)

Hydrophilic fumed silica

AEROSIL® fumed silica—product groups

Physico-chemical data of hydrophilic fumed silica

Grades	BET surface area [m ² /g]	Loss on drying [%]	pH value
→ AEROSIL® 90	90 ± 15	≤ 1.0	3.7-4.7
→ AEROSIL® 130	130 ± 25	≤ 1.5	3.7-4.5
→ AEROSIL® 150	150 ± 15	≤ 1.5	3.7-4.5
→ AEROSIL® 200	200 ± 25	≤ 1.5	3.7-4.5
→ AEROSIL® 255	255 ± 25	≤ 1.5	3.7-4.5
→ AEROSIL® 300	300 ± 30	≤ 1.5	3.7-4.5
→ AEROSIL® 380	380 ± 30	≤ 2.0	3.7-4.5
→ AEROSIL® OX 50	50 ± 15	≤ 1.5	3.8-4.8
→ AEROSIL® TT 600	200 ± 50	≤ 2.5	3.6-4.5
→ AEROSIL® 200 F	200 ± 25	≤ 1.5	3.7-4.5
→ AEROSIL® 380 F	380 ± 30	≤ 2.0	3.7-4.5
→ AEROSIL® 200 Pharma	200 ± 25	≤ 2.5	3.5-5.5
→ AEROSIL® 300 Pharma	300 ± 25	≤ 2.5	3.5-5.5

The data represents typical values.

2.2.2.1.3. How particles flow in water-oil interface

Dommersnes and coworkers (12) published a study about how electric fields can alter the colloidal formation at the oil-water interface. They found that a ribbon-shaped film is formed when underwent by DC electric field, additionally behavior of the ribbon changed with respect of the orientation of the field (see Figure 2.3a). They observed a ribbon in less than a minute after mixing fluid with solids and in about 4 minutes the drop becomes transparent due to clay migration to the ribbon in the direction of the field. This ribbon-shape formation along the droplet surface suffered a slightly disrupt when electric field is stopped which indicate that clay bound are irreversibly under this conditions.

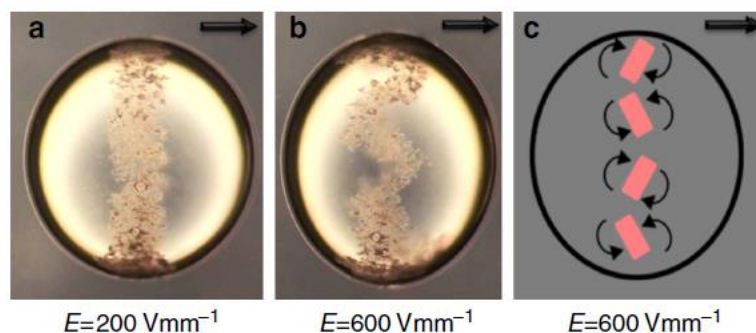


Figure 2.3 – Break up of clay ribbon into rotating domains. Ref (12)

Clay particles form a ribbon under a DC electric field when mixed with the external fluid (12), this behavior can be divided into two processes: first clay particles move from the drop bulk to the interface, and secondly an assembly of the ribbon film with strong adherence on the drop surface. Therefore emulsions stability is assured due to capillary bidding, that is when a particle is trapped in a capillary barrier with substantial energy cost of moving to either side of the liquid interface this effect is also studied by Averyard et al (13).

Additionally it was proved that the width of the ribbon depends on the clay concentration, thus when clay concentration was 1.5% the ribbon almost covered the surface, on the contrary when 0.5% the ribbon is narrow (12).

On the other hand when subjected to AC electric field the colloidal particles migrates to what so called equator or the poles of the droplet, this is called dielectrophoresis (DEP) effect, which can also be applied to remove particles from broken-up droplets. The power of the electric field also affects the ribbon-shape formation at the oil-water interface. At lower clay concentration, if electric field strength is increased ribbon breaks up into several counter-rotating colloidal assemblies, particles that are less conducting than their surrounding liquid can spin in DC Electric fields (see Figure 2.3) (12).

2.3. Overview of EOR

Enhanced oil recovery has been developed for a long time in the petroleum industry. Several methods including chemical injections of surfactants or polymers, also the application of heat through thermal techniques and the most common-applied water or gas flooding are some examples of technologies applied in the oil industry with the only objective to improve the oil recovery of fields in secondary and tertiary production stages.

Farouq (14) explains several non-thermal techniques that are currently still applied in oil recovery, including water and polymer flooding, gas injection, solvent stimulation and other methods. In his paper it is pointed out the importance of heavy oil fields, with oil viscosities within the range of 50-500 cp for moderately viscous to thousands in heavy oils. Heavy and intermediate oils reservoir constituent the vast majority of oil resources world widely.

Oil recovery techniques for this type of reservoirs are addressed to reduce the viscosity of the oil by applying thermal techniques such as steam injections or in situ combustion. However in most of the cases limited economic resources or reservoir conditions such as thin reservoirs, high permeability, great depth, etc., make unfavorable the application of such techniques (14).

Therefore non-thermal techniques are considered in most of the cases to be applied for increasing the oil recovery, which in heavy oil reservoirs may be challenging due to high viscosity, thus low mobility of the fluid may be expected and inefficient sweep can be experienced. Oil displacement is more efficient when the mobility of the displacing fluid is less than the displaced fluid (oil), therefore the challenge is to generate a low mobility drive fluid in a cost-effective manner.

On the other hand water flooding is frequently used as secondary recovery. This technique may be optimal when limited economic resources exist and when displacing oils with similar mobility. However in viscous oil reservoirs the low mobility of the oil makes this method inefficient, water viscosity is hundreds lowers than heavy oil, hence mobility is much greater than the oil and unfavorable mobility ratio has place, the viscosity difference cause channeling or fingering in the reservoir sweep and an early water breakthrough. Ending up with high water water-oil-ratio (WOR) and low sweep efficiencies of oil displacement (14) (15).

Chemical injection is often useful for improving the sweep in the reservoir and different issues may be solved by the use of chemicals. On one hand by polymer injection water mobility may be decreased, thus a favorable mobility ratio can be obtained and volumetric sweep efficiency are optimized. Injection of polymer may not reduce the residual oil saturation in the reservoir but results in an improvement of displacing front stability and better oil recovery can be obtained compared to other techniques such as water flooding (15).

Another chemical injection is by using surfactants, this recovery technique reduces the capillary forces that may retain the small oil droplets trapped in the reservoir porous media. As result residual oil saturation may be decreased by increasing the oil displacement, thus the oil recovery. Despite chemical flooding may lead to convenient results in oil recovery, this technique usually cannot be

economically applied in viscous reservoirs since the amount of chemical needed may be uneconomically sustainable (14) (15).

Additionally rock permeability can also has a great impact in oil recovery. Reservoir heterogeneity may lead to thief zones in which the displacing fluid tends to channel quickly due to higher permeability, thus low sweep efficiency may be obtained due to uncovered zones. Therefore a fluid injected at low cost is more likely to reduce fluid mobility in a “piston-like” manner displacement when low permeable zones are swept or in present of reservoir with lower heterogeneity (14).

Several methods have been used to reduce the permeability of high permeable zones. Injection of polymers and gels or cross-linked aldehydes are typical agents that can be injected for the profile modification. However these techniques only affects the closet region to the wellbore due to fast action of the agents, once in place gels are immobile. Usually this injection is followed by waterflooding which in most of the cases finds a new path between the gels and decreasing the permeability reduction effect in the formation.

Due to the inconveniences presented above and such others with thermal and non-thermal techniques, the oil industry has found in the emulsion flooding an attractive technology for increasing the oil recoveries avoiding the low oil displacements and sweep efficiencies obtained in waterflooding and high investment required in the chemical injection, and also proving to be an excellent agent for profile modification reducing the permeability of high permeable zones.

2.4. Emulsions in EOR

Several labs and in-field experiments have been carried out, and in most of the cases water-in-oil or oil-in-water emulsions have showed improvements in oil sweep in the tertiary recovery and increases in oil recovery compared to water flooding.

Emulsions flooding basically consist on a preparation on surface of a lyophobic emulsion, which is thermodynamically unstable and not possible to be formed spontaneously at the reservoir. Emulsions as was mentioned previously are constituted by water, oil and an emulsifying agent. This immiscible and stable mixture is injected in the reservoir and studies have shown that both water-in- oil and oil-in-water emulsions flooding can lead to convenient results in oil recovery increasing.

Farouq (14) mentions that emulsion flooding is basically covered by four mechanisms: emulsification and entrainment, wettability reversal and emulsification and entrapment. This last dominates the viscous oil reservoirs displacement.

McAuliffe (16) explains the concept of emulsion flow in a porous media. He states that if an oil- in-water emulsion is injected in the reservoir, the droplet enters a pore, and if its radius of curvature is smaller than the radius of the pore it will experience a constriction dominated by a capillary pressure greater in the front than in the back (Figure 2.4). This effect is called “Jamin” (17) and it will be evident when more droplets are trapped.

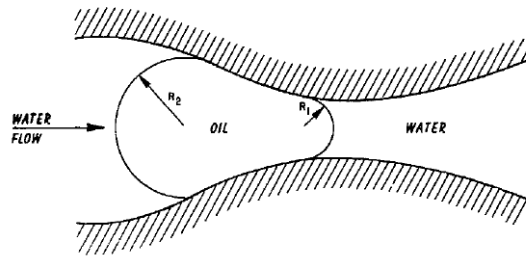


Figure. 2.4 – An oil Droplet entering a pore constriction. Ref (16).

As mentioned before, emulsions in heavy oil displacement are dominated by this type of entrapment, when moving downstream and encounter a small pore throat. This is an indication of emulsion effectiveness, in oil-in-water emulsions oil droplets should be slightly larger than the pore throat in the porous medium (16).

Emulsion flooding is usually followed by water flooding (16). However due to water is the external phase then emulsions it will tend to flow through preferable water flooding paths (water-wet rock surfaces) entering the more permeable zones, as being trapped in the porous medium, flow is restricted and effective permeability of the water is decreased and driving water flooding is forced to flow in less permeable zones, resulting in greater sweep efficiency.

The entrapment process may occur only if the injected emulsion droplets size is adequate to achieve the constriction in the porous throat all along the formation. Bragg (9) suggests that the lower limit of rock permeability can be determined by laboratory test where emulsion flows through a series of rocks of decreasing absolute permeability that known in advance. Procedures may include pressure drop measures across the core at measured flow rates that indicate if emulsion has been trapped in the porous media or passes without constriction through it.

2.4.1. Emulsion flooding experiments

Several experiments to analyze the effectiveness of the emulsion injection have been executed, however literature is still limited about this method. One of this experiments was carried out by Demikhova et al. (18), in it a sand pack using quartz Ottawa sand was flooded with two oil-in-water emulsions prepared separately EM1 and EM2. The dispersed phase was represented by two ionic liquids (called IL1 and IL2) used in each emulsion respectively. An emulsifying agent was used in aqueous phase. Ninety percent of emulsion droplet size had 5 μm . Additional properties of the components of the emulsion may be found in the paper. A total of nine displacement tests were carried out, varying parameters such as temperature, water salinity, permeability, porous media and emulsion concentration. Emulsion flooding was considered as tertiary recovery followed by water displacement, secondary recovery was covered by waterflooding.

Results showed that in all cases both emulsions EM1 and EM2 lead to increase the oil recovery obtained by water flooding after emulsion entrapment. Additionally was found that the use of an organic or inorganic anion in the dispersed phase of the emulsion will impact the recovery results. Although it is not clearly indicated which one generated the best results, it is stated that the emulsion that used the IL2 showed better results with recovery increasing up to 17%. Moreover at reservoir conditions including sandstone representative sample and reservoir temperature up to 79°C it was obtained 29% additional recovery by the tertiary recovery with emulsion displacement. The experimental result is shown in Table 2.2, which was showed in the referenced paper (18).

Table 2.2- Experimental data of oil recoveries during water and emulsion injection in porous medium, Ref (18).

	Sand (0.35 D) distilled water	Sand (3.7 D) dist. water	Sand (2.1 D) sea water	Berea (0.21 D) dist. water	Berea (0.33 D) dist. water	Berea (0.65 D) brine
Emulsion	S_{or} (%) / additional oil recovery (%)					
Em1 (10 %)	53.5/3.4	-	-	41/15.3	-	-
Em2 (10 %)	56.8/17.7	-	-	34/22.8	-	-
Em2 (1 %)	-	34.8/17.7	55.87/23 37.3/16.5	-	16.7/12	65.4/29

It was concluded (18) that emulsion injection changes the water preferential paths by blocking the porous media in high permeability zones as well supported by the adsorption of hydrophobic droplets in rock surface that change the wettability of the rock to oil-wet. This factor improves the volumetric sweep allowing to improve the oil recovery by displacing the viscous but mobile oil in the porous media.

McAuliffe (19) executed what is considered one of the very limited emulsion flooding jobs at field level. Injecting 236000 bbl of a 14% oil-in-water emulsion at section of the midway-sunset oil field in California, USA. A caustic oil-in-water emulsion was prepared, containing 70% of Midway sunset crude oil with 14° API mixed with 30% fresh water phase contained 1% sodium hydroxide, prepared in 450 bbl batches in 500 bbl tanks. The average droplet diameter was 3 μ m and 200 cp of viscosity, which is considered easy to pump.

The recovery displacement was carried out by water and emulsion flooding intervals. In 1962 waterflooding began for about three years followed by a fresh water cushion injection. In 1967 emulsion flooding was started with an increasing concentration up to 14% oil in water emulsion, by 1968 a total on 236000 bbl of emulsion containing 33000 bbl of crude oil were injected equivalent to 3 PV. Emulsion flooding was followed by the injection of 4PV of fresh water and resumed the saline water injection afterwards (19).

Results for waterflooding shows that by 1967 fluid production increases with no increase in oil production, therefore it is inferred that water sweep efficiency is low due to reach the production wells, leaving a high residual oil saturation values in the field. Results shown in Figure 2.5 obtained from referenced paper (19).

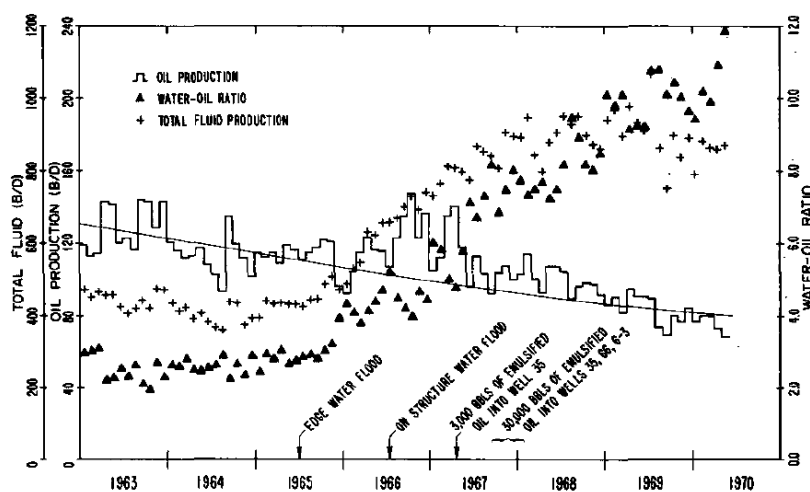


Figure 2.5 – Fluid Production from waterflood area. Ref (19).

On the other hand the emulsion-treated area experienced an averaged stable fluid production. In 1967 emulsion effects were observed with an increasing of both oil production and total fluid production after emulsion was injected for about 4-month long. A total of 55000 bbl of additional oil were attributed to emulsion flooding. Results are shown in Figure 2.6 obtained from referenced paper. Additionally radioactive tracers contained in the injected fluids indicated that better sweep efficiency occurred during emulsion injection, making a favorable change in flood pattern after emulsion injection. It was concluded that the injection of emulsified oil decreased fingering and increased volumetric sweep efficiency, attributed by a formation heterogeneity correction (19).

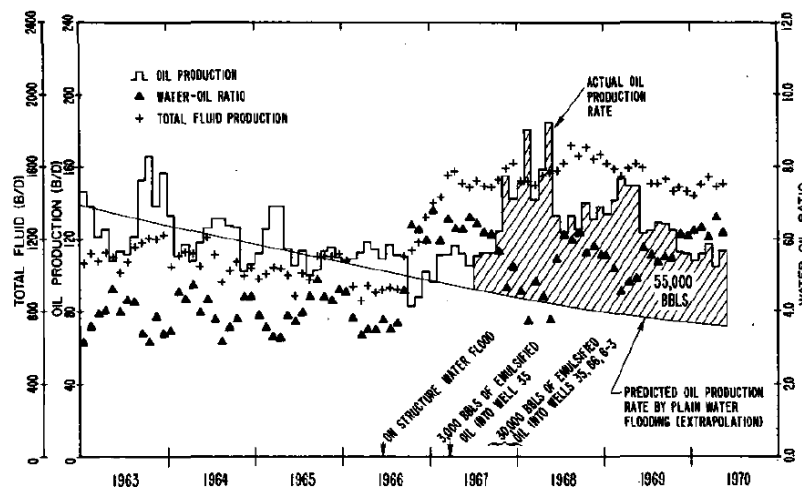


Figure. 2.6 – Fluid Production from emulsion-treated area. Ref (19).

2.4.2. Emulsions properties based on experiments

McAuliffe (19) also shows interesting conclusions of flow properties of oil-in-water emulsions based on lab experiments. On one hand at the moment of emulsion preparation it is important to consider that a synthetic surfactant can help to emulsify a not-achieve emulsion of crude oil with lower content of organic acids and a sodium hydroxide. A nonionic synthetic surfactant is required if the emulsion has saline water as continuous phase, presented in many reservoirs. Additionally it is indicated that not enough caustic may be insufficient to neutralize organic acids to create an emulsion. On the other hand excess of sodium hydroxide produce very viscous emulsion in some cases greater than the based oil.

In terms of bulk viscosity, it was found that emulsions tend to have the viscosity of the continuous phase, thus if water is the aqueous phase the emulsion viscosities will tend to be around 1 cp even when using crude oils with viscosities about 3500 cp. Table 2.3 shows different values of emulsions viscosities obtained from different oils, observe that even when the viscosity of the dispersed oil is 1000000 cp the emulsion viscosity is 12 cp. This characteristic allows the oil-in-water emulsion to be injected easily in the reservoir avoiding injectivity issues due to high viscosities (present in water-in-oil emulsions), additionally since emulsion purpose is to block high permeable zones then low viscosity lead to higher mobility and it is more likely for the emulsion to flood and decrease the permeability to the water, forcing the waterflooding to swept less permeable zones (19).

Table 2.3 – Viscosities (at 75°C) of oil-in-water emulsions prepared from different crude oils. Ref (16).

Percent Oil in Emulsion	Emulsion Viscosity (cp)		
	Midway-Sunset 15A	Casmalia	Boscan
80	1,200	1,200 to 5,000	
70	185	200	800
60	28		55
50		12	14
40	6		
20	1.6		
10	1.1		
Oil Viscosities, cp	3,600	1,000,000	180,000

Additionally experiments (19) show that below 50 percent of oil content the emulsion behaves as a Newtonian fluid; for a higher content of oil the emulsion changes and starts to behave as a pseudo non-Newtonian fluid that is a fluid which its flow varies with pressure and its viscosity lecture depends on the shear rate used to measure the viscosity.

This property was analyzed by flowing the emulsion through a core varying the pressure, results indicate that permeability reduction is more effective at lower pressure difference (results shows in Figure 2.7), since emulsion entrapment in a smaller pore throat is a combination of viscous and capillary forces in the porous medium, and entrapment will occurs if the pressure at the rear of the droplet is equal to the pressure on the back and will remain until the pressure is higher enough to let the droplet deforms and continue flowing. Therefore since the highest pressure difference occurs near wellbore this will help to easy injection into the reservoir avoiding infectivity issues and due to pressure difference reduction occurs as the distance from the wellbore increase, thus emulsion effectiveness for permeability reduction increases with the displacement (19).

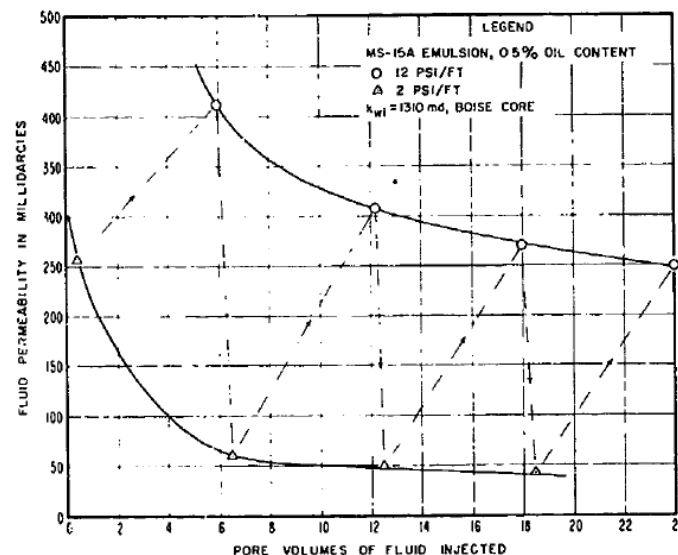


Figure 2.7 – Pseudo non-Newtonian flow of the oil-in-water emulsions in porous media, Ref (16).

Rocha de Farias and coworkers (20) concluded that oil droplets can be deform and cross pore throats of smaller size due to a competition between viscous and capillary forces, the balance is represented by the capillary number (N_c) given by equation 2.13, where μ is the viscosity of the continuous phase, v is Darcy velocity and σ is the interfacial tension:

$$Nc = \mu.v/\sigma \dots \dots \dots (Eq. 2.13)$$

Cobos et al. (21) Executed some experiments about the art and found that the capillary number has a strong effect when the larger droplets flow through the porous media. The pressure gradient of the flow will not change due to droplet deformation when passes through a constriction if the capillary number is above defined critical value. Therefore as stated before the mobility may be controlled at a certain distance from the injection well.

Emulsion droplets size is a key parameter of quality and lead to determine its effectiveness in reducing permeability in high permeable zone to increase sweep efficiency. McAuliffe (16) mentioned that droplets size can be altered either by varying the concentration of sodium hydroxide or by use of different oil. However for the offshore reservoir fields in the North Sea injection of sodium hydroxide will result in precipitation of minerals in the reservoir that may altered permanently the permeability in undesired zones. Figure 2.8 shows that as the sodium hydroxide increase the droplet size distribution tends to be narrow at the smaller sizes resulting in sustained stability throughout the time of injection.

