UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

TÍTULO: EFFECT OF LOSAL WATER FLOODING ON W/O EMULSIONS STABILITY

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímico

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A mi querido padre, por su incondicional apoyo en mis decisiones de vida.

Jordy Sarmas Farfan

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Jordy Sarmas Farfan

RESUMEN

El continuo agotamiento de las reservas de crudo y la falta de descubrimiento de nuevos yacimientos han motivado a los países, cuyas economías dependen del petróleo, a implementar técnicas de recuperación mejorada de petróleo (EOR). La inyección de agua de baja salinidad (LoSal) es una técnica EOR que ha ganado gran importancia debido a su gran potencial de uso y a la simpleza de su aplicación. Las investigaciones en este tema atribuyen la acción EOR, mostrada por el LoSal, a diversos mecanismos, relacionados con las interacciones sustrato/crudo/salmuera, incluyendo el flujo de emulsiones. Las emulsiones son útiles en la recuperación mejorada de petróleo debido a que pueden actuar como agentes de control de movilidad que mejoran la eficiencia de los fluidos inyectados. En el presente trabajo, se evaluó la capacidad emulsionante de una muestra representativa de crudo, proveniente de la región amazónica ecuatoriana (Campo Sacha). Para ello, se propuso un conjunto de cinco actividades: a) la primera actividad consistió en comparar el recobro de crudo mediante recuperación secundaria e inyección de agua de baja salinidad a través de simulación computacional con el software Computer Modelling Group (CMG-IMEX); b) las siguientes tres actividades consistieron en evaluar el efecto de la reducción de salinidad, el tipo de catión y la temperatura en la estabilidad de emulsiones mediante pruebas de botella y un aparato de separación de agua y aceite; c) para la última actividad, se utilizó microscopía óptica y el software ImageJ para analizar la morfología de las emulsiones generadas. Los resultados obtenidos en la simulación computacional muestran que el recobro de crudo es mayor mediante la inyección LoSal. Además, experimentalmente, se determinó que las macroemulsiones más estables, con una mejor dispersión de fases, se obtienen mediante la reducción de la salinidad de la fase acuosa o el incremento de la concentración de cationes divalentes, tales como el calcio y el magnesio. Por otra parte, utilizando una adaptación a la norma ASTM D1401, se observó que las bajas temperaturas también conducen a macroemulsiones más estables. Finalmente, se puede concluir que el crudo del Campo Sacha responde positivamente a la inyección de agua de baja salinidad, en términos del fortalecimiento de las emulsiones, y consecuentemente, esta técnica muestra gran potencial de aplicación en procesos de recuperación mejorada locales.

Palabras clave:

LoSal, macroemulsiones, Ecuador, Recuperación Mejorada de Petróleo.

ABSTRACT

The continued depletion of crude oil reservoirs and the lack of new oilfields discoveries have encouraged the countries, whose economies depend on crude oil, to implement enhanced oil recovery (EOR) techniques. Low salinity (LoSal) water flooding is an EOR technique that has gained great importance because of its potential for use and the simplicity of its application. Investigations on this subject attribute the enhanced oil recovery action, shown by low salinity water flooding, to several mechanisms related to substrate/crude/brine interactions, including emulsion flow. Emulsions are useful in enhanced oil recovery because they can act as mobility control agents that improve the efficiency of the injected fluid. In the present work, the emulsifying capacity of a representative sample of an Amazonian-Ecuadorian crude oil, selected from Campo Sacha, was evaluated. A set of five activities was proposed: a) the first activity consisted on contrasting the crude oil recovery during high and low salinity water flooding through a computational simulation in Computer Modelling Group (CMG-IMEX) software; b) the following three activities consisted on evaluating the effect of salinity reduction, cation type and temperature on emulsion stability by using bottle tests and water separability apparatus; c) for the last activity, optical microscopy and software Image J were used for analyzing the morphology of the generated emulsions. Results obtained by computational simulation showed that crude oil recovery is higher during low salinity water flooding than during high salinity water flooding. Experimentally, it was determined that more stable macroemulsions with a better dispersion of phases is accomplished by the reduction of aqueous phase salinity and by the increment of divalent cations concentration, such as calcium and magnesium. On the other side, using the modified ASTM D1401 norm, it was observed that low temperatures also lead to more stable macroemulsions. Finally, it can be concluded that crude oil from Campo Sacha responds positively to low salinity water flooding in terms of emulsions strengthening and consequently, there is potential for local enhanced oil recovery processes application.

Keywords:

LoSal, macroemulsions, Ecuador, Enhanced Oil Recovery.

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Chapter 1: Purpose and significance of the study

1.1 Introduction

Petroleum is nowadays one of the pillars of the world economy. This nonrenewable resource is important because of the vast range of products that derive from it like fuels, polymers and petrochemicals in general. Every year, crude oil is extracted faster than new oilfields discovering emerge. Additionally, not all petroleum in oilfields can be extracted, mainly, because of a lack of suitable and economically viable technology.

Ecuadorian case is not quite different. With proven crude oil reserves of 8.237 billion of barrels in 2017 [1], a half of which cannot be produced through traditional oil recoveries techniques, and a strong economic dependence on this resource, Ecuador also needs to implement Enhanced Oil Recovery (EOR) techniques.

EOR, is a set of technologies that involves the use of fluids, or energy, for increasing the hydrocarbon production from oilfields. [2] Increments in crude oil production during EOR are the result of increments in capillary number, which is the ratio between the viscous and capillary forces, and the action of mobility control agents that improve the sweep efficiencies of injected fluids. [3]

Several EOR techniques are available, whose application and effectiveness will depend on the characteristics of reservoirs, crude oil, among others. Common EOR technologies includes thermal, solvent injection and chemical methods [2]; nevertheless, the use of these technologies can rise considerably the price of crude oil production, forcing its use only when crude oil prices exhibit economical profitability.

Alternative, and less expensive, EOR technologies merely based on the modification of water chemistry have emerged, which have shown successful application both in core flood experiments and oilfield applications. [4,5] One of them is the low salinity (LoSal) water flooding, which consists on injecting water with a low ionic strength. The current knowledge on this technique suggests that, in order to observe EOR, some conditions must be achieved, these include the presence of polar compounds in crude oil, fine clays like kaolinite and illite, initial water with divalent cations and the generation of a salinity shock, that is, a considerable salinity difference between the injected and the formation water. [6]

LoSal water flooding is probably the lowest cost EOR technique, and the one of most immediate application in Amazonian crude oil reservoirs of Ecuador, because of the considerable amounts of fresh water present in that region. When LoSal is used as secondary recovery, it has been reported from tests in sandstones corefloods that, recoveries can be up to 18% of Original Oil in Place (OOIP) higher than secondary recovery using seawater. [7] On the other side, it has been reported from tests in carbonate cores at 110°C, that when LoSal is used as tertiary recovery, it can lead to 2-5 % of recovery of OOIP beyond the secondary recovery with high salinity water. [8] Such numbers are promising by considering that every 1% of OOIP recovery in Ecuador could lead to an additional production of 82 million barrels. With a current price of crude oil barrel of $58.81 [9], it could mean an economic benefit of 4.8 billion of dollars.

In addition, benefits of LoSal water flooding are beyond its EOR action. The reduction of salinity provides other advantages including improvements in flow assurance and compatibility with other EOR technologies, specially the chemical ones.

While encouraging, LoSal water flooding mechanisms of action in EOR are still a subject of speculation and research. There are several mechanisms proposed for explaining this phenomena including, wettability alteration, fine particle migration, increased pH, Multicomponent Ion Exchange (MIE) and emulsions flow. [6,10]

Emulsion flow theory is based on the fact that emulsions can occur during crude oil production because of the coaction of natural surfactants and pumping agitation. According to this theory, if dispersed phase droplets get a similar size, or even higher, than reservoirs pore throats (as macroemulsions), then capillary pressure will trap the droplets creating a sort of “obstruction” that will drive the flow of liquids towards previous unswept zones, improving in this way the mobility control. [10] Pressure response under LoSal water flooding experiments is consistent with that theory, however, this model is valid provided that LoSal water flooding conditions favor the formation and prevalence of emulsions. [10]

The present work evaluates the effect of LoSal water flooding on emulsions stability, which in turn can act as mobility control agents for local EOR processes. The particularity of this work is that the emulsifying capacity of a selected crude oil from Campo Sacha, operated by Petroamazonas EP, in Ecuador and its corresponding formation water have been evaluated under lab-simulated LoSal conditions.