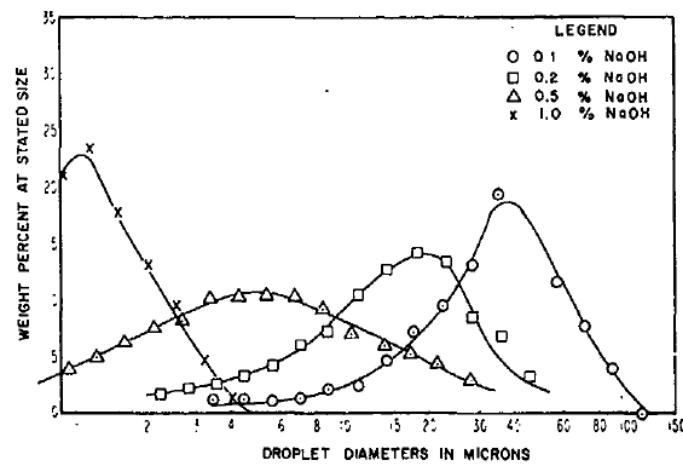


Figure 2.8 – Size distribution of emulsions prepared with crude oil and sodium hydroxide solutions. Ref (16).

As was mentioned before emulsions flooding is less effective in low permeable zones or tight sands, due to droplet size is required to be smaller than 2 μ m, and emulsion entrapment may have the risk to be entrapped at the beginning of the injection, therefore fingering may not be effectively blocked and sweep efficiencies are not improved as desired. McAuliffe (16) proved this hypothesis by flow an emulsion through three like-permeability cores mounted in parallel, three sets of cores with high, medium and low permeability were flooding respectively. Results show that in the high permeable cores the permeability reduction by the emulsion flooding was observed until the last core. However for the medium and low permeable cores the permeability reduction is only effective in the first core, thus the medium and last core had no affectation.

Finally a comparative oil recovery results to prove once again the benefits of emulsion flooding was reported at McAuliffe (16) work. Same permeability cores were flooded with water and emulsion respectively. Figure 2.9 shows the results of the experiment where is cleared inferred that emulsion flooding lead to higher oil recoveries than the waterflooding, it is concluded that the improvements in fluid displacement are attributed to a correction of heterogeneity in porous media.

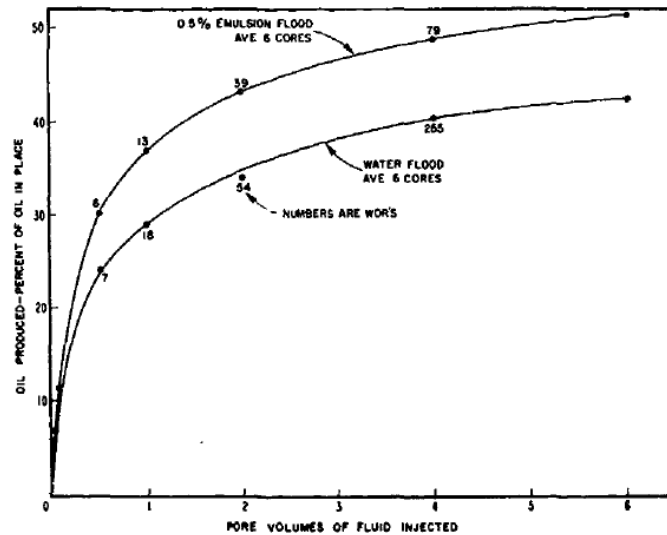


Figure 2.9 – Oil displacement from oil reservoir sandstone cores by water and by 0.5 percent oil-in-water emulsion. Ref (16).

2.4.3. Factors affecting emulsion displacement

Sarma et al (22). pointed out different factors that affect the emulsion flooding process including volume fraction of solvent in the injected emulsion, nature and concentration of the emulsifier, drop size distribution of the injected emulsion, nature of solvent used, emulsion slug size, absolute permeability of the reservoir sand, permeability heterogeneity, mineral content of the sand, flow velocity and viscosity of the oil. Some of these factor been mentioned before, nonetheless the author has established four key parameters by their experiments:

2.4.3.1. Solvent fraction in emulsion

Several samples were tested (22) with different fractions %wt of oil in the emulsion. The results show than increasing the concentration of disperse phase helps to improve the oil recovery. Thus the richest emulsion lead to better results (see Figure 2.10), however even the lowest concentration 10% has the ability to block the porous media and improve the mobility control. Notice that at 0.2 PV approximately the porous media correction starts to have effect and all the emulsions increase the recoveries, however the two highest concentrations shows the best results, this behavior remains but at 1 PV injected approximately the 40%wt emulsion starts to decrease oil percentage, due to apparent loss of mobility control, the reason of this phenomena is not clarified at the literature. Nonetheless all the emulsions by the end of the plotted injection have a narrow margin of performance.

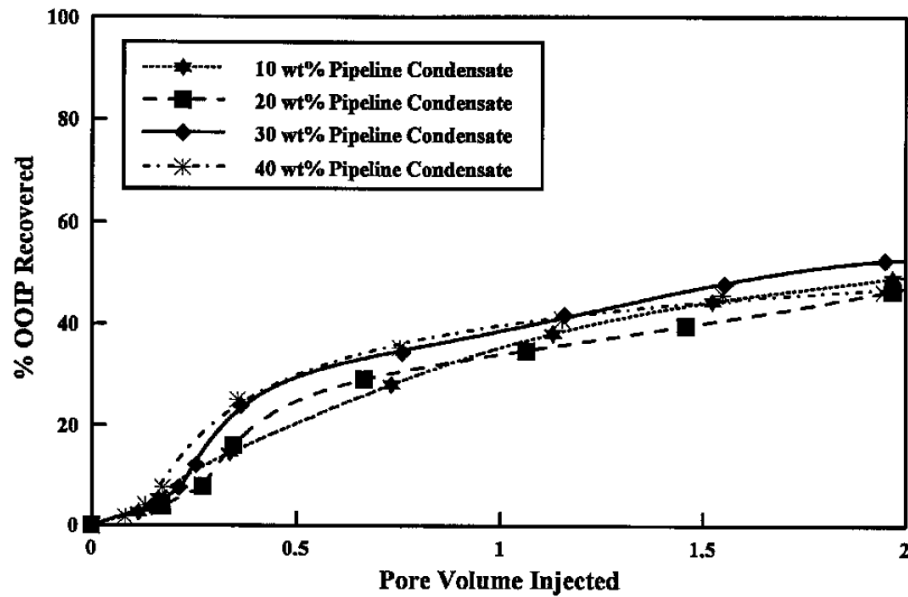


Figure 2.10 – Effect of condensate concentration on oil recovery (1% emulsifier in emulsion, displacing oil). Ref (22).

Additional research in the matter was executed using two lean emulsions with 10% and 5% of dispersed oil respectively (22). Results show in Figure 2.11 indicate almost 20% of additional oil recovery using 10%wt emulsion than 5%wt. Authors suggest that in this case mobility control is not the main mechanism but the viscosity reduction due to the mixing of the disperse phase with the formation oil.

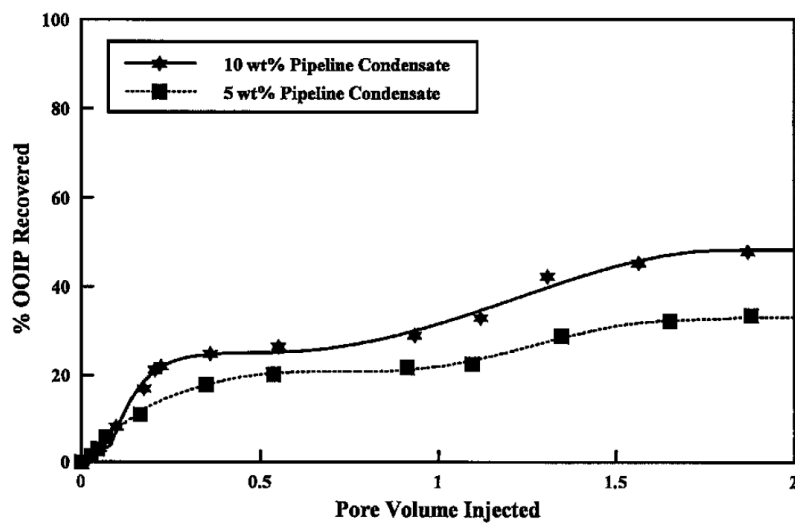


Figure 2.11 – Effect of condensate concentration on oil recovery (0.5% emulsifier in emulsion, displacing oil). Ref (22).

2.4.3.2. Emulsifier concentration

Sarma et al. (22) suggest that at higher emulsifier concentration the stability of the emulsion increase due to decreasing of droplet size distribution, this strength the mobility control capability but would diminish the oil viscosity reduction by dispersed oil and formation oil mixing. Results are supported by experiments shown in Figure 2.12 where the higher the emulsifier concentration the higher the oil recovery.

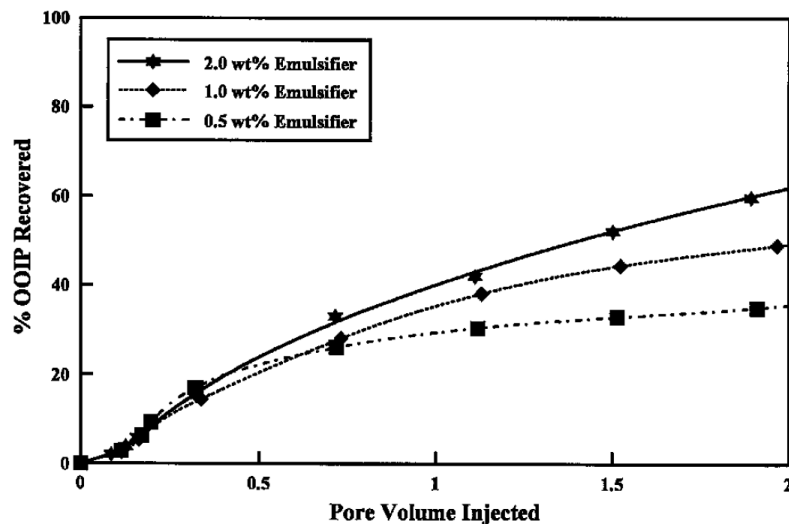


Figure 2.12 – Effect of condensate concentration on oil recovery (10% of oil in emulsion). Ref (22).

2.4.3.3. Oil Viscosity

Results in the literature show that considerable lower oil recoveries are obtained when using a more viscous oil. This result is coherent with the emulsions properties exposed previously, emulsions try to obtain apparent viscosity values closer to the value of the external phase, if viscous oil is dispersed in the emulsion then the flooding process is affected due to the displacement of the oil droplets (22).

2.4.3.4. Flow Velocity

Flow velocity on displacement performance is likely to depend on which mechanism is playing the dominant role. If viscosity reduction by mixing of oil and solvent is important then the performance is likely to be better at lower flow rates. More time would be available at lower flow rates for this mechanism to work. However, if mobility reduction was the dominant mechanism, the performance of very stable emulsions should be insensitive to flow rate, as long as the flow rate is not high enough to increase the pressure gradient to such a high level that the trapped emulsion droplets start squeezing through the pore throats. Nonetheless with moderately stable emulsions the extra time available at lower flow rates may diminish the performance since it may allow the drop size distribution to change towards a less effective size. If in situ emulsification is also a factor, it would become more pronounced at higher flow velocities (22).

3. Experiments Description

Three major experiment procedures are presented in this chapter. Firstly procedure to perform a stability analysis of an oil-in-water emulsion stabilized by clay solid particles. Secondly, a procedure to carry out an oil and solid particles screening in order to determine the appropriate ratio of material solid particles (g)/oil (ml). And finally, a procedure to execute a core flooding by both waterflooding and emulsion-flooding that leads to a permeability reduction impact study.

All procedures found in this chapter are presented in present-tense to facilitate their application as reference by any user in the future.

3.1. Experiment 1: Emulsion Stability & Flotation Analysis

The first stage of experiments involves the preparation of an oil-in-water emulsion, capable to be stabilized by clay solid particles throughout the time.

3.1.1 Description

Objective

Identify an emulsion similar as can be found in produced water, stabilized by clay solid particles. Additionally a flotation analysis of solid particles shall be carried out by being able to study how the stability and behavior of different samples of emulsion is affected by the modification of several parameters.

Oil-in-water emulsion stability using solid-stabilized particles is analyzed. Two different types of fluids will be used as external phase, a synthetic formation water and a low salinity water, and these are mixed with an oil sample from the North Sea respectively. Emulsion stability is intended to be reached by solid-stabilized particles such as clays (kaolinite, bentonite) at different concentrations.

Different parameters such as external phase salinity, solid particles wettability, internal phase concentration and external phase compositions are tested in order to determine its influence in the emulsion stability.

Material:

- Synthetic Formation Water (FW)
- Low Salinity Water (LSW)
- Stock Tank Oil 1 (STO1)
- Solid-Stabilized Particles
 - o Kaolinite
 - o Bentonite
- Measured bottles of 250 ml
- Mixer (Silverson mixer)
- Weight scale

Fluids

<i>Table 3.1.1 - External-Phase Fluid Composition.</i>			
Components		FW (g/l)	LSW (g/l)
NaCl	Sodium Chloride	77.4	10.17
Na ₂ SO ₄	Sodium Sulfate	0.13	-
NaHCO ₃	Sodium Bicarbonate	-	-
KCl	Potassium Chloride	0.42	-
MgCl ₂ ·6H ₂ O	Magnesium Chloride Hexahydrate	3.55	-
CaCl ₂ ·2H ₂ O	Calcium Chloride Dehydrate	21.75	0.11

3.1.2 Procedure

Part I. Preparation of Base Case.

Base case emulsion is prepared by mixing synthetic formation water (FW), stock tank oil 1 (STO1) and hydrophilic solid particles as follows:

- Prepare 2 liters of FW using composition found in Table 3.1.1
- Transfer 240 ml of brine into 4 different samples of 250 ml-vessels each.
- Add solid-stabilized particles (Kaolinite or Bentonite) in each sample based on the quantity found in Table 3.1.2. Mixing simultaneously for about 5 minutes using a Silverson mixer with a high shear square hole head at 6000 rpm. The original solid particles surface is water-wet.

<i>Table 3.1.2 - Emulsion Samples Preparation Quantities.</i>			
Sample N°	FW (ml)	Solid Particles (g)	STO1 (ml)
1	240	1.00	1.00
2	240	1.00	5.00
3	240	5.00	1.00
4	240	5.00	5.00

To increase results reliability, it is decided to measure fluids density with a densitometer DMA 4500M Aston Paar and determine the equivalent mass of each, Table 3.1.3 summarized the calculated data:

Formation water density: 1.06 (g/cm³)
STO1 density: 0.85308 (g/cm³)

<i>Table 3.1.3 - Emulsion Samples Preparation Quantities (g).</i>			
<u>Sample N°</u>	<u>FW</u> <u>(g)</u>	<u>Solid</u> <u>Particles</u> <u>(g)</u>	<u>STO1</u> <u>(g)</u>
1	255.51	1.00	0.85
2	255.51	1.00	4.26
3	255.51	5.00	0.85
4	255.51	5.00	4.26

- d) While mixing add the STO1 carefully using a syringe, based on the mass shown in Table 3.1.3 for each sample. Continue mixing for another 10 minutes.

STO's total acid number (TAN) and total base number (TBN) can be found in Table 3.1.4.

<i>Table 3.1.4 - STO's Total Acid Number (TAN) and Total Base Number (TBN).</i>		
<u>Fluids</u>	<u>TAN</u> <u>(mg KOH /g oil)</u>	<u>TBN</u> <u>(mg KOH/g oil)</u>
STO1	0.1	1.9

- e) Transfer the prepared emulsion immediately to a measuring cylinder of 250 ml and cover it with parafilm. During the observation period samples must remain steady and at room temperature.
- f) Each sample (1, 2, 3 and 4) is observed and volume of free oil after 0.5, 1, 2, 4, 6, 24 and 48 hours is measured in all the samples.
- g) Determine the amount of "free water" column observed either at the top or bottom of each sample.

Part II. Varying (decreasing) external phase salinity.

- a) Low salinity water (LSW) is prepared and intended to be used as external phase, in order to analyze the effect into the emulsion stability with a low salinity environment. LSW uses the composition found in Table 3.1.1 and the rest of the parameters keep constant.
- b) Four samples are prepare using the quantities found in Tables 3.1.5 and 3.1.6 data was calculated using the density of the LSW and STO1.

Initially each sample is with a water (LSW) and solid particles using a Silverson mixer with a high shear square hole head at 6000 rpm. Consecutively the required amount of oil is added and mix for about 5 more minutes.

<i>Table 3.1.5 - Emulsion Samples Preparation Quantities.</i>			
<u>Sample N°</u>	<u>LSW</u> <u>(ml)</u>	<u>Solid</u> <u>Particles</u> <u>(g)</u>	<u>STO1</u> <u>(ml)</u>
1	240	1.00	1.00
2	240	1.00	5.00
3	240	5.00	1.00
4	240	5.00	5.00

Low Salinity Water (LSW) density: 1.005 (g/cm³)

STO1 density: 0.85 (g/cm³)

<i>Table 3.1.6 - Emulsion Samples Preparation Quantities (g).</i>			
<u>Sample N°</u>	<u>LSW</u> <u>(g)</u>	<u>Solid</u> <u>Particles</u> <u>(g)</u>	<u>STO1</u> <u>(g)</u>
1	241.25	1.00	0.85
2	241.25	1.00	4.26
3	241.25	5.00	0.85
4	241.25	5.00	4.26

- c) Transferred each sample to a 250 ml cylinder and cover it by parafilm. During observation period samples must remain steady and at room temperature.
- d) Each sample (1, 2, 3 and 4) is observed after 0.5, 1, 2, 4, 6, 24 and 48 hours and free volume of oil is determined on each.
- e) Determine the amount of “free water” column observed either at the top or bottom of each sample.

Part III. Varying solid-particles surface wettability

Base Case is selected but wettability of the solid particles is modified to a more oil-wet surface, in order to observe how solid particles interacts with the internal phase and its influence on the emulsion stability. The parameter is modified from Part I procedure as follows:

- a) FW composition remains the same as in Part I.
- b) Prepare four samples of solid particles and STO1 using the quantities found on Table 3.1.3 respectively, and mixed manually assuring the closest to a homogenous mixture. Then the four samples are stored at reservoir temperature 80°C for 72 hours.

The kaolinite is naturally hydrophilic, however by allowing and interaction between solid particles and oil at reservoir temperature for an enough time, the high molecular weight polar

hydrocarbons and asphaltenes (if exist) are absorbed onto particles surfaces and wettability may partially be changed to a more oleophilic type.

- c) After 72 hours, take the four samples out from the oven and mix repeatedly until reach a so-called homogeneous sample, consecutively mix with the corresponding FW quantity according to Table 3.1.3, by using a Silverson mixer with a high shear square hole head at 6000 rpm for about 15 minutes.
- d) Transfer each sample to a 250 ml cylinder and cover by parafilm. During observation period samples must remain steady and at room temperature.
- e) Each sample is observed after 0.5, 1, 2, 4, 6, 24 and 48 hours and free volume of oil is determined respectively.
- f) Determine the amount of “free water” column observed either at the top or bottom of each sample.

Part IV. Varying both external phase salinity and solid particles surface wettability

In the fourth part of this experiment there is a combination between parts II and part III (previously shown), thus both the salinity of the external phase and the wettability of the solid particles are modified in order to analyze the favorability of this environment in the emulsion stability. This part is executed as follows:

- a) First solid particles surface wettability is changed to a more oleophilic type by employing the same technique using in Part III step b (four samples are intended to be prepared).
- b) LSW is prepared using the same composition found in Table 3.1.1, this water will be used as external phase in the emulsion.
- c) After 72 hours of interaction between the solid particles and STO1 the samples are taken out of the oven and mixed manually until a so-called homogeneous mixture is reached, next mix with the corresponding amount of LSW quantity indicated in Table 3.1.6, by using Silverson mixer with a high shear square hole head at 6000 rpm for about 15 minutes each sample.
- d) Transfer each sample to a 250 ml cylinder and cover by parafilm. During observation period samples must remain steady and at room temperature.
- e) Each sample is observed after 0.5, 1, 2, 4, 6, 24 and 48 hours and free volume of oil is determined respectively.
- f) Determine the amount of “free water” column observed either at the top or bottom of each sample.

3.2 Experiment 2: Solid Particles and Oil Quantity Screening

3.2.1 Description

Flotation experiments in section 3.1 were intended to analysis both emulsion stability and the behavior of emulsion under different scenarios of fluids variations. However emulsion preparation in

the practice will require a procedure in which oil droplets protection is assure and no more material than needed is used.

Therefore in the Experiment 2 procedure several screening tests will be carried out in order to determine the appropriate quantity of solid particles per milliliter of oil that must be added to the emulsion in order to assure stability by effective attraction and coverage of oil droplets by solid-particles and at the same time avoiding using more solid particles material than needed.

As soon as the solid-particles/oil quantity rate is determined, the emulsion will be injected in the core following by synthetic water flooding to analyze both porous media blocking and heterogeneity correction effects.

3.2.2 Procedure

The screening rate comprises two parts, the first one corresponding to screening of solid particles using kaolinite and bentonite. Secondly an oil screening is required to saturate the solid particles in the emulsion is assed.

Materials

- Solid particles: Bentonite, Kaolinite
- Synthetic formation water
- Stirrer: Silverson and Magnetic
- Beaker to contain 1 Liter of fluids
- Recipient for storage, 1 Liter of fluids

Solid-Particles Screening

Quantity of solid particles per milliliter of oil will be determine by the following procedure:

- a) Prepare 1 Liter of formation water with the composition shown in Table 3.1.1
- b) Measure 1 milliliter of STO1 (oil); according to STO1 density 0.854 [g/cm³] this volume is equivalent to 0.854 g to be precise. This quantity of oil was determined at the maximum in which the concentration of oil in the emulsion is less than 1000 ppm following the environmental rules (with 1 ml it is obtained 852 ppm).
- c) Pour the prepared FW on an appropriate beaker and start first with the magnetic stirring at 800 rpm (this is determined by the maximum rate at which magnet spinning is stable in the vortex), it is important that all experiments are done with the same magnet size and shear stirring rate.
- d) Add the 1 ml of STO1 gently with the help of a syringe, observe if the oil is appropriate mixed with the formation water.
- e) Start adding 0.2 g of solid particles, continue the stirring for 5 minutes, and observe the behavior of the mixing process. Is there an appropriate coverage of oil droplets? Is there any free oil?
- f) Stop stirring and observe how the emulsion stability is for about 5 minutes. If free oil is observed then start stirring again at the same rate and add 0.2 g more of solid particle. Repeat this process until observe that there is no free oil floating on the surface.

- g) It is expected that by the magnetic stirring the size of droplets are not small enough to create an stable emulsion, therefore more material is required to capture the oil big droplets, resulting in a less efficient process and waste. Therefore more shear stirring energy is require. Observe if this is the case and continue with next step.

Note: Since it is require to apply more energy in the stirring process to create smaller enough droplets to be covered by the solid particles, thus Silverson stirring will be used to create a stable emulsion and will be transfer afterwards to magnetic stirring to see if stability can be maintain under this conditions.

- h) Pour the prepared FW on an appropriate beaker and start stirring with Silverson mixer (or another with sufficient energy) at 6000 rpm. Next 1 ml of STO1 is added gently with the help of a syringe, observe that this energy rate is enough to create an emulsion.
- i) Start adding 0.2 g of solid particles, continue stirring for 5 minutes, and observe the behavior of the mixing process.
- j) Stop stirring and observe emulsion behavior for about 5 minutes. If free oil is observed start stirring again at the same rate and add 0.2g more of solid particle. Repeat this process until observe that there is no free oil floating on the surface.

Note: However it is possible that no free oil may be observed, due to solid particles are efficient to protect oil droplets regardless the size. Therefore it is required to observe the level of oil saturation and the size of droplets that are formed. At lower solid particles concentration the bigger the size of droplets because the quantity of kaolinite is not enough to and efficient coverage.

- k) When no free oil is observed in the surface, transfer the emulsion to magnetic stirring (the same magnet size is required) at a lower rate of 300 rpm for about 5 minutes. Observe if the emulsion remains homogenous and the size of droplets formed.
- l) Stop stirring for 5 minutes and observe if there is free oil that indicates the break of droplets. Additionally observe if the accumulation is observed floating over the top or sink at the bottom of the beaker.
- m) If there is no free oil it is an indicator of emulsion stability under lower stirring and that small droplets can be obtained at 6000 rpm. Secondly, observe the size of the droplets formed when lowering the stirring rate, continue if big droplets are observed if not continue to stop "o".
- n) Transfer the beaker to the Silverson stirring and repeat steps j to m until observe that the size of small droplets can be preserved when magnetic stirring.
- o) Determine the exact point when the quantity of solid particles can assure both no free oil, thus efficient stability of emulsion and no waste of material. It is expected that in the process the accumulation on the top starts sinking to the bottom.
- p) Determine the grams of solid particles per milliliter of oil required for a stable emulsion.

- q) Additionally can be determined the point of grams of solid particles per milliliter of oil that will past from oil-saturated (floating in the surface) to more particles-saturated (sinking towards the bottom).

Oil Screening

Quantity of milliliters of oil per gram of solid particles will be determined by this procedure:

- a) Prepare 1 Liter of formation water with the composition shown in Table 3.1.1
- b) Measure 1 gram of solid particles, in this procedure clay particles (kaolinite) are recommended, however this procedure shall be used for any type of solid particles that meet the required conditions.
- c) Pour the prepared FW on an appropriate beaker and start stirring with Silverson mixer (or another with sufficient energy) at 6000 rpm. In this case the procedure starts directly with a high shear rate due to high energy is required to break the added oil into small droplets at each step. Add 1 g of the selected solid particles.

Note: In this procedure it will be analyze the moment when solid particles stop being accumulated at the bottom and starts to be oil-saturated and migrate to the surface. No free oil is expected to be observed due to great volume is required to reach that point and results may exceed the environmental law.

- d) Add the 1 ml of STO1 gently with the help of a syringe, continue stirring for 5 min and observe the color of the mixture.
- e) Stop stirring and observe the changes within 5 min. Observe if the accumulation on the bottom starts to move upwards towards the surface. If so continue with point “h”.
- f) If there is no migration, start stirring for 5 min at the same rate and add 0.5 ml of solid particles. Observe the physical appearance of the mixture.
- g) Repeat points “e” and “f” until see the indicated changes.
- h) Stop stirring and place the mixture in a closed bottle for observation.
- i) Determine the quantity of milliliters of oil per gram of solid particles needed to saturate the solid particles. Thus there will not be free oil due to efficient coverage of droplets and not waste of material.

3.3 Experiment 3: Core Flooding

3.3.1 Description

Objective

From the previous chapter the appropriate ratio solid-particles/oil was calculated to avoid waste of material and at the same time guarantee efficient protection of oil droplets to coalescence. Once screening experiment was concluded, the core flooding test was ready for execution.

One of the advantages of emulsion injection is to lowering the permeability heterogeneity (high permeability zones) in the porous media that lead to early breakthrough of displacing fluid in an oil recovery practice. By being trapped in porous throat, emulsion droplets block and decrease the permeability in high permeable zones to avoid fast water breakthrough and forcing the sweep of lower permeability zone to increase the oil recovery.

Therefore in Experiment 3 a core flooding test was executed in order to analyze the impact in rock permeability when and emulsion of different oil concentrations is injected in the core. This experiment was carried out in three different stages: first the core initial permeability was calculated, following by emulsion flooding and finally changes in permeability were assessed.

Materials

For this experiments the following equipment are required, Figures 3.3.1A-C show pictures of some actual equipment used for the execution, additional some valves are required, this are showed in the pictures below:

1. Piston Cell for Emulsion
2. Piston Cell for Formation Water
3. Core Holder
4. Core
5. Pressurized oil Vessel to maintain over burden pressure
6. Pressure transmitter
7. Magnetic Stirrer
8. Stirring Magnet
9. Water Pump

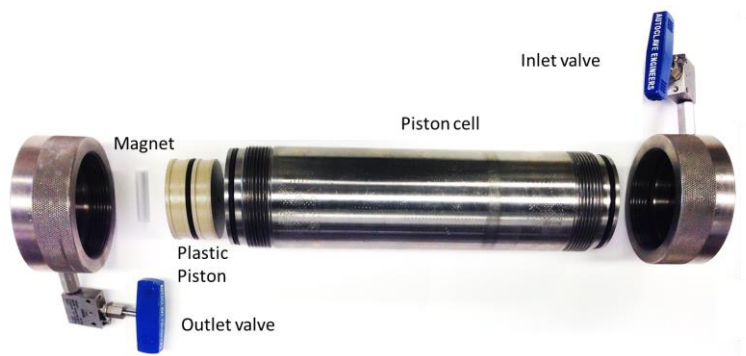


Figure 3.3.1A – Piston Cell for emulsion & magnet used in the core flooding experiment assembly.

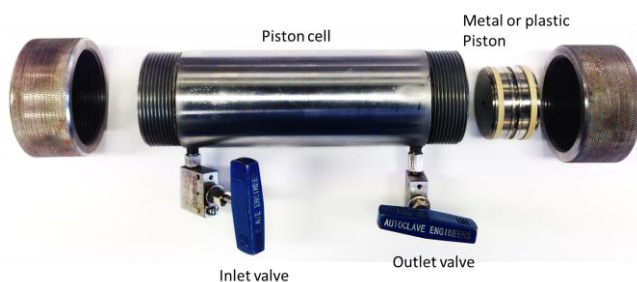


Figure 3.3.1B – Piston Cell for Formation Water used in the core flooding experiment assembly.

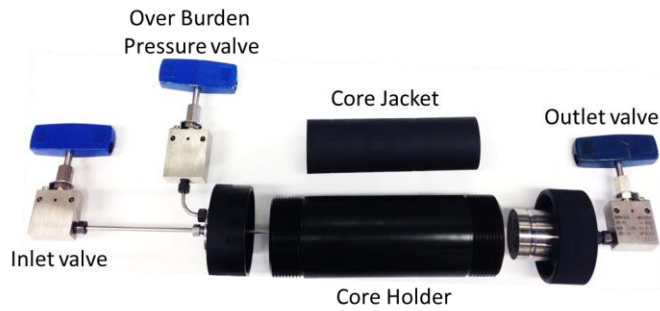


Figure 3.3.1C – Core holder used in the core flooding experiment assembly.

3.3.2 Procedure

3.3.2.1 Experiment Assembly

Initially all the listed equipment must be set in the correct way to perform the core flooding, Figure 3.3.2 shows the process flow diagram that was used to execute this experiment.

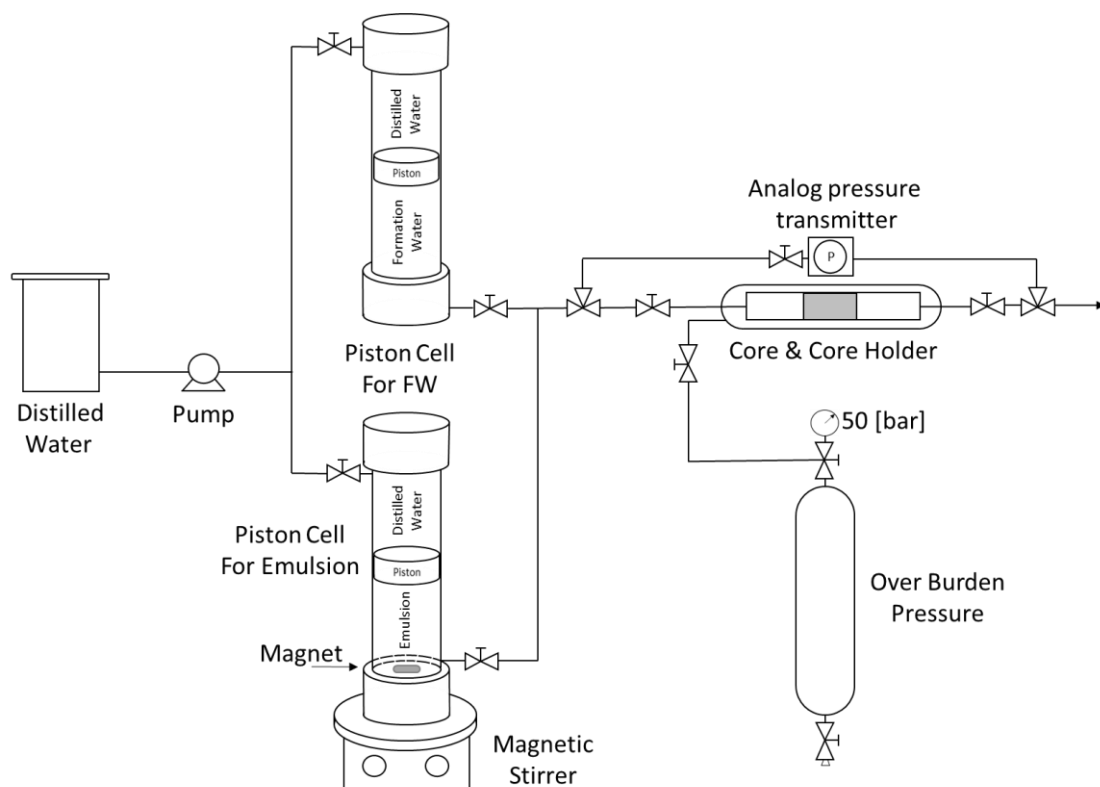


Figure 3.3.2 – Process flow diagram for core flooding.

The fluid used for water flooding was Formation Water (FW) with a composition showed before in Table 3.1.1. The porous media used was a Bentheim core with 25% porosity approximately, additional characteristics are summarized in Table 3.3.1 and were used to calculate that core had 21.5 [cm³] pore volumes.

Table 2.3.1 - Porous media

Type	Benthein
Weight (g)	176.80
Diameter (cm)	3.71
Length (cm)	8.02
Cross Section (cm ²)	10.82
Bulk Volume (cm ³)	86.74
Porosity	0.25

Additional information:

- Pressure transmitter measured the differential pressure along the core, this information was given in percentage with a range between 0-5 [bar].
- A triangle shape magnet was used to maintain a more uniform stirring vortex, nonetheless a cylindrical rounded shape has shown same results.
- Water pump was setting at maximum pressure of 40 [bar], thus 10 [bar] below the overburden pressure (increasing the pore pressure and overburden pressure gradually must be considered to avoid crashing when a chalk rock is used).
- In order to assure there is no air in the system, the core was flooded with Formation Water (FW), first at a rate of 5 [ml/min] for 30 [min], followed by a rate of 0.5 [ml/min] during 24 hours, this flooding was assumed to displaced big bubbles but also the smallest bubbles of air that may be trapped in the core.

As mentioned before this experiment comprises three different stages, the first one is to determine the initial permeability of the porous media, followed by emulsion flooding and finally changes in core permeability are analyzed.

3.3.2.2 Determination of Initial Permeability

Permeability determination can be perform at any time of the experiment, however in all the cases it must be executed with the same fluid for coherence and comparative results. In this experiment permeability was calculated in all the cases by formation water flooding (unless something else is mentioned), Figure 3.3.3 shows the correct valves setting that must be checked before experiment is initiated.

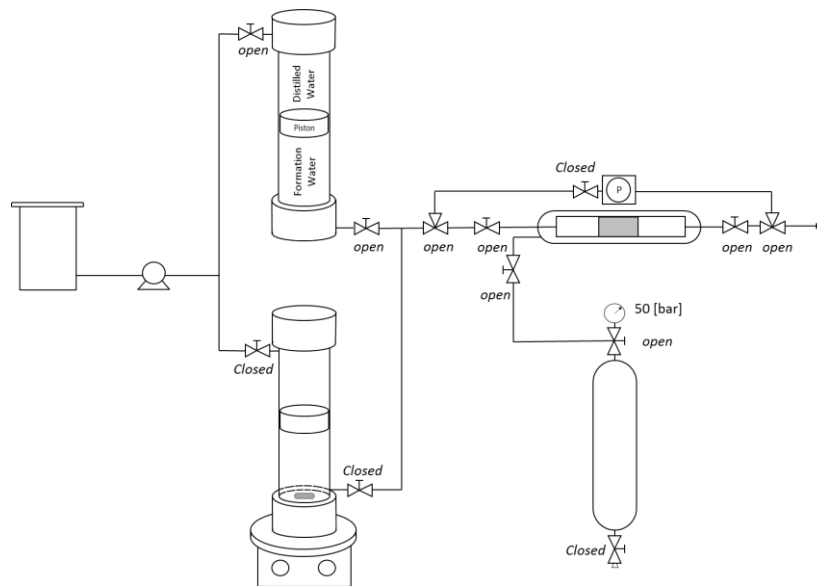


Figure 3.3.3 – Valves setting for Formation Water Flooding.

Initial permeability is calculated as follows:

Procedure:

- a. Set valves configuration according to Figure 3.3.3.
- b. Check pressure transmitter indicates 0% (or closer), this indicates that pressure measuring is on progress.
- c. Set water pump at a rate of 10 ml/min and press RUN.
Note: If Figure 3.3.2 is observed once water pump is activated, distilled water fills the upper part of the piston cell pushing the formation water into the system. Fluids in the piston cell are never mixed since complete seal of piston must be assured.
- d. If pressure transmitter is connected to logging:
 - Observed when water breaks through.
 - Monitor pressure until pressure build up stops, then allow the system to stabilize for about 2-3 minutes.
 - Select carefully three (3) point measurements from the most stable tendency.
- If pressure transmitter is not connected to logging:
 - Observed when water breaks through
 - Write the delta pressure indicated in the pressure transmitter screen every minute.
 - When pressure gets stable write the delta pressure indicated in the pressure transmitter screen every 30 seconds, for about 2-3 minutes.
 - Select carefully three (3) point measurements from the most stable tendency tracked from the last 2-3 minutes.
- e. Stops pumping, and set the water pump at 5ml/min then press RUN.
 Repeat step "C", then continue with point "f" afterwards.

- f. Stops pumping, and set the water pump at 1ml/min then press RUN. Repeat step “C”, then continue with point “g” afterwards.
- g. Finalize the experiment by stop pumping by pressing STOP at the pump. And close all the valves
- h. By this point 9 total differential pressure (ΔP) measurements must be selected. Three measurements for each pumping rate, which represents the most stable points at each stage.
- i. Since the differential pressure value is given in percentage it must be converted to pressure units (in this case [bar]), thus (where “Pressure Difference (%)” represents each selected point) Eq. 3.3.1:

$$\text{Pressure Difference [bar]} = \text{Pressure Difference (\%)} * \frac{5}{100\%} \dots \text{Eq. 3.3.1}$$

- j. Porous media permeability is calculated by the use of the Darcy equation for flow of incompressible fluids through porous media (equation 3.3.2), data from Table 3.3.1 must be included, thus:

$$Q \left[\frac{\text{ml}}{\text{s}} \right] = \frac{k [\text{Darcy}] * \mu [\text{cp}] * L [\text{cm}]}{A [\text{cm}^2] * \Delta P [\text{atm}]} \dots \text{Eq. 3.3.2}$$

Where;

Q, injected fluid flow rate, [ml/s]

μ , injected fluid viscosity; [cp].

This value was measured by a viscometer

$\mu_{\text{Formation Water}} = 1.2 [\text{cp}]$

L, core length; [cm]

A, cross section area, [cm²]

ΔP , Pressure Difference, each of the points calculated in step “g”

Alternative equation 3.3.2 can be converted to determine the absolute rock permeability, where 0.0168879 represents a conversion factor to appropriate units

$$k [\text{Darcy}] = \frac{1}{60 \left[\frac{\text{s}}{\text{min}} \right]} * \frac{1}{0.986923 \left[\frac{\text{Atm}}{\text{Bar}} \right]} * \frac{Q \left[\frac{\text{ml}}{\text{s}} \right] * \mu [\text{cp}] * L [\text{cm}]}{A [\text{cm}^2] * \Delta P [\text{atm}]}$$

$$k [\text{Darcy}] = \frac{1}{59.21538 \left[\frac{\text{s}}{\text{min}} \frac{\text{Atm}}{\text{Bar}} \right]} * \frac{Q \left[\frac{\text{ml}}{\text{s}} \right] * \mu [\text{cp}] * L [\text{cm}]}{A [\text{cm}^2] * \Delta P [\text{atm}]}$$

$$k [\text{Darcy}] = 0.0168879 \left[\frac{\text{s}}{\text{min}} \frac{\text{Atm}}{\text{Bar}} \right] * \frac{Q \left[\frac{\text{ml}}{\text{s}} \right] * \mu [\text{cp}] * L [\text{cm}]}{A [\text{cm}^2] * \Delta P [\text{atm}]}$$

- k. Fill up Table 3.3.2 with the calculated values:

Table 3.3.2 – Permeability Calculations Sheet.

<u>Experiment Stage</u>	<u>Oil Concentration (ppm)</u>	<u>Q (ml/min)</u>	<u>Delta Pressure (%)</u>	<u>Delta Pressure (Bar)</u>	<u>Permeability (Darcy)</u>
1. Initial Permeability	(Formation Water Injected)	10			
		5			
2. Permeability After Emulsion Flooding	"Place the value of emulsion oil concentration used prior permeability calculation"	10			
		5			
3. Final Permeability	(Formation Water Injected)	10			
		5			
		1			

- I. Check the calculated points by plotting Q vs ΔP plot, then slope of points tendency should be close the values found at the experiment.

3.3.2.3 Emulsion Flooding

Once the core initial permeability was calculated then the system was ready to be flooded with the prepared emulsion indicated at the beginning of this chapter in Description section. As mentioned before the quantities used results in an emulsion with an oil concentration of 852 ppm. Additionally Figure 3.3.4 shows the correct valves setting that must be checked before emulsion flooding experiment is initiated.

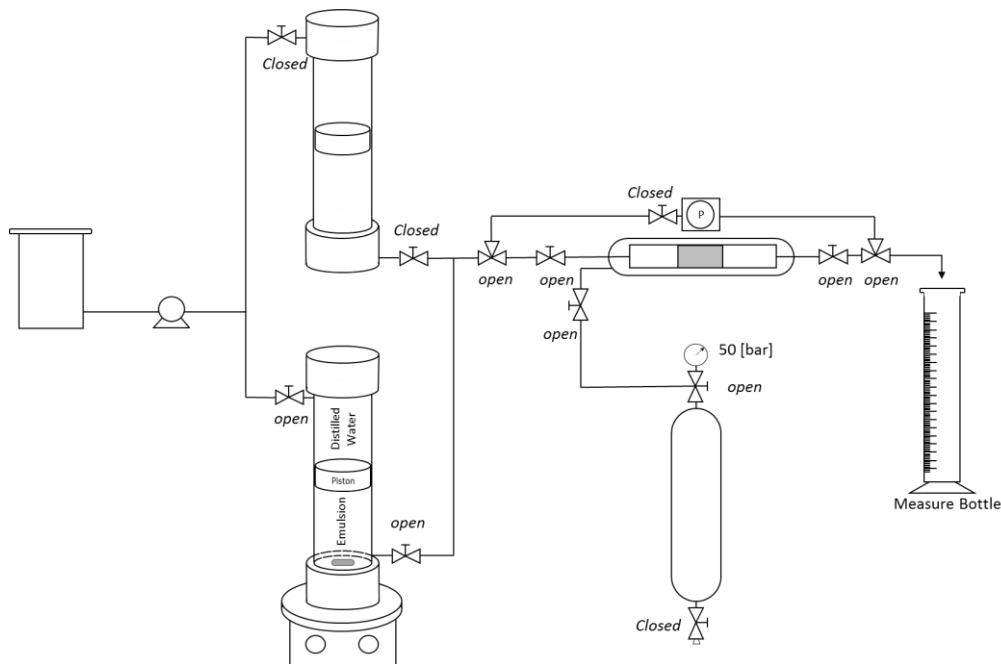


Figure 3.3.4 – Valves setting for Emulsion Flooding.

Emulsion flooding was executed as follow:

Procedure:

- a. Place a measured bottle at the end of the experiment setting, as showed in the Figure 3.3.4 since injected pore volumes must be measured constantly.
- b. Set valves configuration according to Figure 3.3.4.
- c. Check pressure transmitter indicates 0% (or closer), this indicates that pressure measuring is on progress.
- d. Set water pump at a rate of 0.5 ml/min and press RUN.
Note: If Figure 3.3.2 is observed once water pump is activated, distilled water fills the upper part of the piston cell pushing the Emulsion into the system. Fluids in the piston cell are never mixed since seal of piston must be assured.

e. If pressure transmitter is connected to logging:

- Observed when fluid breaks through.
- Monitor pressure constantly to avoid abrupt pressure increase that indicates flow blocking. If so, then experiment must be suspended and formed mud cake must be removed from the core injection face.
- When fluid breaks-through initiate monitoring the pore volumes injected by the lecture in the measured bottle placed at the system outlet.
- Finalize the experiment when three (3) pore volumes have been injected in the core.

If pressure transmitter is not connected to logging:

- Observed when water breaks through
- When fluid breaks-through initiate monitoring the pore volumes injected by the lecture in the measure bottle placed at the system outlet.

- Write the pressure difference (ΔP) indicated in the pressure transmitter screen.
Note: It is suggested to read this value every 5 minutes or even more often based on the pressure readings variances. The more values the more reliable results can be analyzed.
 - Finalize the experiment when three (3) pore volumes have been injected in the core.
- f. Turn off the pumping by pressing STOP at the pump.
- g. Close all the valves.
- h. Calculate the permeability after the emulsion flooding. Using the Procedure found in section 3.3.2.2.
- i. Fill up Table 3.3.2 with final results.

3.3.2.4 Determination of Final Permeability

The purpose of using emulsion as secondary or tertiary recovery is to lower the rock heterogeneity throughout the reservoir production zone. By blocking the high permeable zones porous media and forcing the water flooding injected afterward to sweep the lower permeability zones where un-swept oil is still pending (trapped) for being produced and thus increase the oil recovery.

Therefore this final test was intended to analyze the impact of emulsion injection, by permeability assessment after emulsion flooding ended.