The work in this thesis is presented as follows:

Chapter 2 includes a review of the literature about (i) EOR and its state in Ecuador, (ii) LoSal water flooding, (iii) the use of emulsions as mobility control agents and (iv) the emulsification phenomena.

Chapter 3 details the methodology followed in the experimental set-up. First, a computational simulation was made by using Computer Modeling Group (CMG) software for estimating the crude oil recovery associated to LoSal water flooding and comparing it with secondary recovery. Data considered for this exercise was taken from Abduraman and Kunnas.[11,12] Then, LoSal water flooding effect on emulsion stability was evaluated via bottle tests under simulated lab conditions, the experiments proposed were an adaptation of the work of Wang and Alvarado.[13] Finally, the emulsions generated were analyzed via optical microscopy and the software ImageJ.

Chapter 4 covers the results of the experimental set-up and discussions.

Finally, Chapter 5 includes the conclusions and recommendations of the research.

1.2 Objectives

General:

To probe that LoSal water flooding working conditions enhance the stability of emulsions formed between a sample of Ecuadorian-Amazonian crude oil from Campo Sacha and its corresponding formation water.

Specifics:

- ✓ To compare the secondary oil recovery and LoSal water flooding by using CMG software.
- ✓ To determine the effect of LoSal conditions (salinity shock and divalent cations) on emulsion stability.
- ✓ To evaluate the effect of temperature on emulsion stability.
- ✓ To analyze the morphology of the generated emulsions and its relation to the emulsifying behavior.

2.1 Enhanced Oil Recovery

Crude oil production is categorized as primary, secondary and tertiary. Initially, crude oil remains deep in the reservoirs at elevated pressures and, after drilling, it tends to ascend as a consequence of the pressure difference (primary). With the continuous depletion of the reservoir, the inside pressure diminishes so, fluids like water are injected in order to maintain the internal pressure sufficiently high (secondary). After a certain time, crude oil production decrease and water production increase, even when considerable amounts of crude oil remains in the reservoir. This give rise to tertiary recovery and the enhanced oil recovery methods.

Enhanced oil recovery, EOR, is a set of technologies that involves the use of fluids, or energy, in order to increase the hydrocarbon production from oilfields above the traditional techniques. [2] The objective of EOR methods are to reduce the capillary and interfacial forces for improving the displacement efficiency, or to improve the sweep efficiency by reducing the mobility ratio between the displacing and the displaced fluid. [3] Commonly, EOR has been associated with tertiary recovery but it can also be present at any production stage. [2]

EOR methods can be classified as thermal, chemical and miscible or solvent injection.

Thermal: Thermal methods are applicable to heavy oils and deal with processes of injection, or *in-situ* generation, of thermal energy for increasing the temperature of the oil and reduce its viscosity. [14] Thermal methods includes steam injection, steam flooding, Steam Assisted Gravity Drainage (SAGD), air injection, in-situ combustion and others. [2] The most popular thermal methods are: steam injection, with ongoing projects in heavy oil sandstones reservoirs of Canada, Venezuela, California, Indonesia, Russia and Oman, and in-situ combustion, with projects in heavy oil sandstone reservoirs in Canada, US, India and Romania. [14]

Chemical: The objective of chemical methods is to increase the capillary number, which is the ratio between the viscous and the capillary forces (Eq1), this is possible through an increment of water viscosity, with polymers, and a reduction of interfacial tensions, with alkali and surfactants. It includes surfactant-polymer (SP) flooding and alkali-surfactant-polymer (ASP) flooding. [2] The most successful cases of chemical EOR, specially polymer flooding, have been reported in China, and based on this success, other countries like Oman, Canada, USA, India, Argentina, Brazil, Austria and Argentina have developed similar projects. [14]

$$N_c = \frac{\mu V}{\sigma} \qquad \text{(Eq1)}$$

Where:

N_c: capillary number

μ: dynamic viscosity of the liquid

V: characteristic velocity

σ: interfacial tension

Solvent injection: It is based on the miscibility of the injected fluid with the oil phase and it involves the use of hydrocarbon miscible fluids, carbon dioxide and nitrogen & flue gas. [2] The injection of CO_2 is the most popular EOR method in this group. There are around 100 commercial CO_2-EOR projects, mainly concentrated in Texas and Canada. This EOR method is applicable for light oil in both sandstones and carbonate reservoirs. Hydrocarbon gases are other solvents used for light oil reservoirs, which are used in EOR projects of Alaska, Canada, Libya and Venezuela. The success of such projects is dependent on the availability of solvent sources near the reservoirs. [14]

In addition to traditional classification, it can also be considered the EOR methods by using a chemistry-controlled water. This is the case of low salinity water flooding, whose degree of novelty and benefits has made of it an interest topic in research and field tests.

2.1.1 State of EOR in Ecuador

In Ecuador, Ministry of Natural Non Renewable Resources is the government entity responsible for policy decisions about hydrocarbons. Whereas that, crude oil production in Ecuador is distributed between the National Oil Company, Petroamazonas EP, and private companies. In 2018, the total crude oil production was 188.8 million of barrels, at a rate of 517 200 barrels per day, of which 146.35 million were produced by Petroamazonas EP [15]. Proven crude oil reserves in Ecuador are 8.237 billion of barrels at 2017 [1], located mostly in Amazon region (See Fig 1).

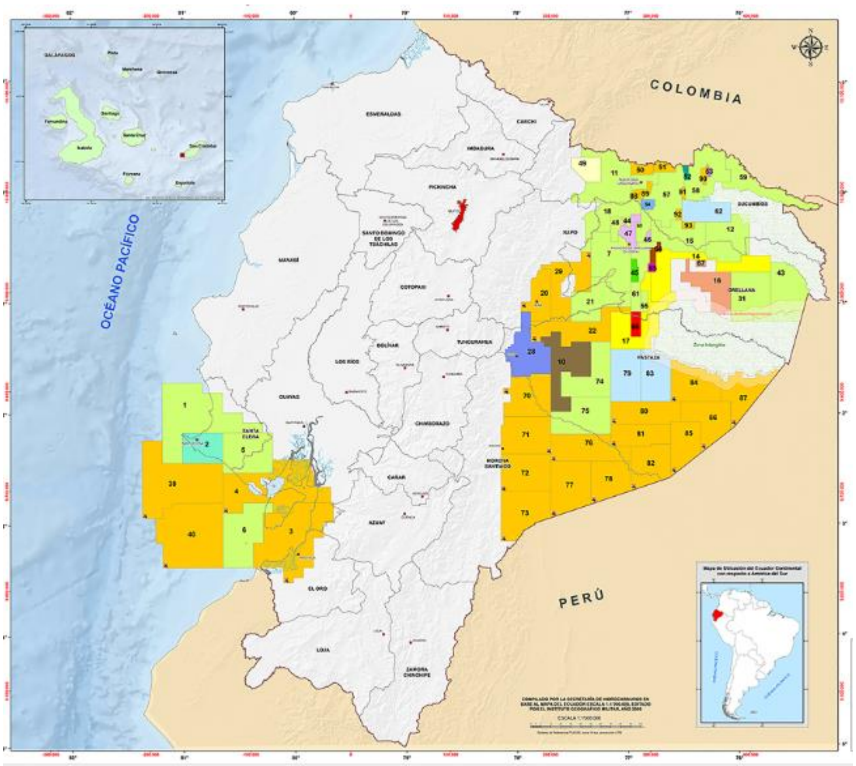
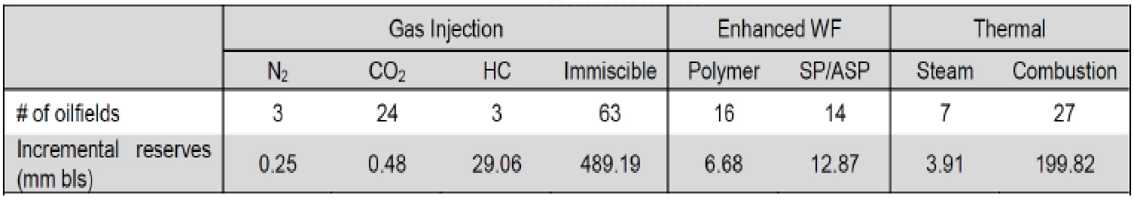


Fig1._ Location of reservoirs in Ecuador.