Procedure

- a. Check that all the valves in the system are closed.
- b. Remove the mud cake in the injection face of the core, by opening the core holder by following the following sub-steps:
 - i. Open the valve of inlet pressurized oil (oil must be considered as the oil used for overburden pressure throughout this sub procedure) to relieve the overburden pressure.
 - ii. Place the core holder vertically to avoid oil spills over, and remove the upper cap, place the “depressurized” oil in a bottle.
 - iii. Remove the core jacket carefully, assuring that no oil contacts the porous media.
 - iv. Clean the equipment by removing all the oil.
 - v. Once the core is released, clean it with formation water (never use any other type of water or fluid).
 - vi. Clean the core holder injection face by removing with formation water (never use any other fluid) the mud cake that may be accumulated, do it at the outlet face if required.
 - vii. Reassemble the core holder with the core in the same position at the beginning of this experiment, and set the overburden pressure at 50 [bar]. This procedure must be done carefully due to neither core must not be in contact with oil, nor any air should be accumulated at the porous media.
 - viii. Close all the valve of the system.
- c. Use the procedure showed in section 3.3.2.2 to calculate the final permeability.
- d. Fill up the Table 3.3.2 with final results.

4 Experiment Results & Discussion

The information contained in this chapter is presented in the same way as indicated in the Experiment Description section 3. Therefore three major experiment results are shown, Firstly Emulsion Stability and Flotation Analysis, followed by Solid Particles and Oil Quantity Screening and finally Core Flooding results. Each one of these experiments involve several Tests, therefore for simplicity each chapter will discuss the respective results at the end.

4.1 Experiment 1: Emulsion Stability & Flotation Analysis

4.1.1 Test 1: Emulsion Stability using Kaolinite as solid-particles

Different solid particles were intended to be tested, to observe their effectiveness as a stabilizing agent. As was explained before, solid particles get attached to the surface of oil droplets and protect them for aggregation and coalescence that lead to phase separation and emulsion break up.

For the Test 1 the oil “STO1” was selected as dispersed phase and Kaolinite was used as solid particles. The previously explained procedure in section 3.1.2 was followed, therefore four samples were prepared, and each one of them was tested under four different scenarios (referred as “Parts” in the procedure) where one variable was modified at a time, thus:

- a) BASE CASE- FW: Use of formation water as external phase, composition found in Table 3.1.1.
- b) LSW: Use of low salinity water as external phase, composition found in Table 3.1.1.
- c) Oleophilic kaolinite: base case was selected and kaolinite particles surface was modified to a more oleophilic wettability
- d) Oleophilic kaolinite & Low salinity water: use of modified wettability kaolinite in a low salinity environment.

The following pictures in Figure 4.1.1A-D show behavior throughout the time for each of the four samples of Table 3.1.3, under the four scenarios listed in the procedure

Part I: Base Case – Using Formation Water and water-wet solids

Part II: Using a Low Salinity Water

Part III: Using oil-wet solid

Part V: Part II + Part III

(BLANK SPACE ON PURPOSE)

Sample 1









								FW – Base Case
								LSW
								Oleophilic Kaolinite
								LSW Oleophilic Kaolinite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.1A – Sample 1 under four different scenarios. Test 1 using Kaolinite.

The Base Case of Sample 1 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Kaolinite as Solid Particles and 0.85 g of oil “STO1”. Sample 1 was tested under four scenarios accordingly to Procedure 3.1.2

Sample 2







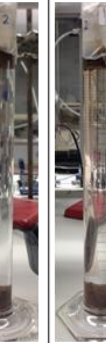



















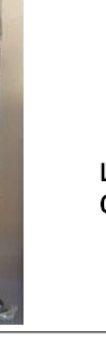
								FW – Base Case
			Not Available		Not Available	Not Available		LSW
								Oleophilic Kaolinite
	Not Available					Not Available		LSW Oleophilic Kaolinite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.1B – Sample 2 under four different scenarios. Test 1 using Kaolinite.

The Base Case of Sample 2 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Kaolinite as Solid Particles and 4.26 g of oil “STO1”. Sample 2 was tested under four scenarios accordingly to Procedure 3.1.2

Sample 3








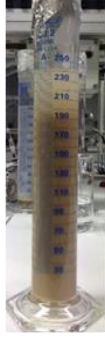
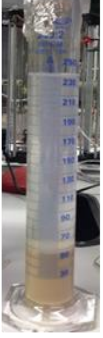













					Not Available			FW – Base Case
					Not Available	Not Available		LSW
	Not Available				Not Available			Oleophilic Kaolinite
					Not Available	Not Available		LSW Oleophilic Kaolinite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.1C – Sample 3 under four different scenarios. Test 1 using Kaolinite.

The Base Case of Sample 3 contains 255.51 g of FW composition found in Table 3.1.1, 5 g of Kaolinite as Solid Particles and 0.85 g of oil “STO1”. Sample 3 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 4




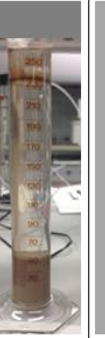




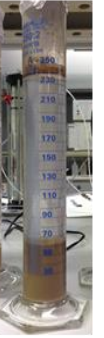















				Not Available	Not Available			FW – Base Case
				Not Available	Not Available	Not Available		LSW
				Not Available	Not Available			Oleophilic Kaolinite
						Not Available		LSW Oleophilic Kaolinite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.1D – Sample 4 under four different scenarios. Test 1 using Kaolinite.

The Base Case of Sample 4 contains 255.51 g of FW composition found in Table 3.1.1, 5 g of Kaolinite as Solid Particles and 4.26 g of oil “STO1”. Sample 3 was tested under four scenarios accordingly to Procedure 3.1.2.

4.1.1.1 Results Discussion

Pictures show that the behavior of emulsion flotation changes according to both the amount of solid particles and the volume of oil used in the emulsion. Results indicate that in all the cases there is no free oil observed floating as separate phase on the top of the solution, therefore kaolinite has the ability to attract oil droplets and create a layer protection that avoids coalescence between particles.

Additionally, if stirring energy stops, the protection of kaolinite remains effective and after 48 hours the emulsion stability is still observed. However this type of emulsion behaves differently than others where the internal phase is totally dispersed all along the continuous phase. In this Test it was observed that emulsion is affected strongly by the shear rate since initial oil droplets will vary their size according to the energy used for dispersion.

It was also observed that kaolinite and oil droplets remain disperse as long as the stirring continues, as soon as it stops the oil droplets covered by solid particles will float or sink based on the solid particles and oil quantity ratio used. Therefore after 48 hours it is observed that if the amount of kaolinite is lower or closer to 0.25 grams per milliliter of oil used then solid particles and oil mixture is likely to float to the top of the solution. On the other hand for a higher value of quantity ratio (1g-5g of Kaolinite /ml of oil) the mixture will always sink at the bottom indicating that probably the quantity of solid particles exceed the required. However this ratio value will be analyzed further to determine the exact values at which a change in the flotation has place.

To confirm that flotation behavior is related to density difference, densities of all fluids were measured, the following results were obtained:

Formation Water (FW) density: 1.06466 [g/ml]

Low Salinity Water (LSW) density: 1.00522 [g/ml]

Oil (STO1) density: 0.85308 [g/ml]

According to fabricant kaolinite density is 0.961 [g/ml],

Therefore when mixture ratio between solid particles and oil is lower as sample 2 (0.2g of kaolinite /ml of oil), thus low amount of kaolinite is protecting the oil droplets and density is closer to oil making the column floats. On the contrary if the mixture rate is closer to Samples 1, 3 or 4 (1-5g of kaolinite /ml of oil), the density will be closer to kaolinite making the mixture column sinks to the bottom. A sample from the solid-oil column from sample 3 was obtained and density measures was 1.01331 [g/ml] therefore mixture density is greater than synthetic water. This is also possible to be observed by the color of the mixture column, where a darker color is seen when floating and a lighter brown color is obtained if mixture sinks due to oil concentration.

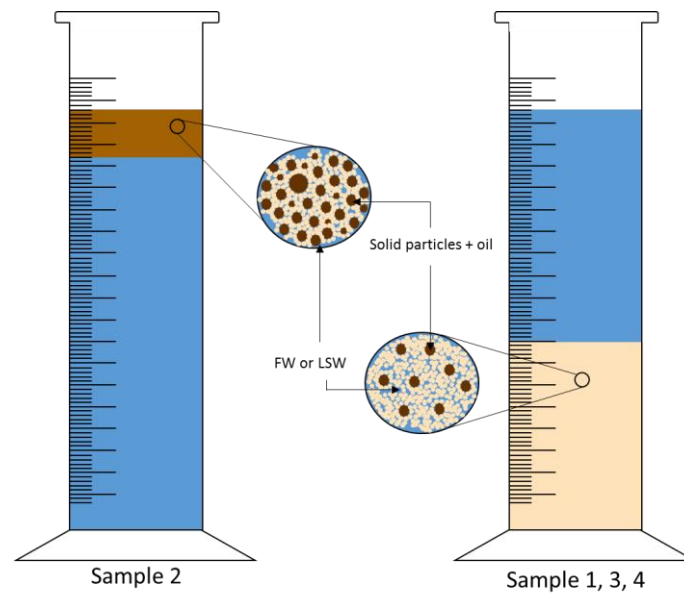


Figure 4.1.2 – Flotation effect of emulsion samples.

However particles are dispersed in the formation water without affecting the stability, moreover a homogeneous dispersion can be obtained at any time if stirring is applied since coalescence has no place between oil droplets. Figure 4.1.2 explains this statement in a more graphical way. Observe that the average size of the droplets is the same in both cases, even though the size was not determine in this Test it is likely to expect similar oil droplet size due to the same stirring energy was applied in both cases.

Kaolinite flotation can be analyzed by the volume of “free water” or clean water column observed in each sample after 48 hours of stabilization Figure 4.1.3 summarizes this result. Observe how in all the cases lowering the salinity of the water lead to have more volume of clear water (“free water”). On the other hand change the wettability of solid surface to a more oil-wet only have an impact in sample 4, therefore this parameter is consider not relevant for Test 1.

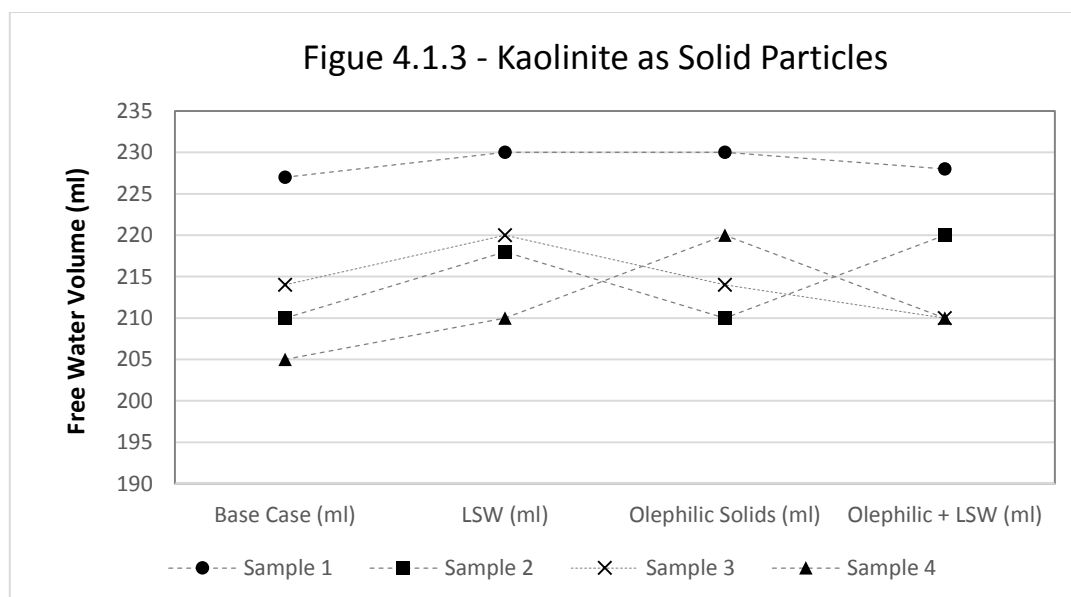


Figure 4.1.3 – Free water volume in emulsion samples under four different scenarios using Kaolinite as solid particles.

4.1.2 Test 2: Emulsion Stability with Bentonite

For the Second Test different solid particles were analyzed to observe their effectiveness as a stabilizing agent. Bentonite was selected for this test due to its well-known properties to create tight mud cakes in drilling processes, thus a smaller particles size was expected to cover the oil droplets.

For this Test 2 the oil “STO1” was selected as dispersed phase, and Bentonite was used as solid particles. Following the previously explained procedure in section 3.1.2 four samples were prepared, each one of them was tested under four different scenarios (referred in procedure as Parts) where one variable was modified at a time, thus:

- a) BASE CASE- FW: Use of formation water as external phase, composition found in Table 3.1.1.
- b) LSW: Use of low salinity water as external phase, composition found in Table 3.1.1.
- c) Oleophilic Bentonite: base case was selected and Bentonite particles surface was modified to a more oleophilic wettability
- d) Oleophilic Bentonite & Low salinity water: use of modified wettability Bentonite in a low salinity environment.

The following pictures in Figure 4.1.4A-D show behavior throughout the time for each of the four samples of Table 3.1.3, under the four scenarios listed in the procedure

Part I: Base Case – Using Formation Water and water-wet solids

Part II: Using a Low Salinity Water

Part III: Using oil-wet solid

Part V: Part II + Part III

(BLANK SPACE ON PURPOSE)

Sample 1

























	Not Available							FW – Base Case
								LSW
	Not Available				Not Available			Oleophilic Bentonite
				Not Available	Not Available			LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.4 A – Sample 1 under four different scenarios. Test 2 using Bentonite.

The Base Case of Sample 1 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Bentonite as Solid Particles and 0.85 g of oil “STO1”. Sample 1 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 2





























							FW – Base Case
							LSW
							Oleophilic Bentonite
							LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time

Figure 4.1.4 B – Sample 2 under four different scenarios. Test 2 using Bentonite.

The Base Case of Sample 2 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Bentonite as Solid Particles and 4.26 g of oil “STO1”. Sample 2 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 3











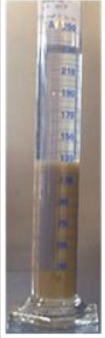










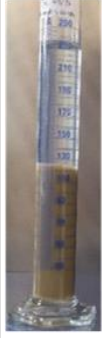
				Not Available	Not Available		FW – Base Case
					Not Available		LSW
							Oleophilic Bentonite
			Not Available	Not Available	Not Available		LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time

Figure 4.1.4 C – Sample 3 under four different scenarios. Test 2 using Bentonite.

The Base Case of Sample 3 contains 255.51 g of FW composition found in Table 3.1.1, 5 g of Bentonite as Solid Particles and 0.85 g of oil “STO1”. Sample 3 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 4





















				Not Available	Not Available		FW – Base Case
					Not Available		LSW
		Not Available					Oleophilic Bentonite
		Not Available	Not Available	Not Available	Not Available		LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time

Figure 4.1.4 D – Sample 4 under four different scenarios. Test 2 using Bentonite.

The Base Case of Sample 4 contains 255.51 g of FW composition found in Table 3.1.1, 5 g of Bentonite as Solid Particles and 4.26 g of oil “STO1”. Sample 3 was tested under four scenarios accordingly to Procedure 3.1.2.

4.1.2.1 Results Discussion

Results in Figures 4.1.4A-D show that the use of Bentonite as solid particle lead to similar result as Kaolinite. Firstly no free oil was observed in any sample, proving not only that this clay is adequate to cover oil droplets efficiently, but also that the size of particles seen in the mixture has a smooth texture, hence a smaller particle size is observed. This is an outstanding property of bentonite when a considerable small droplet size is required for blocking porous media throat.

On the other hand samples showed the same flotation behavior of the mixture solid particles-oil droplets as observed with kaolinite. Thus when the quantity of oil overcomes the solid particles (sample 2) a droplet protection against coalescence is achieved but due to mixture density difference respect the water then the mixture tends float at the surface, otherwise sinks at the bottom when solid particles concentration is greater than 1 g of bentonite per milliliter of oil. This phenomena was explained before and a graphical explanation is given in Figure 4.1.2.

Despite the similar results with kaolinite, there are some remarkable differences obtained with Bentonite use as solid particles:

- Bentonite seems to have smaller particles size, the coverage of smaller particles seems to be achieved, since homogeneous mixture is observed, no big solid particles suspended.
- The “free water” column is lower when using bentonite, thus mixture column of bentonite - oil droplets is higher that Test 1. This results may be obtained due to bentonite density that according to fabricant is 0.817 g/ml. Thus the density different respect the water is lower and particles tends to sink with more distribution along the water column.
- Lowering the salinity of the external phase lead to increase the height of the column bentonite-oil dispersed in the water phase. Also the more bentonite the higher the column (Compare Sample 1 to 3, and Sample 2 to 4). This behavior is more notorious with Bentonite than Kaolinite.
- Since Bentonite has a better coverage of the oil droplet (compare to Kaolinite), then in an over-saturated Sample 2 there is less accumulation at the bottom, most of the mixture Bentonite-Oil is observed at the top due to density difference.
- Effect of changing Bentonite wettability to more oil-wet-like is only observed in Sample 2 with an oversaturated mixture, the attraction of solids to the oil phase is improved thus all particles remains with the oil droplets at the top in less time (faster separation), also no accumulation observed at the bottom. Decreasing the salinity seems to diminish the attraction effect.

“Free water” column was measured in all the samples of Test 2, results are shown in Figure 4.1.5. Observe that when water salinity decreases the free water is lower and, opposite than Kaolinite results, bentonite-oil mixture column increases in all the cases.

Additionally the four samples behaved with the same pattern in each one of the four scenarios, results are more stable than the ones showed in Figure 4.1.3. Observe that changing the wettability of the solid particles to a more oil-wet does not impact the results, since same volume of free water is obtained than when used a water wet particles surface.

Moreover when both oil and bentonite are increased, the volume of free water decrease, however increasing the volume of bentonite (sample 3) appears to have more impact in this effects than when

oil volume is increased (Sample 2). However is important to clarify that this observation must take into account that when oil increase the volume, then it is expected that the majority of the mixture solid-oil particles tend to accumulate more tighten at the top due to density. Otherwise if it sinks then particles tend to distribute more into the water column due to probably density difference is shorter as it was proved with kaolinite mixture sample.

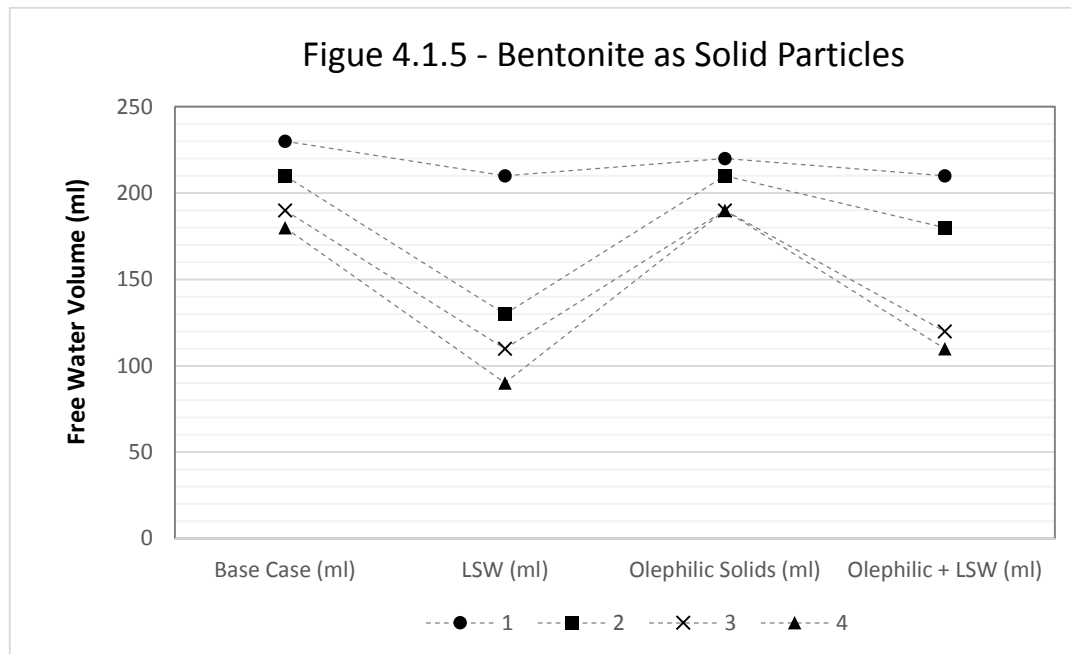


Figure 4.1.5 – Free water volume in emulsion samples under four different scenarios using bentonite as solid particles.

4.1.3 Test 3: Emulsion Stability increasing acidity of the oil

According to Bragg (10) emulsion stabilization by the used of solid particles can be obtained if several factors are considered. When no emulsifier is used for stabilizing the emulsion then oil must content enough polar components to reach stabilization spontaneously, and solid particles will only help to improve the stability in a longer time.

Consequently in Test 3, the polar components of the oil were improved by increasing the acidity of the oil. Thus carboxylic acid components will create micelles, and its polar parts are expected to offer even more protection against coalescence. Despite a proper droplet protection for coalescence was already achieved in Test 2, this property was intended to be upgraded by Test 3.

The acidity of the oil was increased by the use of Palmitic Acid. The amount of required acid was calculated to increase 3 time the Total Acid Number (TAN) of the oil (STO1) which is defined by the amount of potassium hydroxide (KOH) in milligrams (mg) needed to neutralize the acids in 1 gram of oil. Calculation was made as follows:

$$STO1\ TAN = 0.10\ [mg\ KOH/g\ of\ oil]$$

$$Molecular\ Weight\ of\ Palmitic\ Acid = 256.42\ [g/mol]$$

$$Molecular\ Weight\ of\ Potassium\ Hydroxide\ (KOH) = 56.11\ [g/mol]$$

$$\frac{0.10 \left[\frac{\text{mg KOH}}{\text{g of oil}} \right]}{56.11 \left[\frac{\text{g KOH}}{\text{mol KOH}} \right] * 1000 \left[\frac{\text{mg KOH}}{\text{g KOH}} \right]}$$

$$= 1.782 \times 10^{-6} \left[\frac{\text{mol KOH}}{\text{g of oil}} \right]$$

To triplicate the TAN, then

$$= 3 * 1.782 \times 10^{-6} = 5.3466 \times 10^{-6} \left[\frac{\text{mol KOH}}{\text{g of Oil}} \right]$$

$$= 5.3466 \times 10^{-6} \left[\frac{\text{mol KOH}}{\text{g of oil}} \right] * 256.42 \left[\frac{\text{g of Pal. Acid}}{\text{mol Pal. Acid}} \right]$$

$$= \mathbf{1.371 \times 10^{-3} \left[\frac{\text{g of Palmitic Acid}}{\text{g of Oil}} \right]}$$

In the samples we used either 1 ml or 5 ml of oil (0.85308 g and 4.2654 g of oil respectively), to determine the required amount of Palmitic Acid to increase three time the TAN, then:

- $0.85308 \left[\frac{\text{g of oil}}{\text{g of oil}} \right] * 1.371 \times 10^{-3} \left[\frac{\text{g of Palmitic Acid}}{\text{g of Oil}} \right]$
 $= \mathbf{0.00117 \left[\text{g of Palmitic Acid required} \right]}$
- $4.2654 \left[\frac{\text{g of oil}}{\text{g of oil}} \right] * 1.371 \times 10^{-3} \left[\frac{\text{g of Palmitic Acid}}{\text{g of Oil}} \right]$
 $= \mathbf{0.00584 \left[\text{g of Palmitic Acid required} \right]}$

For the Test 3 Bentonite was selected as solid particles based on the results obtained in Test 2. Additionally oil "STO1" was selected as dispersed phase. The emulsion preparation for each one of the four samples remains the same as stated in the previously explained procedure in Section 3.1.2, thus four samples were prepare each one of them was tested under four different scenarios (referred as Parts in the Procedure) where one variable was modified at a time, thus:

- e) BASE CASE- FW: Use of formation water as external phase, composition found in Table 3.1.1.
- f) LSW: Use of low salinity water as external phase, composition found in Table 3.1.1.
- g) Oleophilic Bentonite: base case was selected and Bentonite particles surface was modified to a more oleophilic wettability
- h) Oleophilic Bentonite & Low salinity water: use of modified wettability Bentonite in a low salinity environment.