Amazon region of Ecuador has been exploited over the forty last years, during this period light and medium oil has been extracted, leaving remnant heavy and extra heavy oil in the mature oilfields, whose extraction could require complex technology with environmental precaution because these reserves are located in sensible areas, whose perturbation would attract the objection of ecofriendly communities and media. [16]

Authors like Condor have worked on EOR screening in Ecuador. After reviewing 410 reservoirs distributed in 150 oilfields, it was concluded that an incremental of 700-750 million barrels is possible if the application of EOR methods are optimized (See Tab1). [16]



	Gas Injection				Enhanced WF		Thermal	
	N_2	CO_2	HC	Immiscible	Polymer	SP/ASP	Steam	Combustion
# of oilfields	3	24	3	63	16	14	7	27
Incremental reserves (mm bls)	0.25	0.48	29.06	489.19	6.68	12.87	3.91	199.82

Tab1._ EOR potential in Ecuador. [16]

According to this approach, the most convenient EOR methods are miscible injection and in-situ combustion. Nevertheless, due to the reservoir characteristics, the most applicable EOR methods is miscible gas flooding followed by chemical methods, where the latter ones could lead to a considerable increase in the production, around 1 million in some non-producing oilfields and up to 5 million barrels in producing oilfields. [16]

Other authors like Andrade and Ayala made comparison between different EOR methods in the field MR located in the Cuenca Oriente, concluding that the best alternative is a chemical method (polymer flooding) due to: (i) the high water production in this zone that can be modified and reinjected, (ii) the fewer operational problems and (iii) the higher crude oil recovery. [17]

Also, the technical feasibility of aqueous based EOR application, such as water of controlled salinity flooding, has been reported by Ziritt and Vera, who contrasted the conditions of reservoirs where this technique was successful with the Ecuadorian ones, leading to the conclusion that some reservoirs of Cuenca Oriente in Ecuador compliance with many of the conditions for the application of this technology, such as the connate water, the concentration of divalent cations, kaolinite clay and adequate salinity and temperature. [18]

Finally, it must be pointed out that EOR methods are relatively new in Ecuador and that, the research, development and demonstration of new technologies in this topic are still on initial stages.

2.2 Low Salinity water flooding

Main methods for EOR depends on water because it is used as a carrier fluid for additives. Although, in the last decades, several laboratory experiments and field tests have given water, with an optimum composition, a significant role in EOR processes. [19]

Low salinity (LoSal) water flooding is an EOR technique consisting on the injection of water having a lower salinity than the preceding one in the oilfields.

Injection of water of low salinity has been implemented (in secondary recovery) since many decades ago because of its wide availability and low cost application. However, the EOR potential of this technique was not recognized until Morrow and co-workers, at the beginning of the 1990s, related incrementals of oil recoveries with the composition of water. Since then, several coreflood tests, simulations and field applications have been developed with a successful additional oil recovery in most of them. [20]

The use of water for crude oil production is attractive and has some advantages over other EOR techniques [14], to mention some:

- It can be applied at any stage of production cycle.
- It requires minimal investment (provided the availability of infrastructure for water flooding). Other EOR methods requires investment for infrastructure and injection facilities, changes in tubing and casing, among others.
- The payback is faster even when small amount of additional oil recovery.
- The injection of a low salinity water improve the flow assurance because of the reduction of scale formation and acidification of currents.
- It is compatible with other EOR methods, specially the chemical ones.

2.2.1 Working conditions

Many studies have reported that the following working conditions are necessary for observing the LoSal effect: (i) the presence of clays, (ii) the presence of polar components in crude oil, (iii) the presence of initial or connate water, (iv) the presence of divalent ions in the initial water and (v) a considerable difference between the salinity of the injected and the preceding water. [20]

2.2.2 Mechanisms

In the literature, at least seventeen mechanisms have been related to LoSal effect, and most of them are related to each other, so this section enlist only the major ones.

Wettability alteration: It is the most common suggested mechanism. Drummond and Israelachvili (2002) showed that at pH higher than 9, wettability changes from oil wet to water wet, but at pH below 9, which is the most usual pH range during LoSal, wettability changes towards intermediate-wet (See Fig2). It looks promising considering that mixed-wet cores show lower residual oil saturation, or higher oil recovery than strong water-wet or oil wet cores. [20]

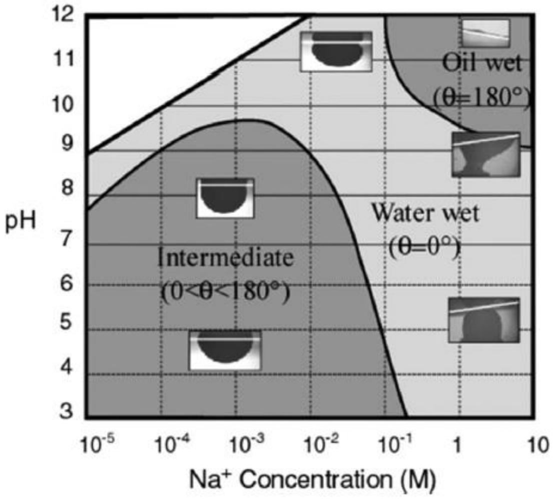


Fig2._ Wettability as a function of pH and salt concentration. [20]

Particle release theory: It has been used for explaining additional oil recovery provided clays existence. According to this theory, if the ionic strength of the injected brine is lower than a critical flocculation concentration that depends on divalent cations, the Electrical Double Layer (EDL) between clays is expanded, and as a consequence, particles get detached from the walls. Once dispersed, clays particles flow with water along high permeability zones and become lodged in the smaller pores, then the formation permeability is reduced and the sweep efficiency is improved. The permeability reduction phenomena has been associated to different processes namely: migration, in which the release and flow of clays causes the pore blockage; swelling, in which the swelling of clays reduce the cross sectional area for flow; and swelling induced migration, that is a combination of the previous processes (See Fig3). [6]

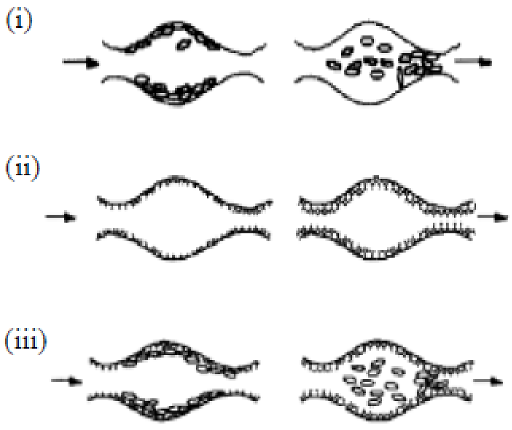
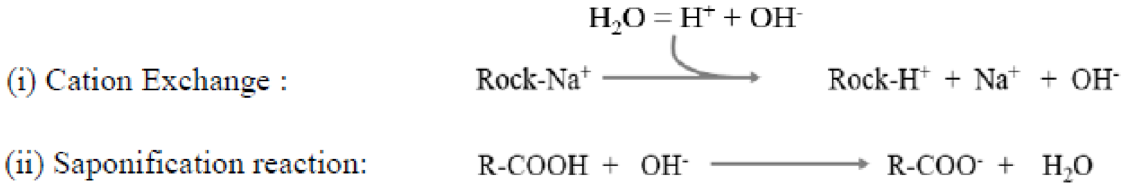


Fig3._ Damage in sandstones containing swelling and non-swelling clays. (i) migration, (ii) swelling, (iii) swelling induced migration. [6]

Increased pH theory: During LoSal water flooding, it is normal an increment in the pH as a consequence of an exchange of Na^+ at the rock surface and H^+ from injected water. The resulting water can act in a similar way to alkaline-flooding, reacting with carboxylic acids and generating *in situ* saponification (See Fig4). [6]



(i) Cation Exchange :

$$\text{Rock-Na}^+ \xrightarrow{H_2O = H^+ + OH^-} \text{Rock-H}^+ + Na^+ + OH^-$$

(ii) Saponification reaction:

$$\text{R-COOH} + OH^- \longrightarrow \text{R-COO}^- + H_2O$$

Fig4._ Mechanisms showing how a LoSal water flooding could derive in an alkaline flooding to promote saponification. [6]

The generated surfactants can reduce the oil and water interfacial tensions, promote the formation of emulsions and hence increase oil recovery. However, this theory is the less probable because pH must be greater than 9 for generating soaps, which is not usual during LoSal water flooding. [6,20]

Multicomponent Ion Exchange (MIE) theory: Divalent cations, such as $Ca^{2+}$and Mg^{2+} at clay surfaces, tend to bind to polar components of crude oil (resins and asphaltenes) forming organometallic complexes and promoting oil wetness on rock surface. Also, organic polar compounds are able to bind directly to rock surface. During LoSal, MIE occurs removing organic polar compounds and organometallic complexes from the surface and replacing them with uncomplexed cations. Several mechanisms have been proposed for explaining this phenomena, but just these related with cation exchange, cation bridging, ligand bridging and water bridging are relevant to the LoSal action (See Fig5). [6]

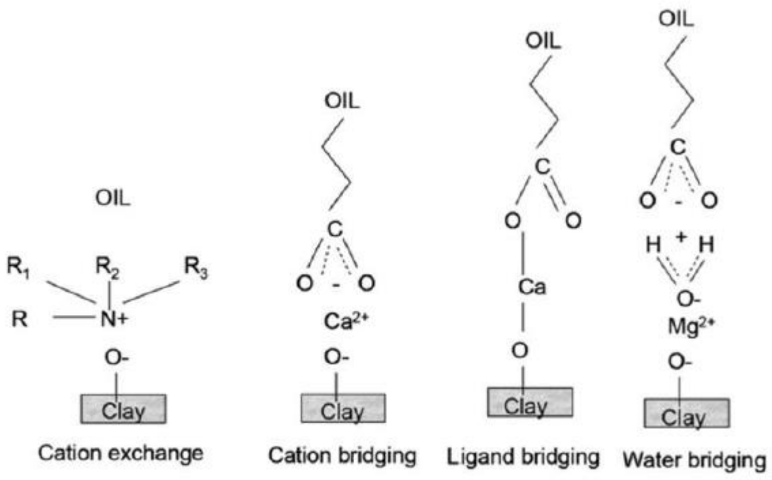


Fig5._ Adsorption mechanisms of crude oil and clays surfaces, directly and via cation. [6]

Flow of in-situ emulsions: The low ionic strength generated during LoSal water flooding can produce more stable emulsions, which in turn can improve mobility ratio between the displacing and the displaced fluid. [10] Emulsions can occur naturally in oilfield operations because of natural surfactants of crude oil, fine solids in the reservoir such as kaolinite, and shear rate provoked by pumping systems. In Fig6, there is a representation of how Water in Oil (W/O) emulsions can improve mobility control. Once W/O emulsions are created, if the water droplets are of an equal or larger size than pore throats, then, capillary pressure could trap the dispersed phase droplets, blocking later displacements and forcing water to flow towards other unswept areas of the porous medium. This mechanisms could provoke a similar effect than particle release but differs in that emulsion flow does not imply a permanent formation damage. [10]

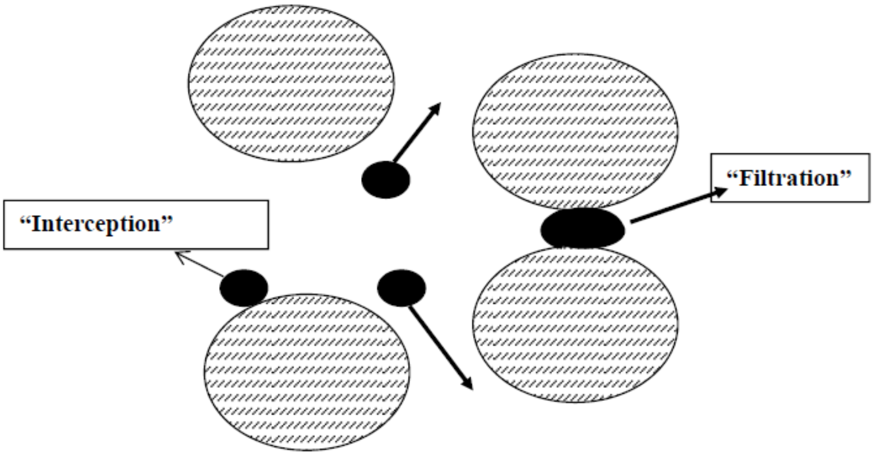


Fig 6._ Schematic representation of EOR mechanism by flow of in-situ emulsions, where black circles represent water. [10]

In the present work, it has been hypothesized that the last mechanism is the one explaining the EOR action of LoSal water flooding. Hence, the following section provides detailed information about how emulsions can act as mobility control agents, which in turn conduct to increments in oil recovery.

2.3 Emulsions as mobility control agents

Mobility control agents are methods for improving mobility ratio, which is defined as the ratio between the mobility of the displacing fluid over the mobility of the displaced fluid. During displacement, mobility ratios lower than 1 are associated with a good swept and therefore, considered favorable; whereas that, mobility ratios greater than 1 propitiate the formation of viscous fingering and a consequent poor oil recovery. [21]

Usually, chemical methods are used to improve the mobility control. Polymer flooding consists on the addition of polymers to the displacing fluid for increasing its viscosity and reducing the mobility ratio. [21] Polymer flooding is a convenient EOR technique for light and intermediate crude oil [22], but this becomes economically unviable for heavy crude oils. Alkali and surfactant floodings are better options for EOR of heavy crude oils, both consisting on the *in situ* generation of emulsions that could drive the flow of crude oil. [23] However, the requirements of chemicals limits the use of these techniques by economic reasons too.

Another technique to increase the sweep efficiency is the use of water and oil emulsions. McAuliffe reported that the injection of emulsions can improve the sweep efficiency in sandstone cores by increasing the heterogeneity of the fluids flow. [24] French, Lorenz and Bertus carried out experiments with externally and in-situ generated emulsions, obtaining reductions in effective permeability in both cases, but with a lower reduction in the case of in-situ generated emulsions. [25]

The mechanism suggested for explaining the additional oil recovery in emulsion flooding is the entrainment and entrapment. The former one consists on the emulsification of crude oil by lowering the interfacial tensions, and the entraining of the resulting emulsion as a continuous phase. [26] And the entrapment is based on the fact that dispersed phase droplets are not small enough to penetrate all pores, occurring entrapments between sand grains, which cause a reduction of water mobility and an increase on sweep efficiency (See Fig 7). [24]