The following pictures in Figures 4.1.6A-D show behavior throughout the time for each one of the four samples under the four scenarios listed in the procedure

Part I: Base Case – Using Formation Water and water-wet solids

Part II: Using a Low Salinity Water

Part III: Using oil-wet solid

Part V: Part II + Part III

Sample 1
































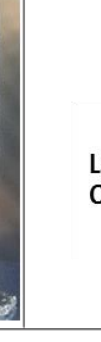
								FW – Base Case
								LSW
								Oleophilic Bentonite
								LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.6 A – Sample 1 under four different scenarios. Test 3 using oil with triple TAN.

The Base Case of Sample 1 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Bentonite as Solid Particles and 0.85 g of oil “STO1” with triple TAN than original. Sample 1 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 2



















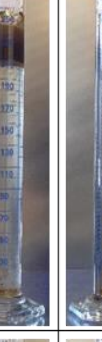

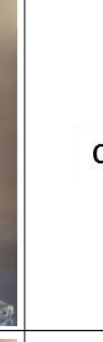







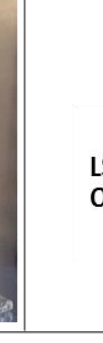
				Not Available	Not Available			FW – Base Case
					Not Available			LSW
								Oleophilic Bentonite
								LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.6 B – Sample 2 under four different scenarios. Test 3 using oil with triple TAN.

The Base Case of Sample 2 contains 255.51 g of FW composition found in Table 3.1.1, 1 g of Bentonite as Solid Particles and 4.26 g of oil “STO1” with triple TAN than original. Sample 2 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 3
















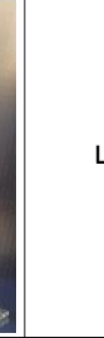



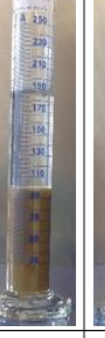
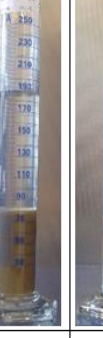
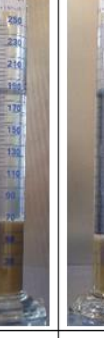

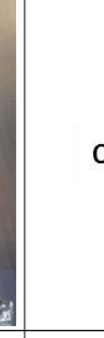








								FW – Base Case
								LSW
								Oleophilic Bentonite
								LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.6 C – Sample 3 under four different scenarios. Test 3 using oil with triple TAN.

The Base Case of Sample 3 contains 255.51 g of FW composition found in Table 4.1.1, 5 g of Bentonite as Solid Particles and 0.85 g of oil “STO1” with triple TAN than original. Sample 3 was tested under four scenarios accordingly to Procedure 3.1.2.

Sample 4
















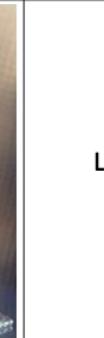







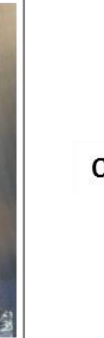








								FW – Base Case
								LSW
								Oleophilic Bentonite
								LSW Oleophilic Bentonite
0.0	0.5	1	2	4	6	24	48 [Hours] – Observation Time	

Figure 4.1.6 D – Sample 4 under four different scenarios. Test 3 using oil with triple TAN.

The Base Case of Sample 4 contains 255.51 g of FW composition found in Table 3.1.1, 5 g of Bentonite as Solid Particles and 4.26 g of oil “STO1” with triple TAN than original. Sample 4 was tested under four scenarios accordingly to Procedure 3.1.2.

4.1.3.1 Results Discussion

Based on numerical calculation the addition of $1.371\text{E-}04$ grams of Palmitic Acid per gram of oil triplicates the total acid number (TAN) from 0.10 to 0.30 [mg KOH/g Oil]. However the procedure to determine the change in the acidity of the non-aqueous solution was not carried out. In this case pH stripes were used instead to measure the pH of the free-oil water solution in Sample 3 for LSW and FW (picture in Figure 4.1.7), results indicate a pH of 5 approximately in both cases, but results are not reliable since do not differ from the pH 5 of the solution on Test 2.



Figure 4.1.7 – pH stripes used for pH of free water solution in selective samples of Test 2 and Test 3.

Increase the acidity of the oil does not affect the behavior of the emulsion, since results showed in Figure 4.1.6 do not differ from the ones obtained in Test 2 with TAN 0.10 [mg KOH/g Oil]. Perhaps in a continuous motion stirring the attraction improvement may be observed.

Free water volume measures in Samples of Test3 are shown in Figure 4.1.8. It is observed the same flotation behavior and conclusions of the Test 2, therefore increasing the acidity of an oil that already achieved stability in a continue phase does not improve or alter the emulsion equilibrium in any different way.

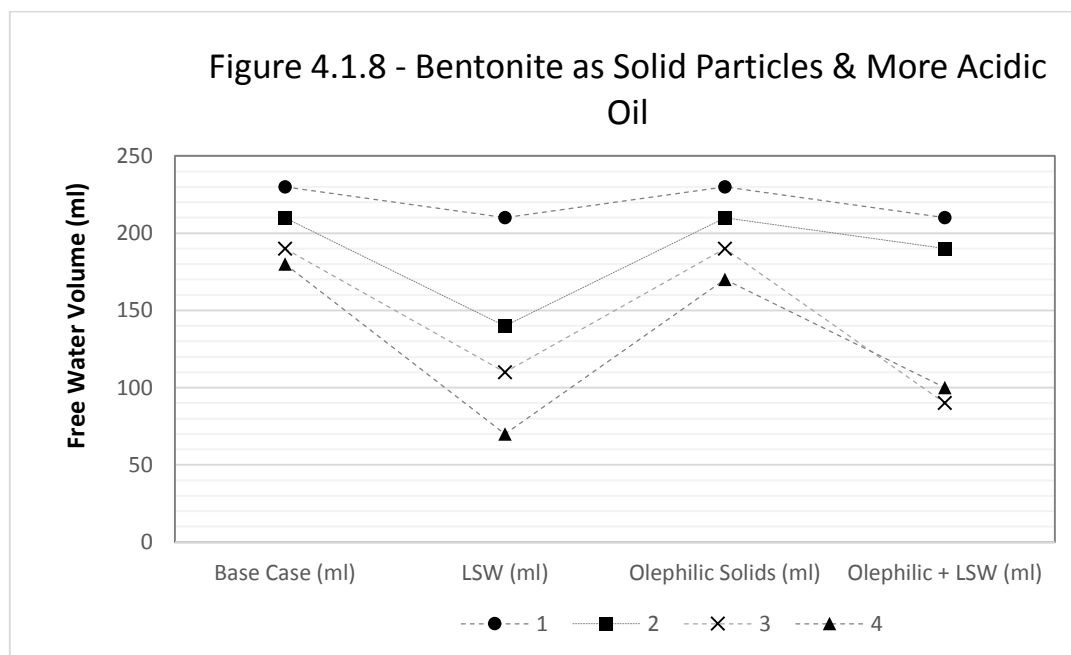


Figure 4.1.8 – Free water volume in emulsion samples under four different scenarios using bentonite as solid particles and more acidic oil (TAN*3).

In all the Test, comparing Sample 1 and Sample 3 both have same amount of oil (1ml) however increasing the amount of solids only increase the column at the bottom, therefore the additional solid particle is excessive. Additionally if comparing Sample 1 with 2 in all the Test it is observe that both have same amount of solid particles (1g) however increasing the amount of oil from 1 ml to 5 ml saturates the equilibrium and particles coverage might be affected and not well accomplished. Therefor the equilibrium point was studied with an oil volume assessment between these two points, results are shown in next chapter.

4.2 Experiment 2: Solid Particles and Oil Quantity Screening Results

These results will show the procedure executed to find the closest value for quantity ratio between kaolinite as solid particles per volume of oil. This estimation was based on a qualitative analysis of the obtained samples and will be shown as a timeline lab execution. Additionally results will be given first for the kaolinite screening with constant oil and formation water quantities and secondly for oil screening with constant kaolinite and formation water quantities. Figure 4.2.1 summarizes the set of experiment performed to determine the correct solid particles (g)/oil (ml) ratio.

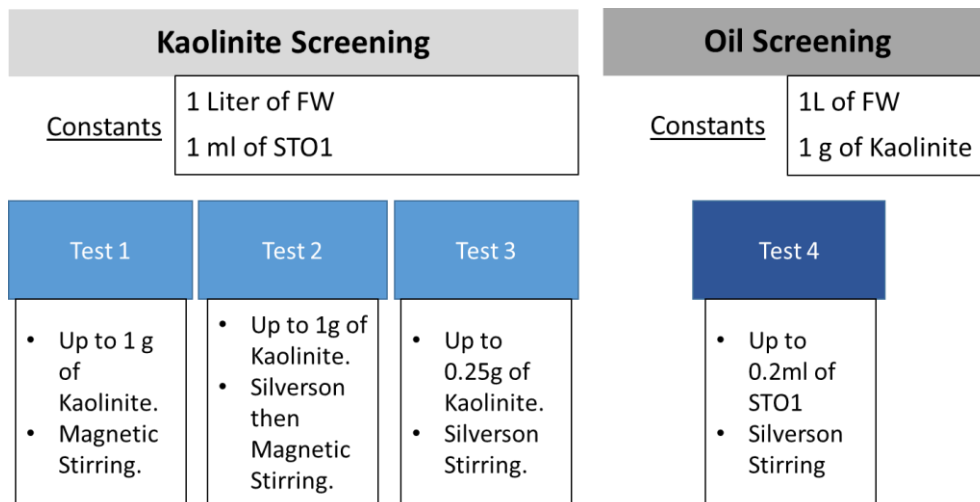


Figure 4.2.1 – Scheme of Kaolinite and Oil screening Test results.

4.2.1 Kaolinite solid particles screening

4.2.1.1 Test 1

In a beaker 1 liter of formation water (FW) and 1 ml of oil (STO1) were added and magnetic stirring initiated at 850 rpm for 5 minutes, Figure 4.2.2 show a set of pictures taken throughout the Test 1. Kaolinite was added starting with 0.2 g and then similar amount was added every 10 minutes (step 3 in the Figure) a darker layer of oil droplets was observed all along the stirring process.

When 1.08 g of Kaolinite were added the stirring was suspended, after 30 minutes was observed that the thin oil droplets layer becomes even darker and aggregation of oil droplets occurred (step 5), this continued to happened for the next hour and by this point kaolinite accumulation was observed at the bottom of the beaker (step 6).

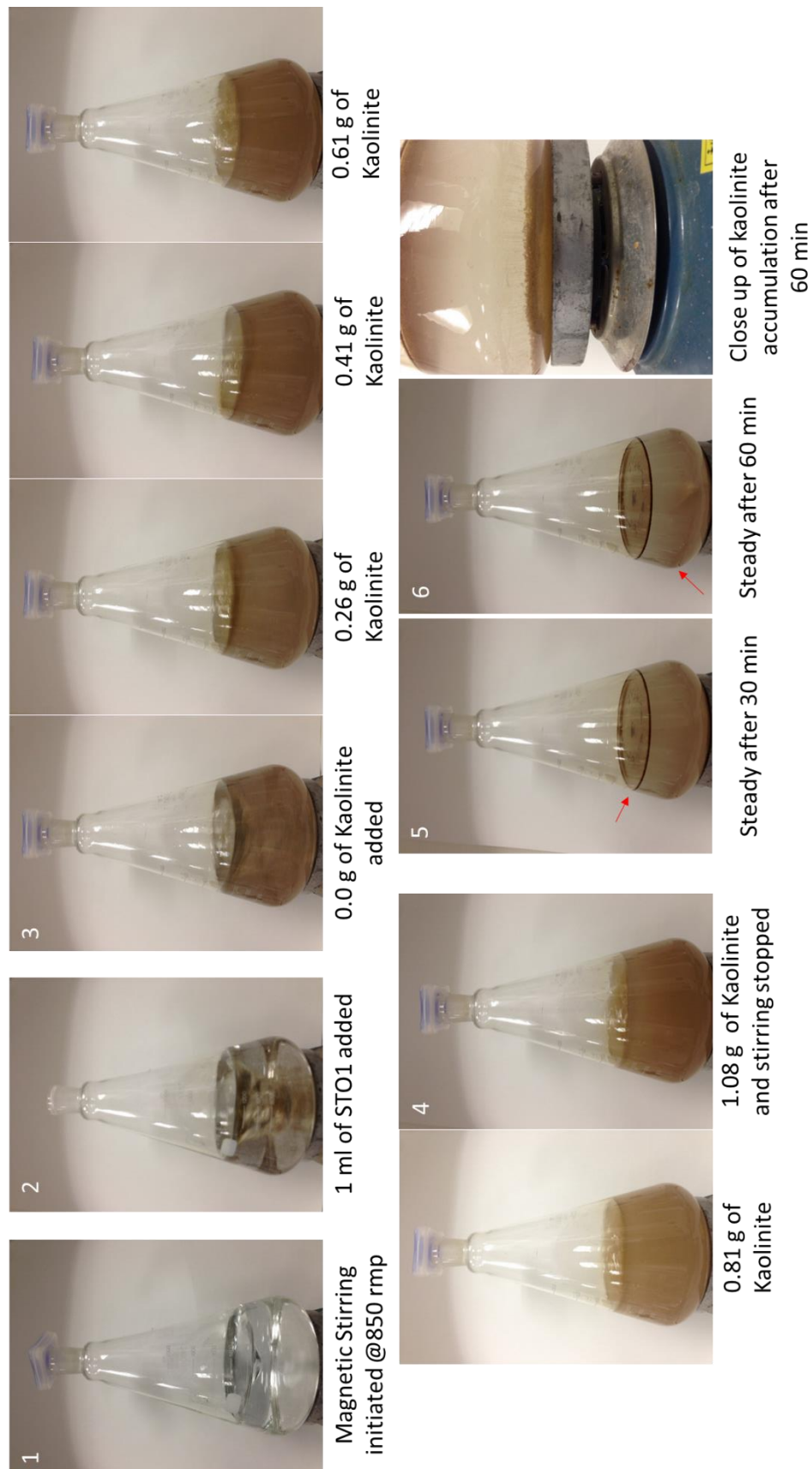


Figure 4.2.2 – Set of pictures for kaolinite screening Test 1.

4.2.1.1.1 Results Discussion

From the beginning of the test a dark layer containing big size oil droplets was observed at the top of the emulsion, therefore magnetic stirring energy is not enough to create small droplets that allows an efficient kaolinite attraction, 850 rpm was the maximum spinning rate that was possible to get an stable magnet spinning. Nonetheless the big droplets were successfully covered by kaolinite and protected from coalescence since after 1 hour the oil layer did not separate but droplets size were too big to consider it a successful dispersion.

As was determined before in the Test of Experiments 1 the use of 1 gram of solid particles is more than the quantity required to cover 1 ml of oil droplets, as a result kaolinite waste is observed by the end of the Test and continue adding kaolinite will result in a fail to improve droplets dispersion since more energy is required to break the oil phase in smaller droplets size.

Since stirring was stopped only until 1 gram of kaolinite was added, is not possible to determine by Test 1 the rate of kaolinite required, for the second test shear rate increasing was applied.

4.2.1.2 Test 2

Since the results obtained in test 1 where big size droplets were obtained due to magnetic stirring, then more energy was required to apply. Therefore for Test 2 Silverson mixer was used to break oil phase in smaller droplets size. Same procedure was followed to perform the experiment. Figure 4.2.3 shows a set of pictures taken throughout test execution.

Stirring initiated with 1 liter of formation water (FW) and 1 ml of oil (STO1), Silverson mixer at 6000 rpm was used to break the oil phase, 0.21 grams of kaolinite were added to assure protection for coalescence and maintain the reached smaller oil droplets size (step 1 in the figure), when no free oil was observed the emulsion was transferred to magnetic stirring at 850 rpm and kaolinite was continued added by 0.2 grams approximately every 10 minutes (step 2).

When 1 gram of kaolinite was added the stirring rate was lowered until 500 rpm to observe if any separation can occurs, however no free oil was detected and stirring stopped. After 15 minutes of steady state no oil droplets or free oil was floating at the surface, and some accumulation was obtained at the bottom of the bottle (step 4). Sample was stored in a close bottle to observe results, after 24 hours of resting all the oil was retained by the kaolinite particles and sank down, free water was obtained for the rest of the emulsion.

4.2.1.2.1 Results Discussion

Increase the shear rate up to 6000 rpm improved significantly the reduction of oil droplets size, and solid particles covered more efficiently. Test 1 and Test 2 has exactly the same conditions regarding emulsion fluids (FW, STO1 and Kaolinite) quantities, however by the moment of stopping the magnetic stirring no dark layer was observed and an apparent homogenous dispersion can be observed, additionally no saturated kaolinite was floating at the surface. Therefore a smaller size averaged distribution can be inferred proving that higher stirring energy is required to obtain stability with solid.

After 24 hours results showed the same behavior as in Experiment 1-Test 1- Sample 1 where the same amounts of solid particles and oil were added in a volume of FW (250 ml). Kaolinite protects the oil droplets successfully but due to excess of kaolinite the density difference sank the oil droplets down to the bottom with the waste of solid particles. Hence 1 gram of kaolinite was proved once more to be more than required to cover 1 ml of oil. For the next test the exact rate of kaolinite in grams per ml of oil to avoid waste without affecting the stability of the emulsion.

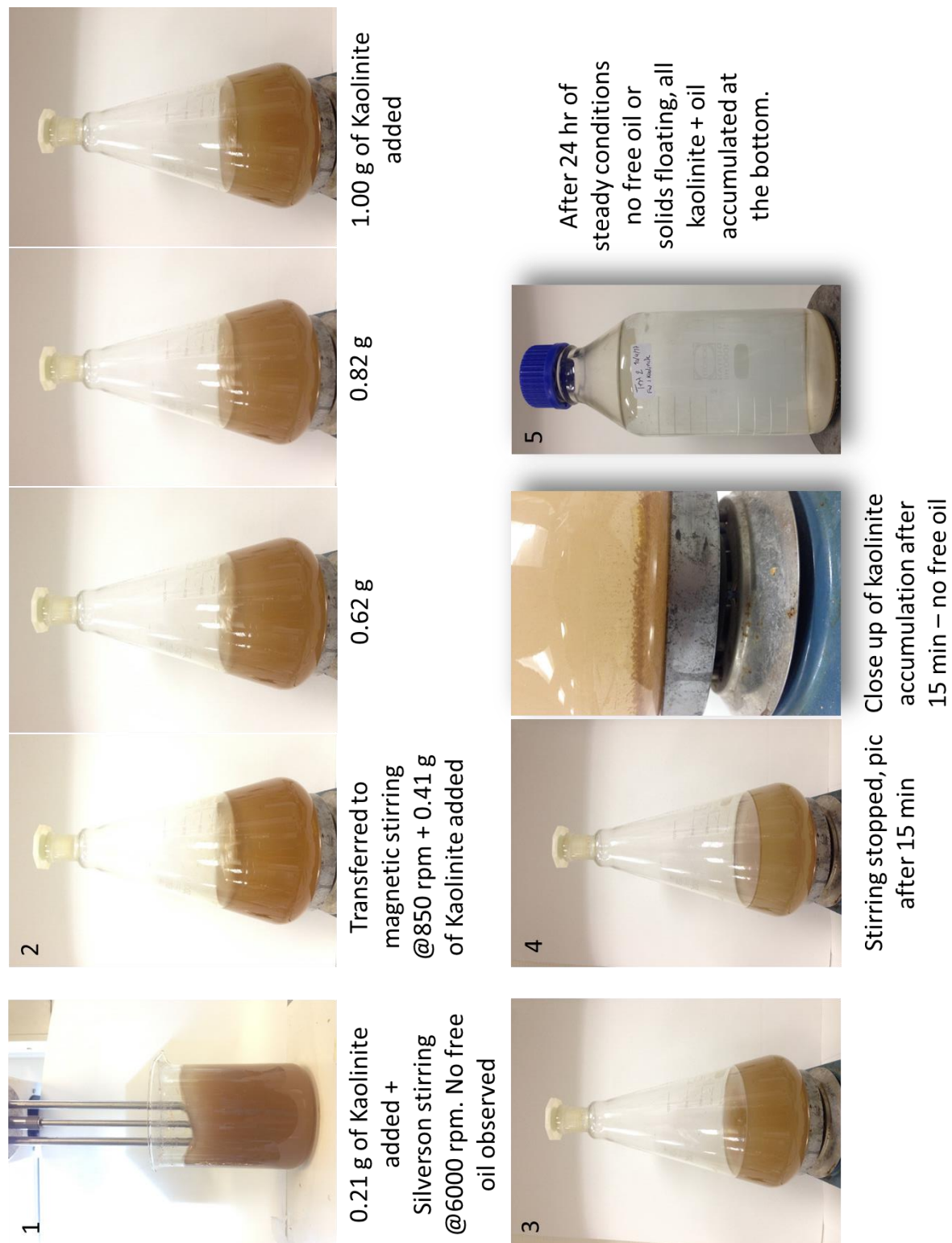


Figure 4.2.3 - Set of pictures for kaolinite screening Test 2.

4.2.1.3 Test 3

The purpose of this test was to determine the required rate of kaolinite that should be used per milliliter of oil dispersed in the emulsion, assuring both a successful coverage of oil droplets dispersed and avoid waste of solid particles material. This test intends to find a value that leads to reduce economical cost when and emulsion flooding is used for oil recovery project.