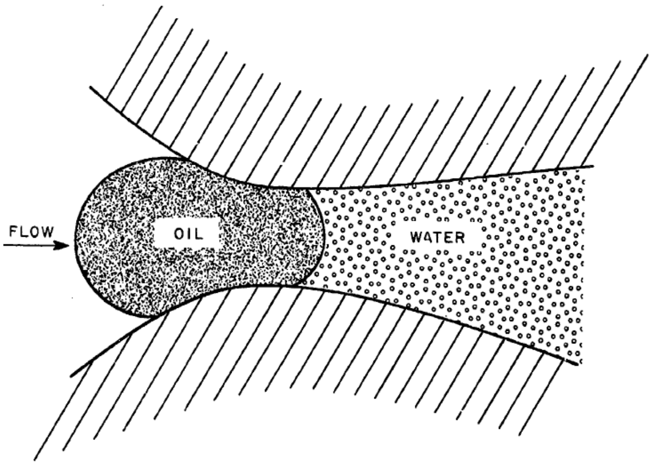


Fig 7._ Schematic representation of a pore throat being blocked by an oil droplet. [25]

As can be seen in Fig 9, not all emulsions are useful as mobility control agents. Dispersed phase drops in emulsions must have an adequate size. The size of the droplets depends on factors such as the type of crude oil, type of emulsifier, flow rate, composition of continuous phase and interfacial properties. [27] For entrapment to occur, drops must be slightly larger than the pore-throat constriction in the porous media. [24] If drops are too small, then they could not act as effective plugs. On the other hand, if drops are too big, their instability would conduct them to experience one of the demulsification steps. [25] For that reason, macroemulsions, whose droplets have a diameter between 1 and 100 μm, are useful mobility control agents. [25]

Emulsion stability is another parameter to take into account, since unstable emulsions allow dispersed droplets to coalesce, and the consequent separation of phases; while more stable emulsions are capable of experiencing entrainment and entrapment mechanisms. [28]

The following section describes the emulsification and demulsification phenomena in an attempt to define the environmental variables and processes that influence the prevalence of emulsions in crude oil reservoirs.

2.4 Emulsification phenomena

2.4.1 Emulsions formation

An emulsion is a system formed by two incompatible phases, one of which (dispersed or internal phase) is immersed within the other (continuous or external phase), whose structure is stabilized by a surface active agent called emulsifier or surfactant. The relative proportions between dispersed and continuous phase can influence the properties of emulsions, and constitute a parameter that can be used to classify them. [29]

Crude Oil produced from reservoirs tends to form natural emulsions with formation or injection water because of mechanical agitation and the presence of emulsifiers. [30] If an emulsion contains drops of water (W) dispersed in oil (O), it is called a water in oil emulsion (W/O) or reverse emulsion. In the other side, if an emulsion contains drops of oil (O) dispersed in water (W), it is an oil in water emulsion (O/W) or normal emulsion. More complex cases are also possible, for example, when small droplets of water are within oil, and in turn, the oil is within a continuous phase of water, it is considered a W/O/W emulsion. See Fig8.

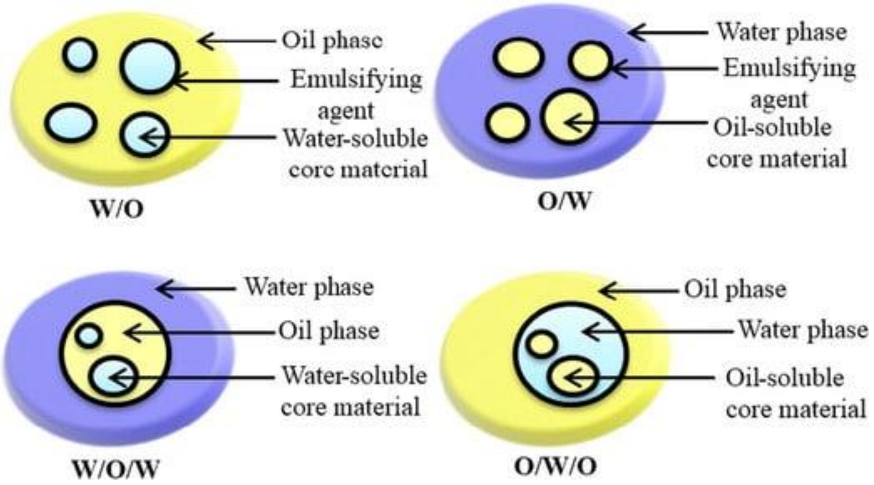


Fig8._ Different types of emulsions. Up, reverse and normal emulsions. Down, complex emulsions.

Crude oil is evidently not soluble in water and the opposite case is also true. Nevertheless, both substances are capable of forming emulsions when the proper conditions are generated. In order to form an emulsion, three requisites are necessary:

- two immiscible liquids;
- agitation for dispersing one phase into another

- emulsifying agents for stabilizing the droplets of dispersed phase within the continuous phase

During petroleum exploitation, especially in secondary and tertiary recovery, all three requisites can be present. Crude oil and water constitute the two immiscible liquids; the agitation comes from pumps and processes of liquid injection; and the emulsifying agents occurs natural in the components of crude oil or can be generated *in situ.* [30]

Emulsifying agents are substances that concentrate at the interface of two immiscible liquids, such as crude oil and water, decrease the interfacial tension between phases and form a film around dispersed phase drops that prevents their coalescence. [30]

There are several emulsifying agents that can be classified in the following manner [30]:

- Natural surfactants, which are macromolecules with interfacial activity formed from the acidic components of asphaltenes, resins, naphthenic acids and porphyrin.
- Finely divided solids or colloids that are capable of forming a physical barrier between phases, as long as they are smaller than dispersed phase drops and capable of being wetted by both phases. Colloids include sand, clay, minerals, residues of corrosion, paraffin, precipitated asphaltenes, and so on.
- Chemicals added during production, whose purpose is to handle problems associated with oil production. It includes corrosion inhibitors, biocides, surfactants and humectant agents.

2.4.2 Stabilization of emulsions

There are three main interaction energies between emulsion drops and also, there are many factors that contribute to the stability of emulsions.

2.4.2.1 Forces between dispersed phase drops

Interaction energies between drops can be attractive (Van der Waals) and repulsive (steric and electrostatic). [31]

The most important Van der Waals attractions in emulsions are the London dispersion forces that arise from charge fluctuations. Dipoles can be instantaneously generated as a result of a charge difference within a molecule, and this temporary dipole induces other dipoles on surrounding molecules. London dispersion forces between molecules, in macroscopic bodies like emulsions, are additive and can result in Van Der Waal attractions that get strong at close distance separation between droplets (See Fig9).

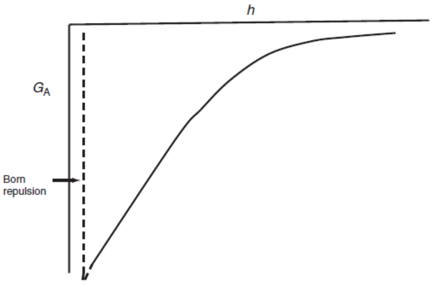


Fig9._ G_A (Van Der Waal attraction energy) as a function of h (distance separation between droplets). [31]

It can be seen that in absence of repulsion agents, such as emulsifiers, flocculation can occurs quickly. Thus in emulsions, in order to counteract this attraction, repulsive forces are necessary.

When charged particles in an emulsion approach each other such that their double layers overlap, repulsion occurs. The extension of the double layer depends on the electrolyte concentration and its valence, in such a way that, a decrease in concentration and a low valence will produce a more extended double layer and a higher repulsion.

A schematic representation of the force – distance curve according to DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek) is shown in Fig. 10, which shows that the sum of Van der Waals attraction and electrostatic repulsions form a primary and a secondary energetic minimum associated with considerable and weak flocculation, respectively, and a maximum that prevents the close approach of the droplets.

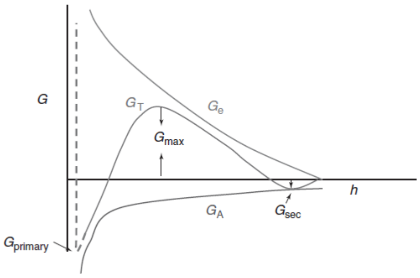


Fig 10._ Representation of interaction energy vs separation distance according to DLVO theory.

Finally, steric repulsions are produced because of the adsorption of nonionic surfactants and polymers at the liquids interface. The thickness of hydrophilic chains produce repulsion as a result of an unfavorable mixing of the chains, G_{mix}, and a volume restriction or elastic interaction, G_{el} . The combination of G_{mix} , G_{el} and G_A gives the total energy according to the theory of steric stabilization. See Fig11.

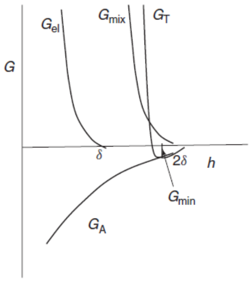


Fig 11._ Representation of energy – distance curve according to the theory of steric stabilization, where small G_{min} values are associated with thermodynamic stability.

2.4.2.2 Factors and properties influencing the stability of emulsions

Emulsion breakage depends on the following factors [30]:

*Interfacial tension and the type of crude oil.*_ Low interfacial tensions are usually related with stable emulsions. Some components of crude oil such as resins, asphaltenes, and other natural emulsifiers can decrease the interfacial tension between crude oil and water, forming stable emulsions.

*Viscosity of phases.*_ A high viscosity of continuous phase makes difficult the approaching of dispersed phase droplets, so making emulsions more stable.

*Density difference of phases.*_ A decrease in the rate of sedimentation is made by decreasing the density difference between phases, making emulsions more stable.

*Volume phase ratio.*_ Decreasing the dispersed phase volume, the distance between drops is increased and the probability of collision between them is decreased too, so emulsion stability gets increased.

*Droplet size.*_ Small droplets, with a narrow size distribution, are related with stable emulsions.

*Interface ageing.*_ With the passage of time, the film between interphase, produced by adsorption of natural surfactants, becomes thicker and more rigid. Film in the interphase can also enlarge with the successive formation of emulsifiers in process of photolysis, oxidation and so on, producing more stable emulsions.

Temperature._ An increase of temperature produce less stable emulsions, whether from reduction of rigidity of: interfacial film, adsorption of natural surfactants or viscosity of continuous phase.

Composition of brine._ Low-salinity brine is related with stable emulsions. Additionally, the presence of divalent cations, like calcium and magnesium, can compact the films at the interface producing more stable emulsions.

2.4.3 Emulsion breakdown

Demulsification, the separation of emulsions into their components, involves three steps: sedimentation or creaming, flocculation and coalescence (See Fig12). [10]

Sedimentation occurs in W/O emulsions when water droplets settle down because of their higher density than crude oil. Gravitational sedimentation is governed by Stokes' law (Eq2), which allows to calculate the settling velocity, v, for a solid sphere with a small Reynolds number in a viscous fluid, without taking into account the presence of emulsifying agents and the coaction of other demulsification stages.

$$v = \frac{g\, d^2(\rho_w - \rho_o)}{18\, \mu_o} \qquad \text{(Eq2)}$$

Where:

v: settling velocity (cm/s)

g: gravity acceleration (cm/s^2)

d: droplet diameter (cm)

ρ_w: droplet density (g/cm^3)

ρ_o: continuous phase density (g/cm^3)

μ_o: continuous phase viscosity (P)

On the other hand, creaming is an analogous process to sedimentation that occurs in O/W emulsions when oil droplets arise as a result of their lower density than water continuous phase.

Flocculation, or aggregation, is sometimes the first stage in emulsion breakage. During flocculation, dispersed phase drops tends to clump together forming aggregates. At this point, drops are close to each other, even joined at some points, but do not lose their identity.

During coalescence, droplets of dispersed phase join together in order to form bigger drops. This process is irreversible, leading to a decrease in the number of droplets. Finally, the phase separation occurs with the correspondent emulsion breakdown.

Unresolved emulsion droplets tend to accumulate at interface and form an emulsion pad, which is undesirable because it can slow the normal demulsification process, increase the residual oil in the treated water and increase the Basic Sediment and Water (BS&W) of the treated oil, among others.

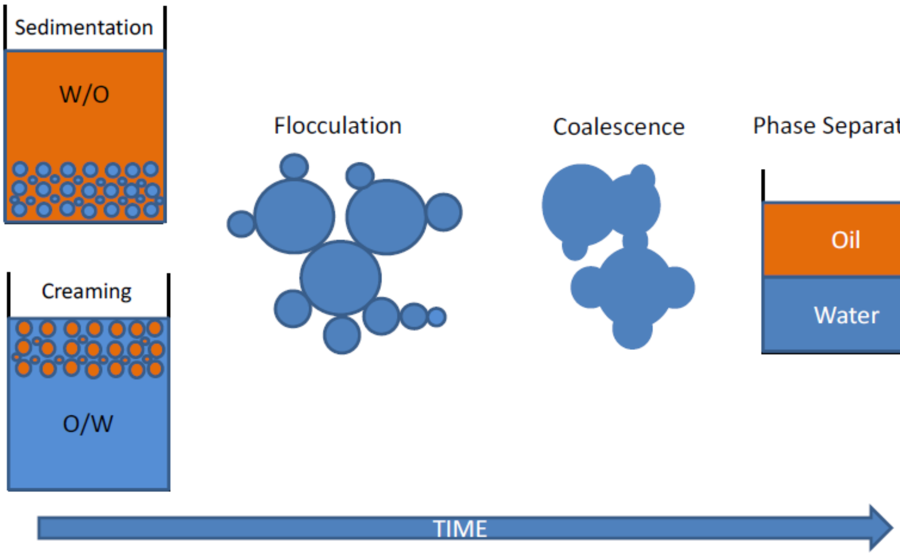


Fig12._ Scheme of demulsification stages for a W/O emulsion. [10]

2.4.4 Measurement of emulsion stability

Emulsion stability refers to the capability of emulsions to resist changes over time. Stability of emulsions is influenced by the constituents of the phases and the formation conditions. Some properties of the droplets can be used to evaluate emulsion stability such as concentration, size, charge, rheology, among others. [32]

Visual observation can provide the first method to evaluate emulsion stability, however, this technique can be used just to monitor gravitational separation such as sedimentation phenomena because of the limitations of human eyes. Other phenomena like flocculation and coalescence can be successfully measured by other instrumental methods such as microscopy, particle size analysis, charge analysis and rheology. [32]

2.4.4.1 Optical Microscopy

Microscopy is based on the study of objects that, because of its reduced size, cannot be analyzed directly by visual inspection. Images generated by a microscope can be several orders of magnitude larger than the original object.

Several types of microscopes, including optical, electron, atomic force and confocal fluorescent microcopy can be used to monitor emulsions, but for the objectives proposed in this work, optical microscope is enough.

Using microscopy, it is possible to see and measure the size and size distribution of drops, and so obtain information about emulsion stability and characteristics. Flocculation can be noticed when equally-sized droplets get closer each other without forming new ones. While on the other side, a non-flocculated emulsion will show homogenously distributed droplets of small size. [32]

Even when microscopy is a simple, intuitive, fast and cheap technique, the subjectivity of the results make necessary the use of additional analytical sources.

2.4.4.2 Bottle tests

Phase separation methods are based on measuring the amount of resolved phase from emulsions, either naturally or by external forcing. According to this technique, the smaller the dispersed phase resolved volume, the more stable the emulsion is. [10]

Even when this technique provides a simple tool for measuring emulsions stability, the demulsification process is studied as a whole, that is, it is not possible to discriminate the occurrence of different demulsification steps. Also, this technique is not adequate for tight-stiff emulsions or emulsions with a not sharply defined interface. [10]

2.4.4.3 Light scattering

Particle size, particle size distribution (PSD) and particles concentration in an emulsion can be measured by light scattering techniques. Based on the operating principle, there are two types of light scattering, static (SLS) and dynamic (DLS).