As well as in the previous test, a Silverson mixer at 6000 rpm was used to mix 1 liter of formation water with 1 ml of oil (STO1) with the required energy to obtain a homogeneous dispersed phase. After 5 minutes the stirring stopped to observe how oil droplets aggregate and then coalescence finally produce separation when neither solid particles nor emulsifier is added to stabilize the emulsion, as can be observed in Figure 4.2.4. It is likely that oil polar components are not enough to guaranty stability and dispersion of the oil droplets, then regardless the applied energy or the droplets size the use of solid particles is required to improve the stability process.

Test 3 was executed by several stages, since a thorough analysis is required, Figure 4.2.5 show a set of pictures of the experiment execution. Additionally this test is intended to prove that once emulsion stability is achieved with a high shear energy mixer then a lower energy could be enough to maintain a homogenous distribution of the disperse phase as long as the motion goes on. This topic is important when emulsion is injected in a core or reservoir for analysis, since fluid injected must guarantee a homogenous concentration of oil in the formation water phase, otherwise a mud-cake can be formed at the injection face of the porous media and affects the results negatively, however this analysis will be performed and showed in the next chapter when emulsion flooding was carried out.

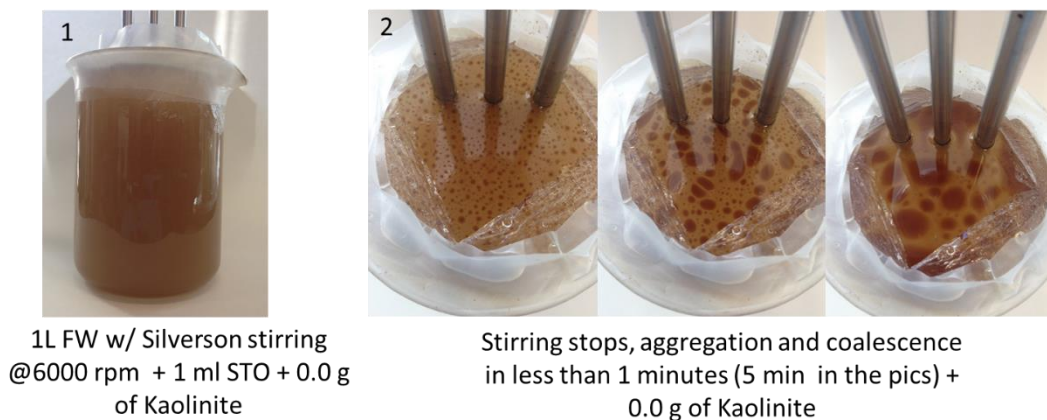


Figure 4.2.4 – Aggregation and coalescence of oil phase in absence of solid particles or emulsifier.

The first stage began stirring the emulsion at 6000 rpm with the Silverson mixer. When 0.15g of kaolinite were added stirring stopped and some bubbles with very small size and oil at their surface appeared floating at the surface (step 6 in the Figure 4.2.5). However due to none free oil is floating the emulsion is transported to a magnetic stirring.

Emulsion was mixed at 300 rpm for about 5 minutes, after this time bubbles aggregated and exploded leaving free oil behind that was accumulated at the spinning vortex. Additionally emulsion passed from a homogenous dispersion to particles aggregation and big size particles was observed spinning around.

Stirring stops and after 10 minutes of steady state most of big size droplets covered by kaolinite were floating at the surface. Although no free oil is observed, the emulsion is considered not efficiently stable due to droplets size increasing due to aggregation.



Figure 4.2.5 – set of pictures for Stage 1 of Test 3 for Kaolinite screening.

In the second stage emulsion stirring was restarted with the Silverson mixer at 6000 rpm, another 0.05 g of kaolinite were added to complete 0.2g of solid particles in total, mixing lasted for 5 minutes. Figure 4.2.6 shows picture for second stage of experiment execution. Stirring stopped and lighter brown bubbles (almost transparent) were observed floating at the surface (step 11 in the Figure 4.2.6).

Once again the emulsion was transported for stirring with magnets at 300 rpm for about 5 more minute. At the beginning the same aggregation of oil was observed at the vortex but with smaller size and in the form of foam (no free oil), however after 1 minute of stirring droplets with kaolinite started to aggregate again forming bigger particles but with smaller size than stage 1.

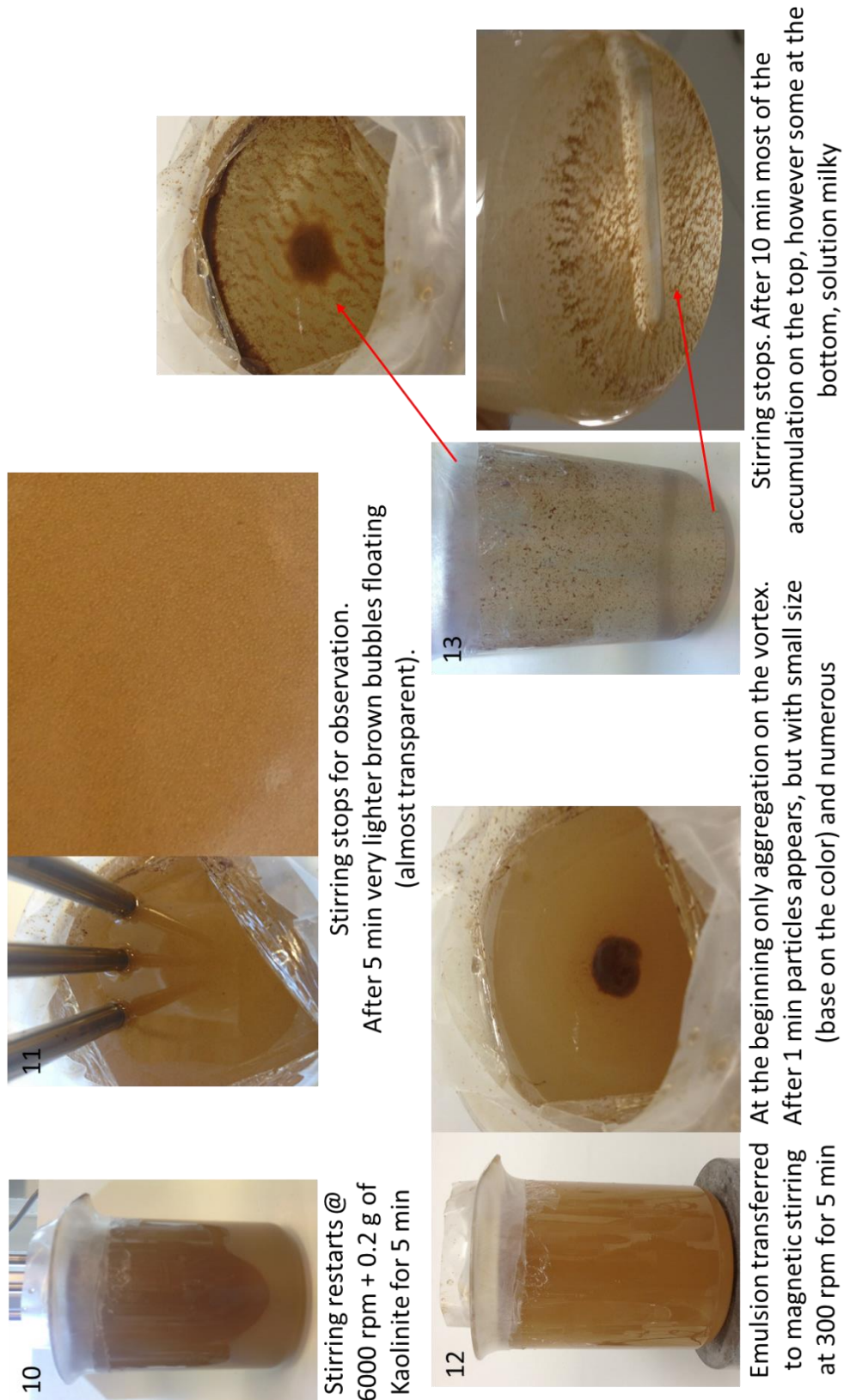


Figure 4.2.6 - set of pictures for Stage 2 of Test 3 for Kaolinite screening.

Magnetic stirrer was turned off and after 10 minutes most of the droplets and oil droplets were accumulated at the top, however some material started to deposit the bottom of beaker. Due to majority of oil were floating then a third stage were performed.

For the third stage high shear rate restarted with the silverson mixer at 6000 rpm, kaolinite were added to complete a total of 0.25 g of solid particles added to the emulsion for droplets protection. After 5 minutes stirring stopped and some transparent bubbles were observed at the surface. Figure 4.2.7 shows set of picture of the experiment workflow.

Emulsion is transferred to magnetic stirrer at 300 rpm for about 5 more minutes. Again foam accumulation is seen at the vortex but smaller and with light brown color. After 2 minutes particles aggregation had place, to solve this the spinning rate was increased to 500 rpm. Nonetheless was noticed that aggregation occurred principally because magnet spinning was intermittent, thus stirring rate was decreased to 300 rpm but assuring continuous movement, as result lower aggregation and average particles size was observed (step 18 in Figure 4.2.7).

Stirring stopped and after 10 min almost all the oil droplets covered by kaolinite was deposited at the bottom of the beaker, no free oil was observed. Emulsion was stored in a close bottle and after two hours there is no accumulation floating at the surface, and all the material has sank down to the bottom, water is almost clear.

4.2.1.3.1.1 Results Discussion

Emulsion should be prepared at high shear rate energy (6000 rpm in this Test) to assure oil phase breaking into droplet with size sufficiently small to have a homogeneous dispersed phase while stirring motion in applied.

At the first stage 0.15 g of kaolinite were added, and despite the ratio is lower to assure to make the droplets sink at the bottom due to high oil saturation and particles gather in big sizes, it can be considered enough to guaranty a proper coverage or protection to coalescence since no free oil was observed even when there is a steady state (step 9). Nonetheless 0.15g of kaolinite/ml of oil could be a reference point for oil screening in the determination of the point in which a less saturated particles pass from the be sank at the bottom to migrate to the top due to oil concentration increase, but this will be analyzed in the next section.

0.25 g of kaolinite /ml of STO1 at an oil concentration of 852 ppm (this is the oil concentration obtained if the procedure in section 3.2.2 is followed) was found to be the appropriate quantity ratio to guaranty not only that a small-size droplets are efficiently cover and protected from coalescence, but additionally avoiding waste of solid particles material.

The fact that oil concentration is lower than 1000 ppm, follows the Norwegian guidance for disposal water oil concentration. Therefore this emulsion can be prepared by the use of disposal water, hence project economic metrics can be impacted positively due to reinjection of produced water avoiding volumes treatment due to water recycle.

Through the different stages when big size particles were observed, once higher shear rate is applied the dispersed phase is easily broken into smaller droplet, therefore the size of big formed particles can be easily reverted to smaller when the appropriate energy is applied. For further studies it is suggested to analyze the use of Bentonite. It is likely that quantity rates is closer to the found value of 0.25g of Kaolinite/ml of oil. However it was also proved that this clay has smaller solid particles size which can impact the rate determination.

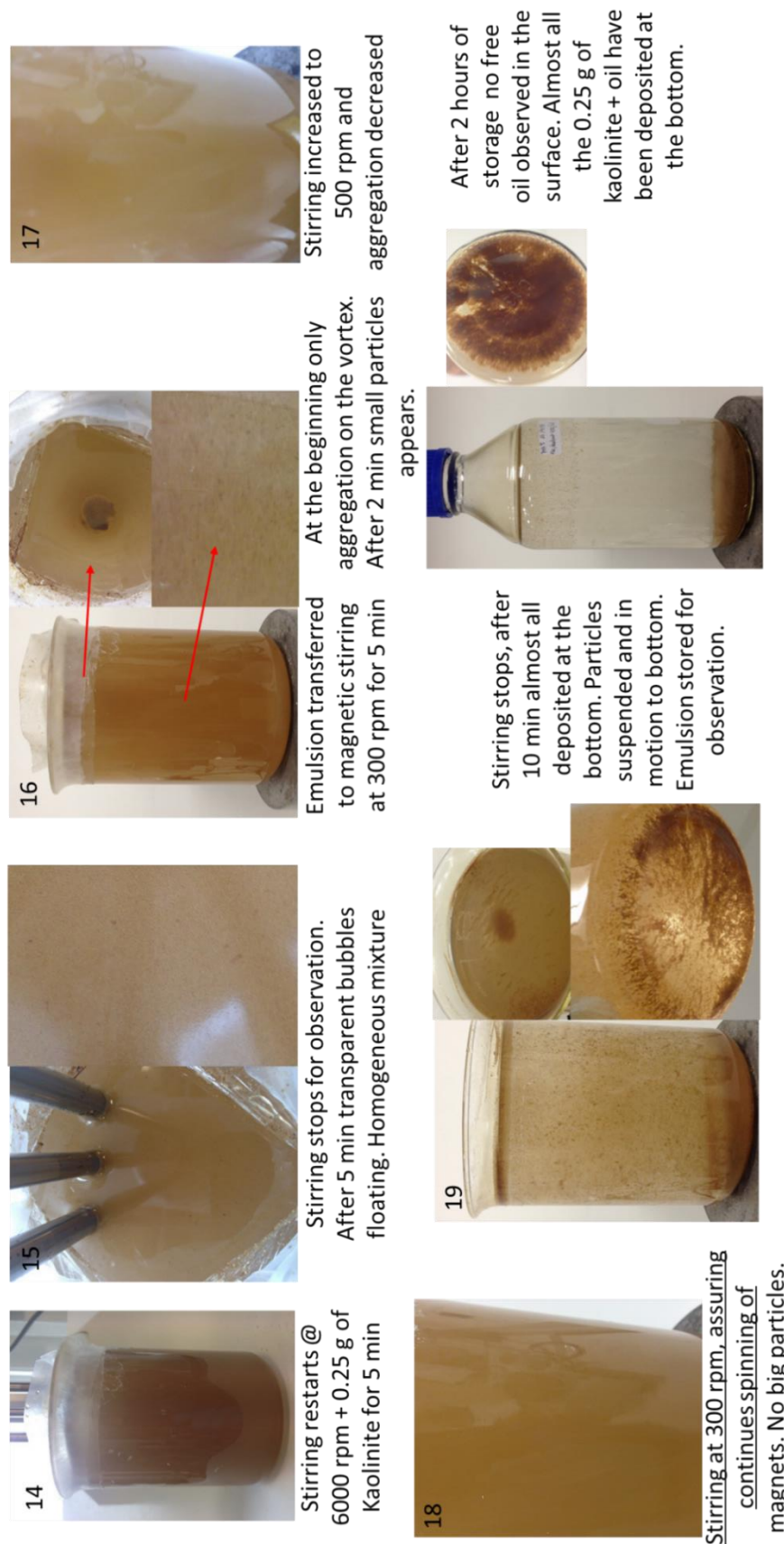


Figure 4.2.7 - set of pictures for Stage 3 of Test 3 for Kaolinite screening.

4.2.2 Test 4: Oil quantity screening

The oil screening was performed in order to confirm or evaluate if results obtained with kaolinite screening behave similarly if process is executed backwards, this test was called Test 4. As explained in procedure section, 1 liter of formation water with 1 gram of Kaolinite was mixed by the used of Stirring mixer at 6000 rpm, in this case continue high shear energy is required throughout the procedure due to a higher volume of oil is expected and new oil added at each time must be broken into smaller droplets. Figure 4.2.8 shows the set of pictures for this Test.

The test began adding 1 ml of oil directly because we know from before that this quantity is considered lower to saturate 1 g of Kaolinite and make particles floating. When 1.5 ml of oil were added stirring stopped and was seen that particles began to fall down to the bottom, thus 0.05 ml of oil was added at a time until complete 2.5 ml of oil added to the emulsion (step 3, 4 in Figure 4.2.8). After 5 minutes of steady state was observed that accumulation at the bottom started to move upwards and motion is slightly turbulent but avoiding the bottom deposit (step 5), emulsion was storage in a closed bottle for monitoring.

After 48 hours of steady state there is no free oil observed. Some droplets with particles were floating at the surface, however most of the material is accumulated at the bottom of the bottle with dark brown color.

Despite the purpose of the experiment was to calculate a rate in which particles started to be saturated with oil and by density difference began to float, the experiment was suspended due to at the moment 2.5 ml of oil addition, the emulsion equivalent to oil concentration of 2126 ppm, surpassing the Norwegian law for disposal water oil concentration.

4.2.2.1 Results Discussion

Solid particles started to be saturated at a rate between **2.0 - 2.5 ml of oil/g of Kaolinite** which is equivalent to 0.4 g of kaolinite/ml of oil since the behavior of the emulsion particles showed in the picture of step 5 in Figure 4.2.8 showed that density of particles started to decrease and tended towards the surface.

However by the Test 3 a rate of 0.25 g of kaolinite/ml of oil was calculated as the closest rate where droplets are efficiently covered by solid particles, this rate suggests that 4 ml of oil are required to be added to the emulsion to saturate 1 g of kaolinite which is a constant value in Test 4. Therefore despite the Test was suspended before reaching this value due to Norwegian law regulations for disposal water; it is possible to confirm that results from Test 3 are partially proven and replied in Test 4 due to the final accumulation at the bottom obtained after 48 hours regardless the apparent particles saturation observed in step 5.

Additionally is important to clarify that Test 4 was executed as a confirmation of results obtained in Test 3. Therefore regardless the results, it was considered that only results of Test 3 are required to continue with the core flooding studies, since the calculated rate of 0.25 g of Kaolinite /ml of oil was a coherent value that was calculated thoroughly.

For further studies it is recommended to finalize with oil screening experiment, and determine the exact rate in which, if the experiment is done backwards, the solid particles are saturated with oil droplets, and analyze if oil in water emulsions are sensitive to the process how the continue phase, dispersed phase and solid particles are mixed.

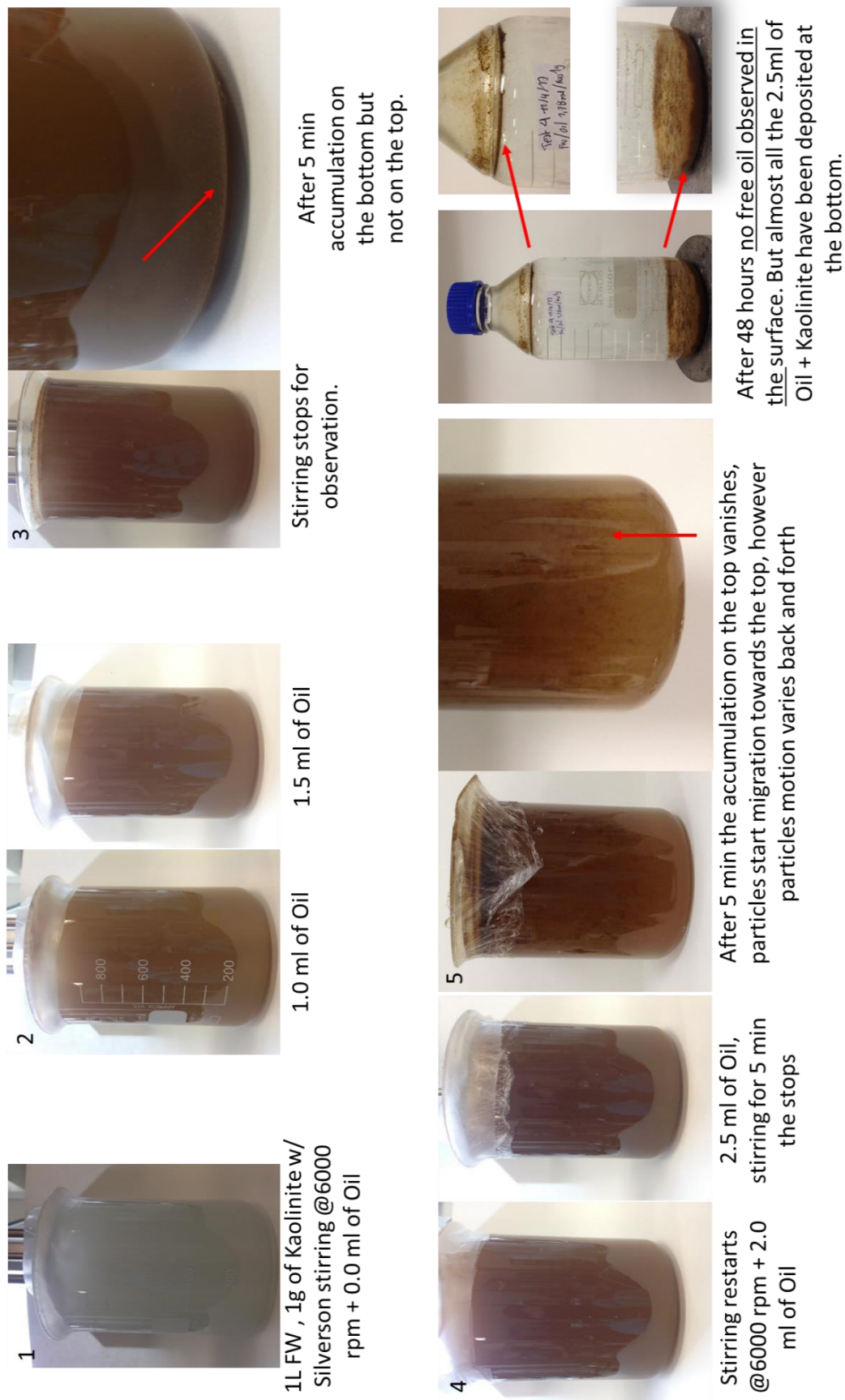


Figure 4.2.8 – Set of pictures of Test 4- Oil Screening.

4.3 Experiment 3: Core Flooding

Results are shown according to how the three stages (3) were explained in the Experiment Description section 3.3.

4.3.1 Initial Permeability

Results from the permeability calculation are comprised in Table 4.3.3. This Information was used to confirm the results shown in Figure 4.3.5.

From the procedure an averaged initial permeability of 1.2 [Darcy] was calculated for the porous media. This value was verified by plotting injection rate [ml/min] vs pressure difference [bar], the equation of the linear tendency line is shown in the plot of Figure 3.3.5, with a final value of slope of 1.37, which confirm the correct calculation of the initial permeability by $1.37 \cdot (1.2 \cdot 8.015 / 10.81) = 1.2$ [Darcy].

Table 4.3.3 - Permeability Calculation Sheet for Initial Permeability.					
Experiment Stage	Oil Concentration (ppm)	Q (ml/min)	Pressure Difference (%)	Pressure Difference (Bar)	Permeability (Darcy)
1. Initial Permeability	N/A (Formation Water Injected)	10	2.42	0.121	1.24
		10	2.46	0.123	1.22
		10	2.50	0.125	1.20
		5	1.27	0.064	1.18
		5	1.26	0.063	1.19
		5	1.27	0.064	1.18
		1	0.25	0.013	1.20
		1	0.24	0.012	1.25
		1	0.25	0.013	1.20

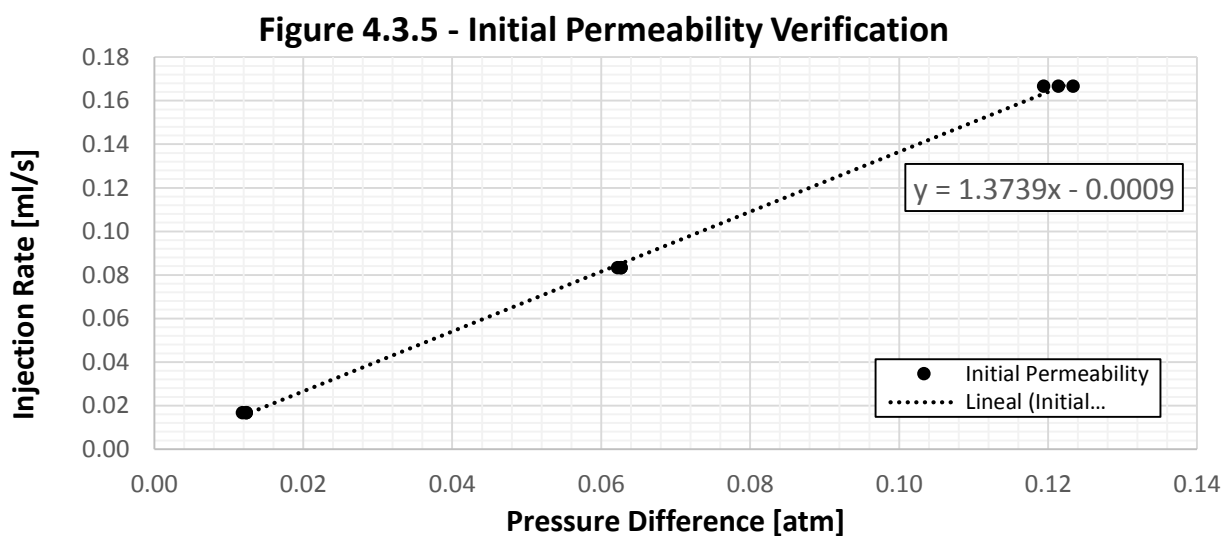


Figure 4.3.5 – Initial Permeability Verification.

Permeability values show consistency and may be considered reliable due to confirmation by plot in Figure 4.3.5. Additionally the averaged value of 1.2 [Darcy] are consistent to the permeability suggested by the supplier.

4.3.2 Emulsion Flooding

An emulsion with an oil concentration of 852 ppm was injected in the core. Pressure transmitter used in the experiment assembly was not connected with logging, therefore the required information was taking manually, and information is comprised in Table 4.3.4. Figure 4.3.6 show emulsion samples taken from the piston cell outlet valve.

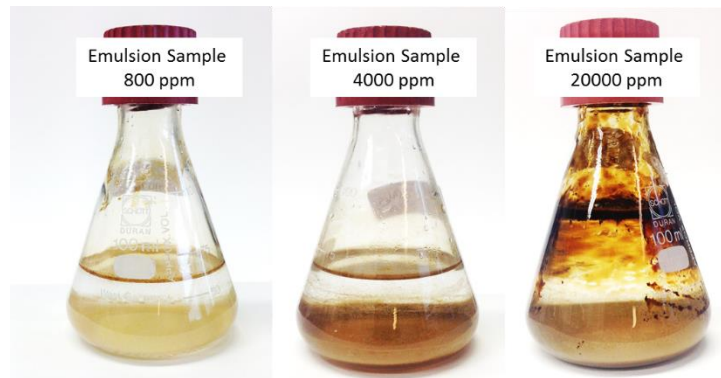


Figure 4.3.6 – Samples of Emulsions used for core flooding.

In total 3.5 pore volumes (PV) were injected, while the fluid breakthrough was monitored there was no oil nor kaolinite particles, thus only formation water was produced, Figure 4.3.7 shows a pic of the measured bottles used to measured pore volumes injected by the breakthrough fluid (several emulsion flooding were needed to execute but this will be explained further in detail) observed the corresponding to 852 ppm approximately. Therefore it was assumed that all the oil droplets and Kaolinite were trapped in the porous media, thus 3.5 PV injected were equivalent to 0.08 ml of oil trapped if emulsion concentration was assumed to be homogeneous along the emulsion.



Figure 4.3.7 – Produced fluids when emulsion flooding was carried out.

Table 4.3.4 – Pressure Difference Values with Emulsion of oil concentration of 852 ppm.

Injection rate (ml/min)		0.5			
Oil Concentration (ppm)		852			
Kaolinite used (g)		0.25			
<u>time (min)</u>	<u>Pressure Difference (%)</u>	<u>Pressure Difference (bar)</u>	<u>Volume Produced (ml)</u>	<u>PV Injected</u>	<u>"Oil Injected" (ml)</u>
0	0.13	0.0065	0	0	0.00
17	0.17	0.0085	8.5	0.4	0.01
39	0.2	0.01	16	0.7	0.02
59	0.18	0.009	30	1.4	0.03
73	0.14	0.007	36	1.7	0.04
91	0.14	0.007	44	2.0	0.04
103	0.13	0.0065	52	2.4	0.05
115	0.13	0.0065	58	2.7	0.06
125	0.13	0.0065	64	3.0	0.06
141	0.13	0.0065	70	3.2	0.07
151	0.13	0.0065	76	3.5	0.08

Observe that pressure values increased gradually until 0.01 [bar], then started to decrease until got stable at 0.0065 [bar], this behavior may be attributed to rupture of kaolinite blocking by the pressurized injected fluid.

Permeability was calculated by formation water injection after the emulsion flooding finalized, this scheme simulates a typical recovery operation at the field, where water flooding is reactivated after emulsion batch has been injected.

According to results a very low pressure difference was measured through the core; 0.0065 [bar], therefore it was concluded that despite oil concentration comply with Norwegian regulation for maximum water disposal oil concentration, this values was too low to assure an efficient porous media blocking, and nonetheless no oil reached the breakthrough.

Regardless differential pressure low values, permeability measurements were carried out. Results can be observed in Table 4.3.5, with and averaged permeability reduction of 1.1 [Darcy].

Table 4.3.5 - Permeability Calculation Sheet.

<u>Experiment Stage</u>	<u>Oil Concentration (ppm)</u>	<u>Q (ml/min)</u>	<u>Pressure Difference (%)</u>	<u>Pressure Difference (Bar)</u>	<u>Permeability (Darcy)</u>	<u>Average Permeability (Darcy)</u>
1. Initial Permeability	N/A (Formation Water Injected)	10	2.42	0.121	1.24	1.2
		10	2.46	0.123	1.22	
		10	2.50	0.125	1.20	
		5	1.27	0.064	1.18	
		5	1.26	0.063	1.19	
		5	1.27	0.064	1.18	
		1	0.25	0.013	1.20	
		1	0.24	0.012	1.25	
		1	0.25	0.013	1.20	
2. Permeability After Emulsion Flooding	852	10	2.68	0.134	1.1	1.1
		10	2.69	0.135	1.1	
		10	2.70	0.135	1.1	
		5	1.30	0.065	1.2	
		5	1.36	0.068	1.1	
		5	1.34	0.067	1.1	
		1	0.28	0.014	1.1	
		1	0.29	0.015	1.0	
		1	0.29	0.015	1.0	
	4200	10	7.03	0.352	0.4	0.37
		10	7.01	0.351	0.4	
		10	7.03	0.352	0.4	
		5	3.37	0.169	0.4	
		5	3.38	0.169	0.4	
		5	3.37	0.169	0.4	
		1	1.20	0.060	0.3	
		1	1.18	0.059	0.3	
		1	1.24	0.062	0.2	
	20000	10	64.90	3.245	0.0	0.05
		10	64.90	3.245	0.0	
		10	64.70	3.235	0.0	
		5	31.78	1.589	0.0	
		5	31.75	1.588	0.0	
		5	31.78	1.589	0.0	
		1	6.75	0.338	0.0	
		1	6.75	0.338	0.0	
		1	6.74	0.337	0.0	

Since blocking was not effective, then an emulsion with an oil concentration of 4200 ppm equivalent to 5 ml of oil dispersed in 1L of FW and 1.25 g of Kaolinite was prepared, the ratio of 0.25 [Kaolinite (g)/ml of oil] was conserved.

Results for emulsion injection can be found in Table 4.3.6, experiment stopped when 3.5 PV were injected. Observe how differential pressure increased continuously as more pore volumes were injected. Additionally Figure 4.3.7 shows that produced fluid is completely transparent, therefore porous media has been saturated with all the oil droplets and kaolinite, thus if homogenous dispersion is assumed, a total of 0.007 ml of oil added and trapped into the porous media. By the end of experiment differential pressure reached 0.4 [bar]

<i>Table 4.3.6 – Pressure Difference Values with Emulsion of oil concentration of 4200 ppm.</i>					
Injection rate (ml/min)	0.5				
Oil Concentration (ppm)	4242				
Kaolinite Used (g)	1.25				
<u>Time (min)</u>	<u>Pressure Difference (%)</u>	<u>Pressure Difference (bar)</u>	<u>Volume Produced (ml)</u>	<u>PV Injected</u>	<u>"Oil Injected" (ml)</u>
0	0.00	0.00	0.0	0	0.00
17	0.17	0.01	9.7	0.4	0.01
24	0.18	0.01	12.0	0.6	0.01
39	0.30	0.02	20.0	0.9	0.02
46	0.58	0.03	23.0	1.1	0.02
49	0.80	0.04	24.0	1.1	0.02
60	1.40	0.07	30.0	1.4	0.03
66	2.10	0.11	32.0	1.5	0.03
72	2.91	0.15	34.0	1.6	0.03
82	2.98	0.15	40.0	1.8	0.04
89	2.70	0.14	44.0	2.0	0.04
91	2.14	0.11	44.0	2.0	0.04
96	2.63	0.13	46.0	2.1	0.05
102	3.51	0.18	50.0	2.3	0.05
111	3.52	0.18	54.0	2.5	0.05
115	4.15	0.21	54.5	2.5	0.05
118	4.57	0.23	56.0	2.6	0.06
130	5.82	0.29	60.0	2.8	0.06
137	5.89	0.29	64.0	3.0	0.06
143	6.60	0.33	68.0	3.1	0.07
146	6.28	0.31	69.0	3.2	0.07
152	7.94	0.40	70.0	3.2	0.07

Despite the continuous pressure increasing, the value of pressure remains lower than 1 [bar]. Nonetheless permeability calculations were carried out. Results can be found in Table 4.3.5, an averaged rock permeability of 0.37 [Darcy] was calculated, thus 0.73 [Darcy] net reduction may be attributed to blocking of emulsion with an oil concentration of 4200 ppm.

Emulsion oil concentration was increased up to 20000. 1 liter of Formation water was mixed at 6000 rpm with 25 ml of oil and 6.4 g of kaolinite (rounded quantities), a ratio of 0.25 g of kaolinite/ml of oil is preserved and was injected at 0.5ml/min rate. Figure 4.3.6 shows a picture of a sample taken from the piston cell outlet, observed that the oil concentration is high enough that some droplets were sticking to the bottle walls, nonetheless when Silverson mixing ended the emulsion had a more homogeneous dispersion on its appearance, therefore the magnetic stirring inside the piston cell may not be high enough at this high oil concentration.

Nonetheless despite the apparent free oil observed in the emulsion sample, there was no oil nor kaolinite particles at the breakthrough, as it can be seen in Figure 4.3.7. Results from emulsion flooding with a 20000 ppm oil concentration emulsion are summarized in Table 4.3.7

<i>Table 4.3.7 - Delta Pressure Values with Emulsion of oil concentration of 20000 ppm.</i>					
Injection rate (ml/min)	0.5				
Oil Concentration (ppm)	20000				
Kaolinite Used (g)	6.4				
Time (min)	Pressure Difference (%)	Pressure Difference (bar)	Volume Produced (ml)	PV Injected	"Oil Injected" (ml)
0	0.00	0.00	0.0	0	0.00
3	1.24	0.06	0.0	0.0	0.00
6	1.37	0.07	0.0	0.0	0.00
7	1.40	0.07	0.0	0.0	0.00
13	1.80	0.09	5.0	0.2	0.00
16	2.05	0.10	7.0	0.3	0.01
21	2.51	0.13	9.0	0.4	0.01
23	2.64	0.13	10.0	0.5	0.01
27	3.15	0.16	12.0	0.6	0.01
35	8.15	0.41	15.0	0.7	0.01
43	16.20	0.81	17.0	0.8	0.02
44	20.50	1.03	19.0	0.9	0.02
47	26.60	1.33	20.0	0.9	0.02
51	37.70	1.89	22.0	1.0	0.02
54	41.80	2.09	23.0	1.1	0.02
57	52.90	2.65	24.5	1.1	0.02
60	49.90	2.50	26.0	1.2	0.03
62	53.50	2.68	27.0	1.2	0.03
67	65.00	3.25	28.0	1.3	0.03
73	84.00	4.20	29.0	1.3	0.03
74	93.00	4.65	30.0	1.4	0.03
75	97.00	4.85	30.0	1.4	0.03
74	100.00	5.00	30.0	1.4	0.03

As showed in Table 4.3.7 pumping finalized when 1.4 pore volumes were injected due to the pressure increased up to 100% equivalent to 5 [bar] which is the maximum value that pressure

transmitter can measured, notice that due to oil and kaolinite quantities increased then the emulsion flooding took more time and displacement reach the breakout after 7 minutes of continuous injection.

Permeability was measured afterwards and results are comprised in Table 4.3.5, a total averaged permeability of 0.005 [Darcy], thus 0.32 [Darcy] net reduction can be attributed to this emulsion blocking. However by this point was needed to confirm if flow restriction was due to emulsion droplets blocking or because a heavy mud cake was formed at the injection face of the core (this will be shown in section 4.3.3).

4.3.2.1 Results Discussion

Emulsion displacement results contained in the prior tables are summarized in the following figures. Observe in Figure 4.3.8 that the 3.5 PV injected of emulsion with an oil concentration of 800 ppm (rounded values for simplicity) does not block the porous media enough to increase the differential pressure, perhaps more volumes of emulsion are required until cause an efficient blocking. Same results are observed when emulsion of oil concentration of 4000 ppm is injected. This conclusion is supported by the linear behavior of the two first mentioned emulsions, in contrast an emulsion with oil concentration of 20000 ppm began with a similar tendency that the lower concentration ones, but after 30 minutes of injection the pressure started to increase abruptly and continuously until experiment stopped when 5 [bar] were reached.

Figure 4.3.8 - Delta Pressure vs time

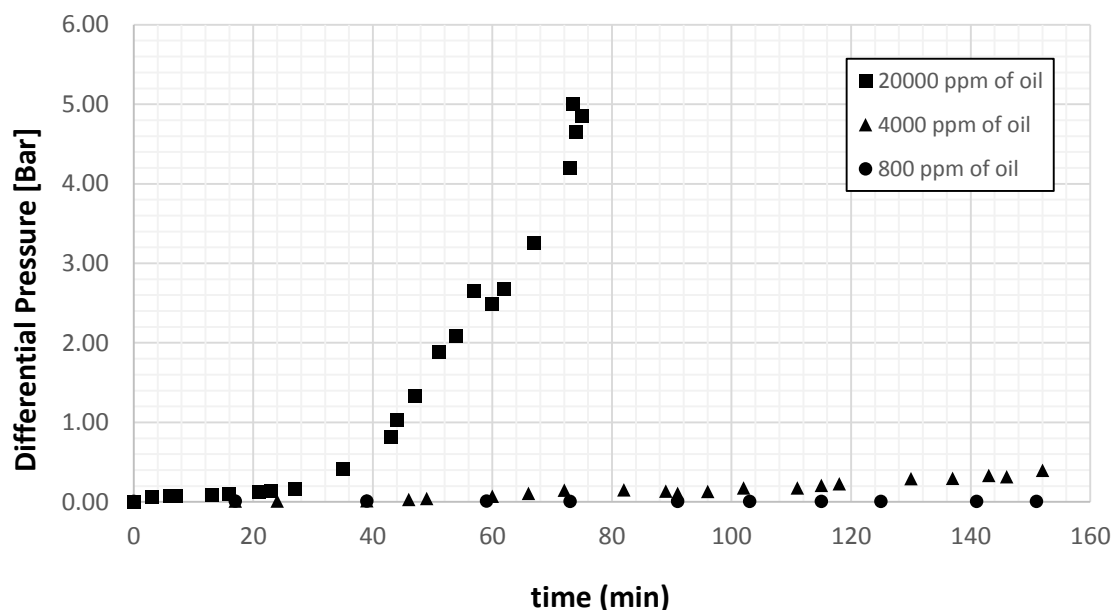


Figure 4.3.8 – Differential Pressure vs Time, Emulsion flooding.

Nonetheless regardless of the notorious pressure difference increasing that infers a flow restriction, Figure 4.3.9 shows that all the three emulsion have almost the same displacement velocity due to the same constant injection rate. However when a tendency line is extrapolated it is possible to observe that after 1 pore volumes have been injected the last emulsion (20000 ppm) reduces its velocity and takes 35 minutes more to reach 3 PV.

Figure 4.3.9 - Pore Volumes Injected vs time

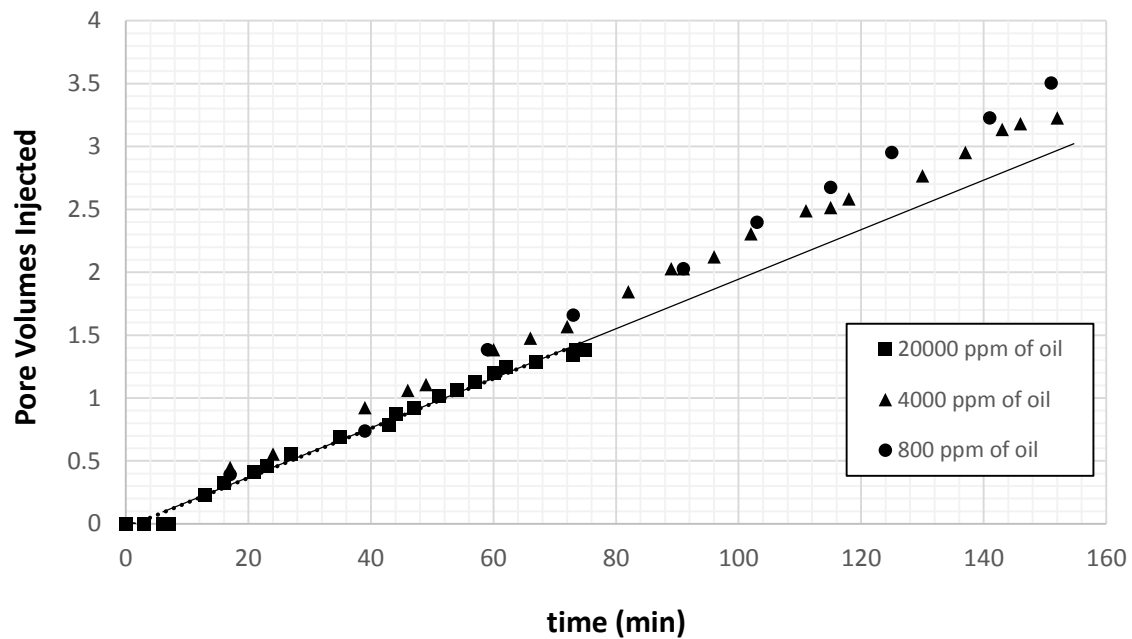


Figure 4.3.9 – Pore Volumes Injected vs Time, Emulsion flooding.

Figure 4.3.10 support previous two figures, it shows the slow increasing of emulsion with 800 and 4000 oil ppm after 3.5 pore volumes are injected. On the other hand an emulsion of 20000 ppm started increasing exponentially when approximately 0.5 PV were injected and this tendency remains until experiment stopped.

Figure 3.3.10 - Pore Volumes Injected vs Pressure

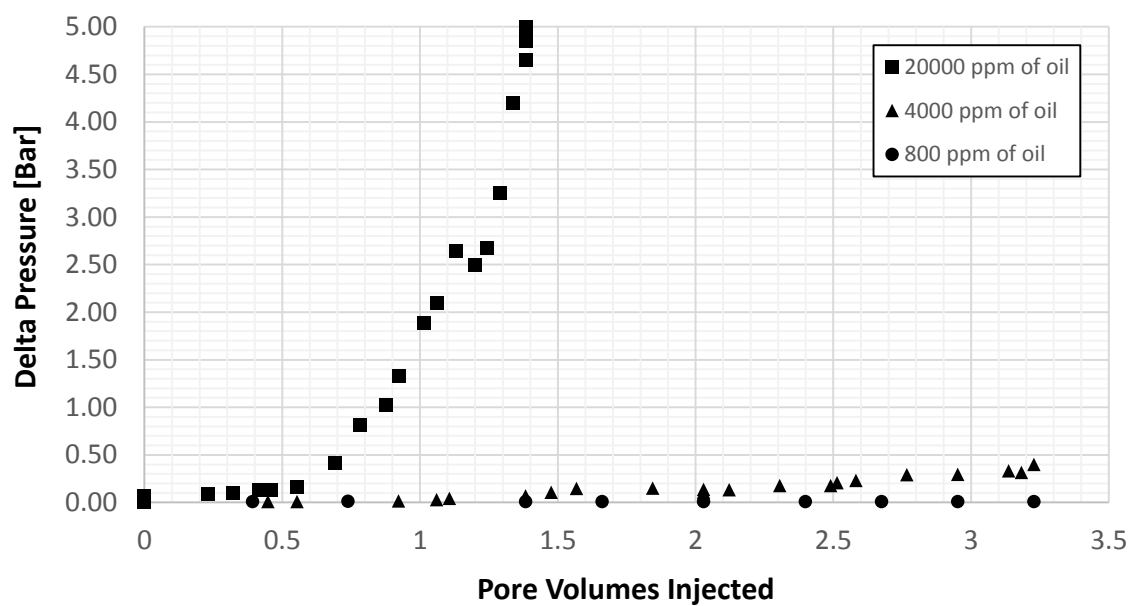


Figure 4.3.10 – Differential Pressure vs Pore Volumes injected, Emulsion Flooding.

Averaged permeability results for each injection rate (instead of using the three values at each rate, averaged value was calculated for simplifications) can be observed in Figure 4.3.11 and its corresponding percentage in permeability reduction at each step. It can be inferred that permeability reduction is a direct result of oil content in the form of dispersed phase at the emulsion. When an emulsion with oil concentration of approximately 800 ppm is injected a reduction of 8.7% in permeability is obtained regarding the initial permeability of 1.2 [Darcy]. Simultaneously 68% in reduction for an Emulsion-4200 ppm and finalizing with a total permeability reduction of 96% by injecting an emulsion-20000 ppm of oil.

However it is important to clarify that each reduction percentage was calculated regarding the initial permeability, therefore since the emulsion flooding experiment were executed in a row by cycles of emulsion and water flooding at each step, the 96% of reduction is the result of oil accumulation by the three emulsions. No additional experiment was executed to determine emulsion permeability by individual core flooding, since determining a specific permeability against oil content is out of the scope of this experiment. Nonetheless an appropriate approach can be obtained by results if each average value is compared with the immediate previous one.