In SLS, a monochromatic light beam, typically a laser, is used to irradiate the sample and a photon detector records the light intensity at different angles (See Fig13). SLS can be used to measure weight average molecular weights and radius of gyration of macromolecules in the range of 100 nm to 1 000 μm. [32]

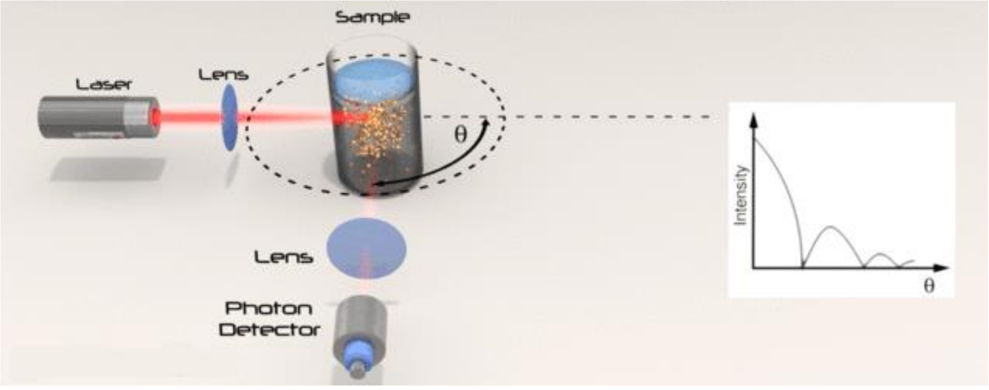


Fig 13._ Schematic representation of an SLS operating principle.

In DLS, a laser beam is used to irradiate a sample and the fluctuating intensity of scattered light is recorded, at a certain scattering angle, as a function of time (See Fig14). By using DLS, it is possible to measure particles sizes from 3 nm to 5 µm, making it useful for emulsion and colloids analysis.

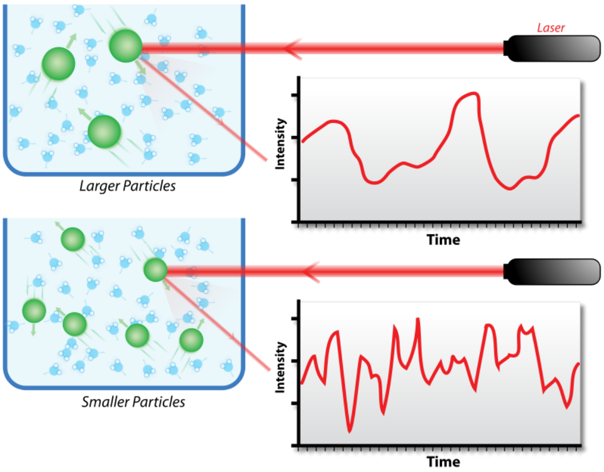


Fig 14._ Schematic representation of DLS operating principle

Both light scattering techniques provide information about concentration and size of the particles thanks to the percentage and angle of backscattered light. A larger percent of backscattered light indicates a higher concentration, while the particles size depends on the scattering pattern. [32]

In Stoke’s law (Eq 1), it is evident that the size of dispersed phase droplets influences the stability of emulsions. Small and homogeneously distributed droplets are associated with a stable emulsion. Therefore, emulsion stability can be measured by light scattering through measurement of droplets size. Additionally, light scattering technique can be used to detect the presence of gravitational processes of demulsification, sedimentation, through measurement of droplets concentration at different sample heights (See Fig 15).

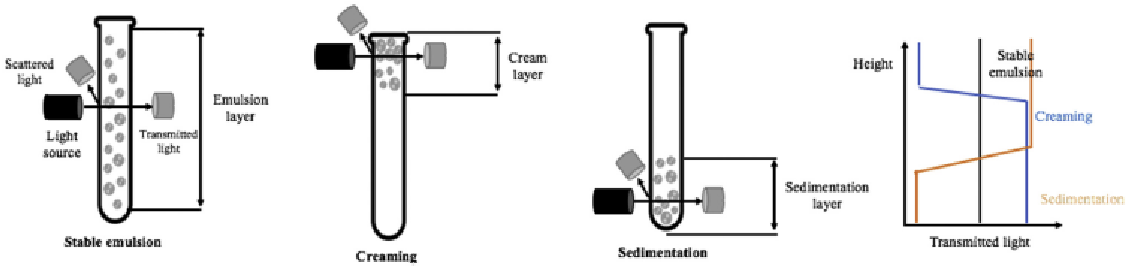


Fig 15._ Representation of how light scattering methods can be used to detect sedimentation processes. [10]

2.4.4.4 Microelectrophoresis

Microelectrophoretic techniques are based on the fact that droplets surfaces exhibit electrical charges. A sample of emulsion is placed in a cell and an electrical field, generated by a pair of electrodes, cause charged particles to move towards oppositely charged electrodes. Therefore, the direction and velocity of the charged particles can offer information about the sign and magnitude of the charges (See Fig16). This technique is used in conjunction with light scattering to monitor the movement of dispersed phase droplets, so emulsions must be diluted (<0.1 %) in order to avoid multiple scattering. [32]

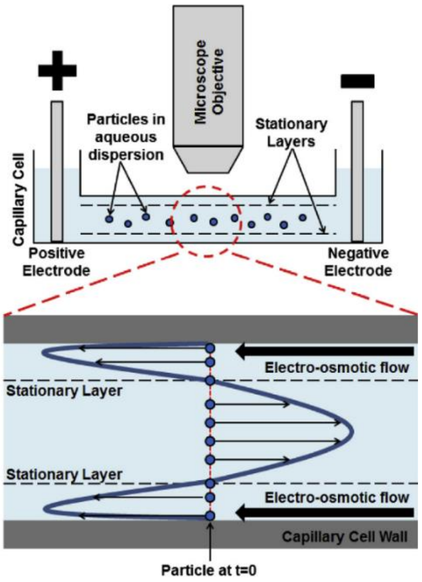


Fig 16._ Scheme of a microelectrophoresis in a capillary cell. Part of the capillary was magnified in order to show the flow velocity profile of particles under electrical field.

A set of five activities was planned for the development of the methodology. The first activity was proposed in order to demonstrate that the increments in crude oil recovery by the implementation of LoSal technology are important. The following two activities were made to probe that LoSal water flooding working conditions, such as salinity shock and divalent cations, affect emulsion stability. Other activity was made for evaluating the effect of temperature on emulsion stability, since conditions at reservoirs can be harsh. Finally, the last activity was oriented to the observation of emulsions morphology for evaluating if the emulsions could experiencing entrapment in porous media in terms of their dispersed phase drops sizes. Table 1 summarizes the activities developed in this chapter.

Activity	Description
1) Computational simulation of crude oil production under secondary recovery and LoSal water flooding	Computer Modelling Group (CMG-IMEX) software was used to compare crude oil production between secondary recovery and LoSal water flooding for a defined situation
2) Evaluation of salinity shock on emulsion stability	Bottle tests were used to determine how the reductions in water salinity influence emulsion stability
3) Evaluation of monovalent and divalent cations in emulsion stability	Bottle tests were used to determine how the cation type influence emulsion stability
4) Evaluation of temperature on emulsion stability	Bottle tests and thermal baths were used to determine how the temperature influence emulsion stability
5) Analysis of emulsion morphology	Optical microscope and Software Image J (developed by the National Institute of Health, USA) were used to take micrographs and calculate the drop size distribution of generated emulsions

Table 1._ Chronogram and description of activities.

The sample of crude oil used was taken on February 24 of 2019 by engineers Bryan Bravo and Patricio Llerena, both from Overtech, under the supervision of the engineer Dixon Taboada, Operation Superintendent of PETROAMAZON EP. The sample site was the Lease Automatic Custody Transfer (LACT) Unit in PETROAMAZONAS EP Central Sacha Oil Field. This LACT unit measures the oil properties for export (API, BS & W), in the case these are not met, the load is automatically returned to the storage tank. Sampling was taken in this unit because it is representative of the whole field as advised by Overtech and Petroamazonas EP engineers.

3.1 Computational simulation of crude oil production under secondary recovery and LoSal water flooding

1. Software: Computer Modelling Group (CMG-IMEX)

2. Procedure:

For simulating LoSal water flooding, the CMG-IMEX software for simulating primary and secondary oil recoveries in conventional and unconventional reservoirs was used. In order to carry out this activity, it was necessary to define: (a) the reservoir geometry and conditions, (b) components, (c) fluids and rock-fluids relations. The Model Builder included in this software was used and the data for its 8 sections were defined in the following manner.