Figure 4.3.11 - Permeability Results After Each Emulsion Flooding

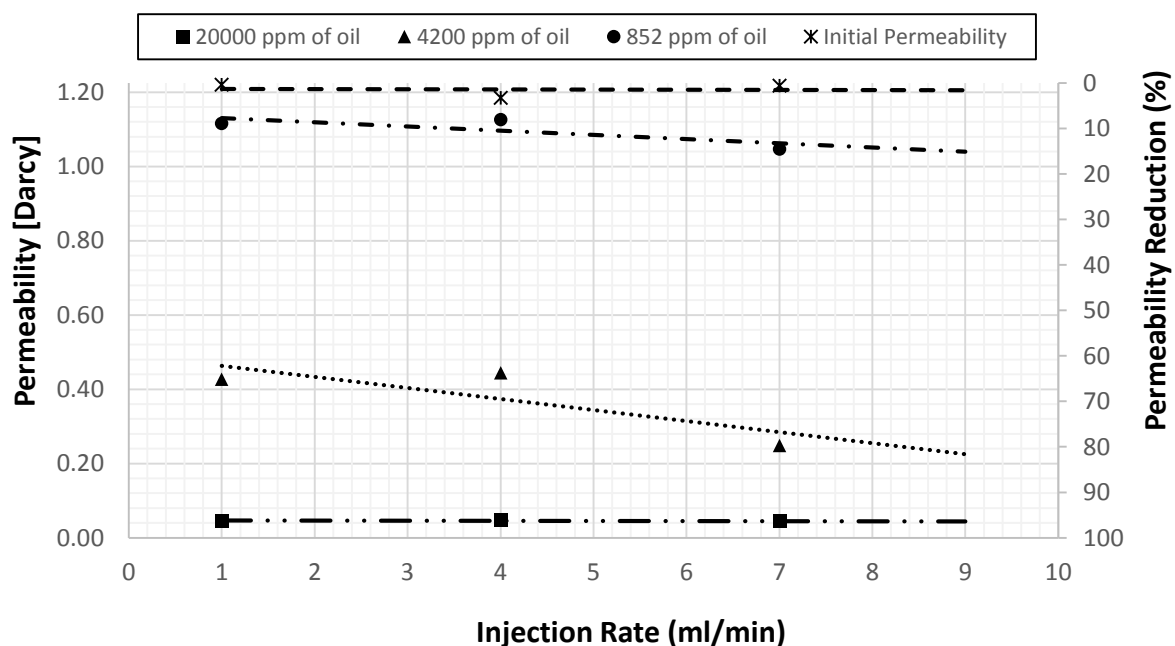


Figure 4.3.11 – Permeability measurements after each emulsion flooding.

4.3.3 Final Permeability Determination

As mentioned before, the permeability values calculated after each emulsion flooding may be attributed to a mud cake accumulated at the injection face of the core causing a flow restriction instead of a heterogeneity “correction” caused by oil droplets blocking reduction. Therefore to solve the uncertainty the core holder was opened and a thin layer of mud cake was observed formed at the injection face shown in Figure 4.3.12. Injection channels were partially blocked and this pattern was replicated at the core front face as observed in the picture. Since final permeability calculation may be affected by the water flow restriction that mud cake may produce, hence both injection face and core front face were washed out with formation water in order to avoid any chemical reaction.



Figure 4.3.12 – Mud cake formed at the front face of the core while emulsion flooding.

With a clean front face the experiment equipment was assembly and water flooding was executed. An averaged final permeability of 0.324 was calculated with the whole core length (8.015 cm). All the results with the different injection rates can be found in Table 4.3.8.

In order to analyze the progression of the blocking effect, the core was cut into slides of about 0.5 [cm] by steps and water flooding was performed to measure the permeability at each new length. Four cuts were carried out in total, picture of the different core can be found in Figure 4.3.13. Core permeability measurement were carried out after each cut, results are compiled in Table 4.3.8. Averaged values were calculated using the values in Table 4.3.8 indicated with gray color. When permeability measurement were done when having 6.96 [cm] (0.87 in fraction) a permeability of 0.704 [Darcy] was obtained, this value was compared to the rest averaged permeability values, thus were not consider valid and reliable due to are out of the linear tendency.



Figure 4.3.13 – Core samples 0.5 [cm] each for permeability variance analysis along the porous media.

Core samples in Figure 4.3.13 show a decreasing progression in oil concentration, thus the first 0.5 [cm] contained the majority of oil droplets and a darker color is seen, in the next 0.5 [cm] fate oil saturation profile is perceived and after it the three left faces have a lighter color. (In the picture light effected the actual color of the samples).

In the theory section 2.4.2 emulsion properties were presented, according to experiment executed by McAuliffe (16) emulsions are considered pseudo non-Newtonian fluid that is affected by pressure, thus it was proved that permeability reduction is more effective at lower pressure difference (see

Figure 2.7), due to oil droplets entrapment in porous media is the results of a combination of viscous and capillary forces, the entrapment will occurs if the pressure at the rear of the droplet is equal to the pressure on the back. Therefore permeability reduction increases as the distance from injection increase since pressure difference decreases.

However by this experiment it was possible to confirm that the previous phenomena is valid only if the droplet size is slightly closer in diameter to the pore throat, otherwise a higher injection pressure is required to favor the emulsion displacement. Results for permeability values throughout the core up to 2.1 cm distance from the injection are shown in Table 4.3.8. In this experiment the highest permeability decreasing of 0.324 [Darcy] is observed in the first 0.5 [cm], most likely due to the injection pressure of maximum 30 [bar] was not enough to force the oil droplets to flow because of its size, particularly at an oil concentration of 20000 ppm. In a field operation this situation would lead to injectivity issues and high bottom hole pressure, thus only the oil trapped closer to injection may be produced, affecting the real advantages of an emulsion in the oil recovery.

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Table 4.3.8 - Final Permeability Calculations Through the Core Length.

<u>Experiment Stage</u>	<u>Core Length (cm) / Fraction</u>	<u>Q (ml/min)</u>	<u>Delta Pressure (%)</u>	<u>Delta Pressure (Bar)</u>	<u>Permeability (Darcy)</u>	<u>Average Permeability (Darcy)</u>
3. Final Permeability	8.015 / 1	10	9.15	0.458	0.33	0.324
		10	9.06	0.453	0.33	
		10	9.08	0.454	0.33	
		5	4.63	0.232	0.32	
		5	4.64	0.232	0.32	
		5	4.66	0.233	0.32	
		1	0.94	0.047	0.32	
		1	0.94	0.047	0.32	
		1	0.94	0.047	0.32	
	7.488 / 0.93	10	4.45	0.223	0.63	0.610
		10	4.46	0.223	0.63	
		10	4.48	0.224	0.63	
		5	2.32	0.116	0.60	
		5	2.32	0.116	0.60	
		5	2.33	0.117	0.60	
		1	0.47	0.024	0.60	
		1	0.47	0.024	0.60	
		1	0.47	0.024	0.60	
	6.94 / 0.87	10	3.51	0.176	0.74	0.704
		10	3.53	0.177	0.74	
		10	3.52	0.176	0.74	
		5	1.82	0.091	0.71	
		5	1.82	0.091	0.71	
		5	1.82	0.091	0.71	
		1	0.39	0.020	0.67	
		1	0.40	0.020	0.65	
		1	0.39	0.020	0.67	
	6.43 / 0.80	10	3.82	0.191	0.63	0.610
		10	3.86	0.193	0.62	
		10	3.86	0.193	0.62	
		5	2.04	0.102	0.59	
		5	2.02	0.101	0.60	
		5	2.03	0.102	0.59	
		1	0.42	0.021	0.57	
		1	0.42	0.021	0.57	
		1	0.42	0.021	0.57	

	5.93 / 0.74	10	3.51	0.176	0.63	0.614
		10	3.49	0.175	0.64	
		10	3.51	0.176	0.63	
		5	1.83	0.092	0.61	
		5	1.81	0.091	0.61	
		5	1.83	0.092	0.61	
		1	0.37	0.019	0.60	
		1	0.37	0.019	0.60	
		1	0.37	0.019	0.60	

4.3.3.1 Results Discussion

Permeability reduction values linked to the actual core used in experiment execution is shown in Figure 4.3.14. Observe the emulsion injection trace marked by a darker color in the first section of the core. After the first 0.5 cm there is no evidence of emulsion injection, supported by the permeability calculation with an average 0.6 [Darcy] in the remaining sections of the core.

In conclusion emulsion injection was capable to reduce porous media permeability with a final permeability reduction of 0.324 [Darcy] equivalent to a permeability reduction of 73% in the first 0.5 [cm] is showed in Figure 4.3.15. Therefore a mud cake affected the final permeability result obtained at the end of the emulsion flooding in 0.274 [Darcy], hence an apparent final permeability of 0.05 [Darcy] was calculated equivalent to misleading reduction of 96%. The permeability reduction decreased drastically to 0.6 [Darcy] equivalent to 50% approximately and is maintained through the rest of the core length.

Additionally it is also possible to consider that permeability reduction was partially affected by precipitation formed in the idle time when the experiment valves were closed but emulsion and formation water remain steady inside the porous media. This hypothesis is supported by the continuous reduction of 0.6 [Darcy] in the analyzed length of the core. However the permeability reduction analysis was executed until reaching 5.930 [cm], it is recommended for further studies to analyze the rest of the core that is used in emulsion flooding to evaluate possible variances.

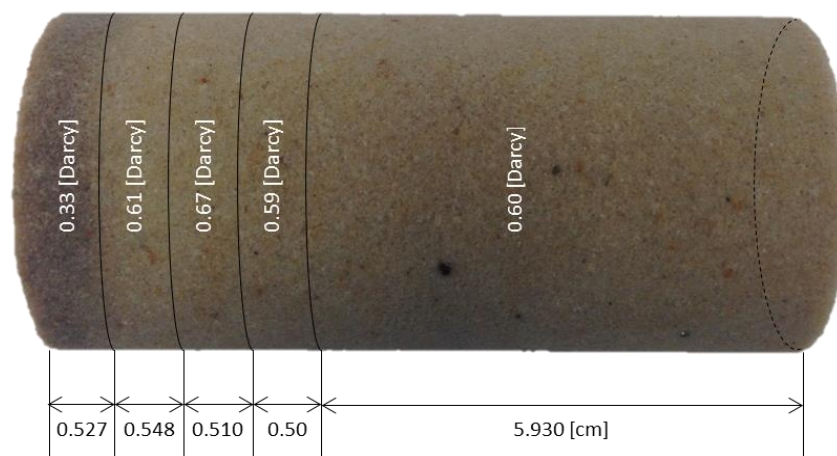


Figure 4.3.14 – Actual core after emulsion flooding, including final permeability results throughout the Core.

Figure 3.3.15 - Permeability Changes After Emulsion Flooding

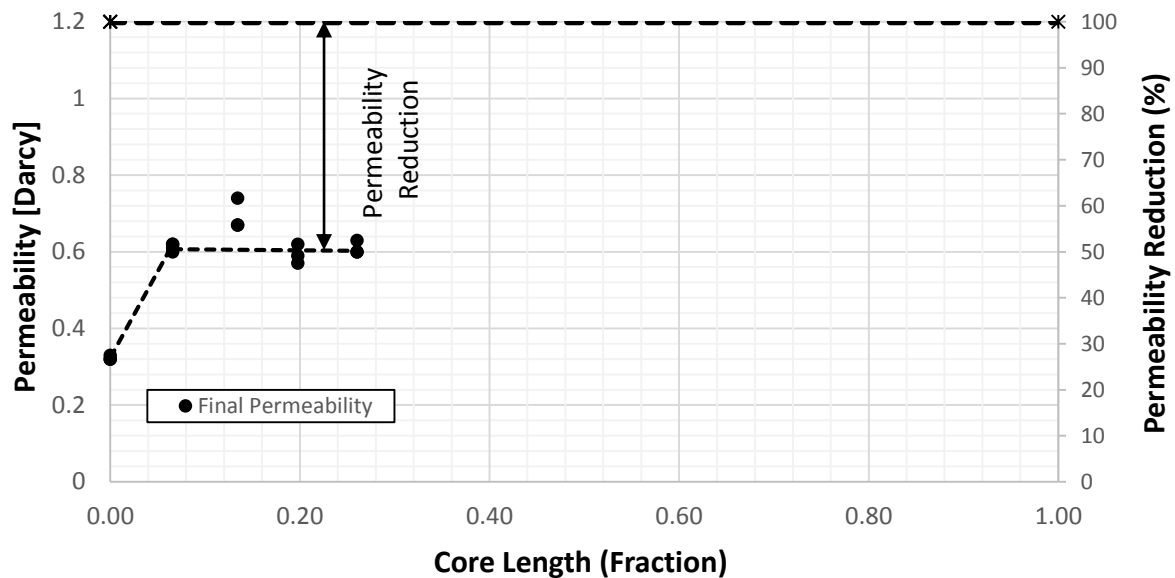


Figure 4.3.15 – Final permeability results throughout the Core.

4.4 Additional Test Suggested for Future Studies

In this study it was determined the suitable ratio of Kaolinite (g)/ oil (ml). However it is recommended to extend the analysis to different types of solid particles such as (9) other clay, quartz, feldspar, gypsum, metal sulfides, metal sulfates, metal oxides, coal dust, asphaltenes or polymers in order to select various candidates that also may also have a water-wet surface to create an oil-in-water emulsion, Bragg (10) suggests a procedure for this selection screening.

On the other hand, in the core flooding experiment was analyzed the final permeability, results indicate a continuous permeability of 0.6 [Darcy] from the 0.5 cm up to 5.930 cm from the front face. However there was a portion of the core that was not analyzed by cuts. It is suggested to carry out the final permeability throughout the whole core, in order to discard precipitation that may affect the permeability reduction, and if not then determine accurately until which point the emulsion effect may be observed.

Additionally before the emulsion flooding, it is recommended to determine the lower limit of the rock permeability, by measuring the differential pressure obtained when flowing emulsions with different ranges of oil droplets size. This procedure will give an indication not only of the lower limit, but also addresses to give an estimation of throat size. Therefore a lower but also a higher limit is determined to avoid the selection of an emulsion that may lead to injectivity problems due to big droplet size.

5 Conclusions

1. Clay solid particles are strongly attracted to the oil-water interface, creating an efficient protection of oil droplets against coalescence. In all prepared emulsion where Bentonite and Kaolinite were used as stabilizer agent there was no indication of free oil at the surface. Once emulsion stabilization is achieved it is less likely to be destroyed. Proving not only that clay particles are adequate to cover oil droplets efficiently, but also that size of clays can be considered small enough to guarantee warranty that even the smallest droplets are covered. This last is important when small pore throat diameter is present in the porous media, since droplets slightly bigger are required to be able to get trapped but small enough to not affect injectivity near to the wellbore.

2. Preparing oil-in-water emulsions stabilized with clay solid particles can be achieved easily with typical lab equipment. However the success in the process requires a great stirring energy, in this study a Silverson mixer was used at 6000 rpm and was enough to obtain an emulsion with small size oil droplets that is essential to allow the clay solid particles to protect adequately and assure stability. Magnetic stirring was also used but is effective only after emulsion stability have been reached with a Silverson mixer (or any other), thus magnetic is only use to apply continuous motion (stirring) and have a homogenous oil concentration in the emulsion while injecting in the core. Otherwise the energy is not enough to create small droplets and the size of droplets would be too big to assure an efficient dispersed phase and cannot be taken as a candidate for core flooding.

3. Oil-in-water emulsion stabilized by solid particles behaves differently than a typical emulsions. The stabilization process is a combination of two phenomena that normally are negative for stabilization but in this case are under control. Creaming and Aggregation (1) between particles were observed in the flotation analysis, however those two never lead to coalescence due to well established protection. Aggregation appears during the steady conditions accompanied by a sort of Creaming effect due to the effect of density difference based on to the amount of clay or oil used. Thus if the ratio between solid particles (g) per oil (ml) is lower than 0.25 [g/ml] (solid particles /oil) the flotation will move towards the surface due to mixture density tend to be closer to oil, otherwise it will sink down to the bottom due to density will shift to solid particles density-like. This density difference applies only when stirring stops and particles move on according to natural buoyancy.

4. When continuous stirring energy is applied and as long as a homogenous oil droplets concentration exists along the water phase, it was proven that emulsion viscosity and density will tend to be closer or similar to the continuous phase (water in this study), as was exposed by McAuliffe's (16) experiments.

5. Solid particles density plays a role in the flotation behavior. Bentonite offers a smooth transition between phases when steady condition, with less free water observed (Figure 4.1.5) compared to their respective for each sample using kaolinite (Figure 4.1.3). Therefore, when steady conditions, a better distribution of the dispersed phase along the continuous phase can be observed when bentonite is used for emulsion stabilization. Nonetheless both Kaolinite and Bentonite offer an effective protection to oil droplets against coalescence.

Additionally bentonite seems to have a smaller size than kaolinite, this was observed by the heavy mud cake formed when equipment cleaning, in all the cases bentonite blocked the filters easily, but also by the size of solid particles suspended, when bentonite was used a homogenous mixture oil-particles was always observed. This characteristic may be useful when a very small oil droplets are required to be fully protected by particles with even smaller size.

6. Lowering the salinity of the external phase decreases the density of the water from 1.06 [g/ml] to 1.005 [g/ml]. This small difference lead to increase the height of the particles-oil column dispersed in the continuous water phase, due to the density difference between both is reduced. Also the more bentonite the higher the column (Compare Sample 1 to 3, and Sample 2 to 4 in Figure 4.1.4). This behavior is more notorious with Bentonite than Kaolinite.
7. Changing the wettability of the solid particles to more oil-wet does not affect the emulsion stability. Therefore if stability is already achieved, either because of oil has the required compounds of asphaltenes or resins or due to the strong attraction of solid particles, then the fact to alter the wettability does not improve the stability. The wettability changing is only required when emulsion is reverted to a water-in-oil emulsion where solid particles with more oil wettability are needed. In this study it only affected the Sample 2 (Figures 4.1.1, 4.1.4, 4.1.6) where oversaturated mixture is presented, the attraction of solids to oil phase is improved then all particles remains with the oil droplets at the top in less time (faster separation), also no accumulation observed at the bottom. Decreasing the salinity seems to diminish the attraction effect.
8. Palmitic acid was added in order to triplicate the Total Acid Number (TAN) in pursuit of improving the emulsion stability, however once stability is achieved by the oil and/or solid particles themselves, acidity change does not affect the behavior or emulsion equilibrium in any way. This is supported by the results showed in Figure 4.1.6 that do not differ from the ones obtained in Experiment 1-Test 2 with TAN 0.10 [mg KOH/g Oil].
9. Emulsion core-flooding is easy to carry out at a lab level. The required equipment can be assembled with typical parts found in any reservoir lab and results obtained are reliable to perform permeability analysis.
10. Determine the initial permeability of the core is essential in order to determine the permeability changes created by emulsion flooding. In this study one core was flooded with three different emulsion with increasing oil concentration at a time. Emulsion with 850 and 4200 ppm required more time to block the porous media than emulsion with 20000 ppm, perhaps with better coverage of the production zone due to the slow motion of oil particles through the core. Being able to perform separate experiments is addressed to assess the desire droplet size and the suitable solid particle required for a particular core. Then executing an individual emulsion flooding (one core for each emulsion) is also strongly suggested.
11. Increasing the oil concentration in the emulsion up to 20000 ppm (maintaining the solid particles/oil ratio) results in a faster blocking of the porous media. Differential pressure exponential increases after 0.5 PV are injected approximately, in contrast lower oil concentration emulsion (852 and 4200 oil ppm) shown a linear behavior indicating slower permeability affectation. Nonetheless the fact that in all the cases no oil droplets were observed at the breakthrough suggests that even with an oil concentration of 852 ppm the oil droplets were trapped and blocking the porous media but since due to low oil concentration it requires more time to see a pressure effect.
12. An apparent permeability reduction from 1.2 [Darcy] to 0.05 [Darcy] equivalent to 96% was observed when emulsion flooding with 20000 ppm oil concentration) finished. However, after core cleaning and mud cake was removed from the injection face, an actual permeability reduction of 0.32 [Darcy] equivalent to 73% was confirmed.

On one hand it is concluded that emulsion injection does work efficiently respect lowering the core heterogeneity by blocking effectively the porous media and decrease up to 73% (in this study) the permeability of the high permeable zone in the core. Additionally solid particles work effectively by

assuring the protection of the oil droplets in the tortuous flow through the porous media, this is important due to oil droplets breaking must be avoid to maintain the permeability reduction and force the water flooding batch to flow through the upswept lower permeable zones.

13. The previous also concludes that increasing the oil concentration in the emulsion to reduce the time of blocking effect must be executed carefully. Because under high oil concentrations more solid particles are required, this can result in injectivity issues closer to the wellbore. As it was possible to see in the Figures 4.3.14 and 4.3.15, the greatest reduction was achieved only in the first 0.5 [cm] of the core and after this point a reduction of 0.6 [Darcy] equivalent to 50% is observed in the rest of the rest of the analyzed length (up to 2.1 cm of the core). This occurred because the penetration of the last emulsion used, containing 20000 ppm of oil, penetrated and got stuck closer to the injection face, probably due to the size of the oil droplets (higher than required) and Test needed to be suspended because exceeded the range of pressure (5 [Bar]). In conclusion at field level high oil concentrated emulsion needs to be monitored carefully due to injectivity issues are likely to occur, thus an efficient permeability blocking along the reservoir is in risk and oil recovery is less likely to satisfy the high expectation for this remarkable technology.

14. The size of droplet particles are less likely to be ensured as the oil concentration in the emulsion increases. In the experiments an oil concentration emulsion with 852 ppm and 4200 ppm shows a smooth penetration in the porous media and a linear (but increasing) differential pressure in the porous media was observed showed a stable flow and blocking. However when emulsion with 20000 ppm oil was injected it got stuck at the front face and pressure difference increased exponentially. Therefore at lab level a Silverson stirring of 6000 rpm cannot assure the appropriated size of the droplet and is possible that the 0.25 g of solid per ml of oil cannot satisfy this level of oil concentration due to calculation was made for 850 ppm in compliance with Norwegian regulation for disposal waters.

15. Emulsion flooding as oil recovery technique is an excellent alternative for re-using the disposal water and lessen the required treatment, saving economical resources for a field exploitation project. In this study an emulsion of 852 ppm oil concentration that comply with the Norwegian regulation for disposal water was used. Obtaining a permeability reduction of 1.1 [Darcy] equivalent of 8.6% when 3.5 PV were injected. This results indicates that this type of emulsion do work as a permeability reduction agent but it requires time to see the effects in pressure measurement, thus 3.5 PV were not enough and probably more pore volumes are required. Also disposal water concentration can be increased up to 4200 ppm (proved in this study) by adding more oil and the needed solid particles and also stable results in pressure difference were observed. Thus disposal waters can be reused in the preparation, with remarkable results.

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