A) Input/Output: This section defines the input/output parameters, such as titles, variables and other information related to output files.

B) Reservoir: This section defines the geometry of the reservoir and some properties of the formation such as width, porosity, permeability, temperature, pressure and saturations of the phases.

C) Components: This sections defines the characteristic of the fluids present in the reservoir such as densities, viscosities, compressibility, etc.

D) Rock-fluid: In this section, relative permeability curves and capillary pressures are defined.

E) Initial conditions: In this section, the initial conditions of the reservoirs are defined. This includes reservoir pressure, depth, water and oil contact and bubble point.

F) Numerical: This section controls the numerical aspects of the simulator, such as time and solver methods, that can be tuned in order to get convergence.

G) Well & Recurrent Data: This section defines the parameters of the well, operation restrictions and the dates of events such as production, flooding, among others.

Note: The numerical values considered for the simulation are detailed in Annexes A.

3.2 Evaluation of salinity shock on emulsion stability

1. Reagents:

69 ml of formation water (characterized in Annexes B), 426 ml of crude oil (characterized in Annexes C), and 189 ml of distilled water.

2. Materials and equipment:

Homogenizer Ultra Turrax T25 Basic, Centrifuge HERMLE Z300, 6 centrifuge tubes of 50 ml, 3 measuring cylinders of 50 ml and 6 beakers.

3. Procedure:

A) Preparation of 100 ml of diluted brine 1% and 10% (v/v): Formation water with distilled water were mixed according to the following proportions:

- 10 ml of formation water and 90 ml of distilled water
- 1 ml of formation water and 99 ml of distilled water

B) Preparation of samples: 2 samples of 100 ml were prepared in the following manner:

- 67 ml of crude oil and 33 ml of brine
- 75 ml of crude oil and 25 ml of brine

(Procedure was repeated with diluted brines at 1 and 10% v/v)

C) Emulsions preparation: The 6 samples were collocated in the homogenizer at 8000 rpm during 3 min.

D) Measurement of emulsion stability: Emulsions samples of 45 ml were collocated in a centrifuge at 3000 rpm 1 hour per day. Then, the volume of resolved water was registered as a function of time during 11 days.

3.3 Evaluation of monovalent and divalent cations on emulsion stability

1. Reagents:

402 ml of crude oil, 2378 ml of distilled water, 13.19 g of NaCl and 637 mg of $CaCl_2$.

2. Materials and equipment:

Homogenizer Ultra Turrax T25 Basic, Centrifuge HERMLE Z300, 6 centrifuge tubes of 50 ml, 3 measuring cylinders of 50 ml and 6 beakers.

3. Procedure:

A) Preparation of synthetic brines of monovalent and divalent cations: Synthetic brine of monovalent cation was made dissolving 13.19 g of NaCl in 1 L of distilled water, while synthetic brine of divalent cation was made dissolving 637 mg of $CaCl_2$ in 1L of water (Calculation for solutions preparation is shown in Annexed D).

B) Preparation of 100 ml of diluted brine 1% and 10% (v/v): Synthetic brines were mixed with distilled water according to the following proportions:

- 10 ml of synthetic brine and 90 ml of distilled water
- 1 ml of synthetic brine and 99 ml of distilled water

C) Preparation of samples: The samples of 100 ml were prepared in the following manner: 67 ml of crude oil and 33 ml of brine. The procedure was repeated with diluted synthetic brines of monovalent and divalent cations at 1 and 10% v/v.

D) Emulsions preparation: The six samples were collocated in the homogenizer at 8000 rpm during 3 min.

E) Measurement of emulsion stability: Emulsions samples of 45 ml were collocated in a centrifuge at 4000 rpm 1 hour per day. Then, the volume of resolved water was registered as a function of time during 11 days.

3.4 Evaluation of temperature on emulsion stability

1. Reagents:

540 ml of crude oil, 71 ml of formation water and 189 ml of distilled water.

2. Materials and equipment:

6 measuring cylinders of 100 ml and Apparatus for water and oil separability.

3. Procedure:

A) Preparation of 100 ml of diluted brine 1% and 10% (v/v): Formation water with distilled water were mixed according to the following proportions:

- 10 ml of formation water and 90 ml of distilled water
- 1 ml of formation water and 99 ml of distilled water

B) Preparation of samples: Samples of 80 ml were prepared in the following manner:

- 60 ml of crude oil and 20 ml of brine

(Procedure was repeated with diluted brines at 1 and 10% v/v)

C) Emulsions preparation: The nine samples were collocated in the homogenizer at 1500 rpm during 5 min at 25°C.

D) Measurement of emulsion stability: Emulsions samples of 80 ml were collocated in thermal bath at 25°C. Then, the volume of resolved water was registered every 5 min during 1 hour. Experiments were repeated with temperatures of 54 and 72°C.

The followed norm was the ASTM D1401-02 available in Annexes E.

3.5 Analysis of emulsion morphology

1. Reagents:

Emulsions 31100, 31010, 31001, NaCl 100%, NaCl 10%, NaCl 1%, $CaCl_2$ 100% and $CaCl_2$ 1% generated in Methodology 3.2 and 3.3.

2. Materials and equipment:

Optical microscope, 6 slides plates for microscope and 6 pipettes.

3. Procedure:

A) Preparation of samples: Crude oil was drained from the centrifuge bottles. Then, a small quantity of the emulsions were extracted with a spatula and collocated in the slides plates.

B) Micrographs in optical microscopy: The samples were analyzed in the microscope with a 10x zoom in the objective lens.

C) Measurement of drops size distribution: Images were processed by the program Image J. Threshold was adjusted to 95% and only droplets with a circularity higher than 0.1 were considered. Finally, the obtained data was tabulated in Microsoft Excel.

Drop size distributions are available in Annexes F.

a) Simulation of secondary recovery and LoSal water flooding:

In order to make estimations about crude oil recovery, core-flood tests or simulations are normally used. In the present work, simulation with CMG IMEX software was considered to compare the variations in crude oil production between normal secondary recovery (HS) and LoSal water flooding (LS) (See Fig17).

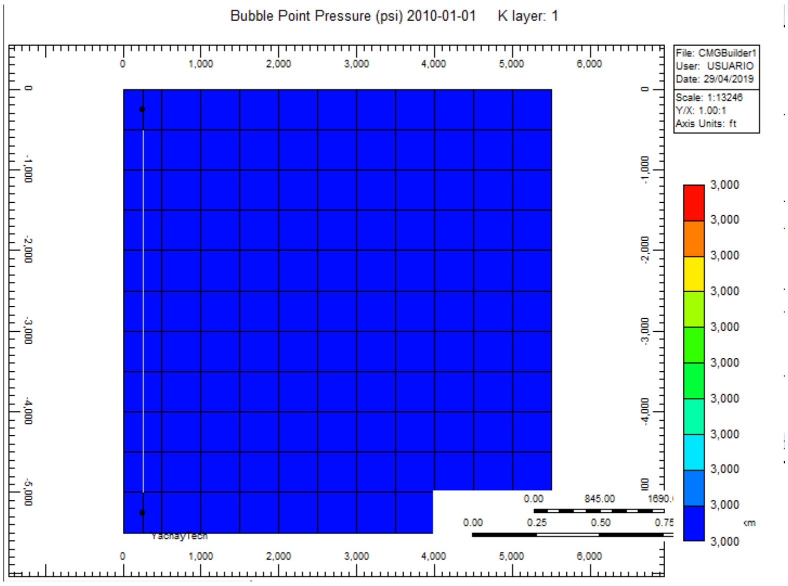


Fig17._ Validity window for reservoir simulation in CMG IMEX, which indicates that all the conditions have been successfully defined and the running can be executed.

A reduction in the salinity provokes changes in the relative permeability curves. LoSal water flooding displaces curves toward water wetness (See Fig18).

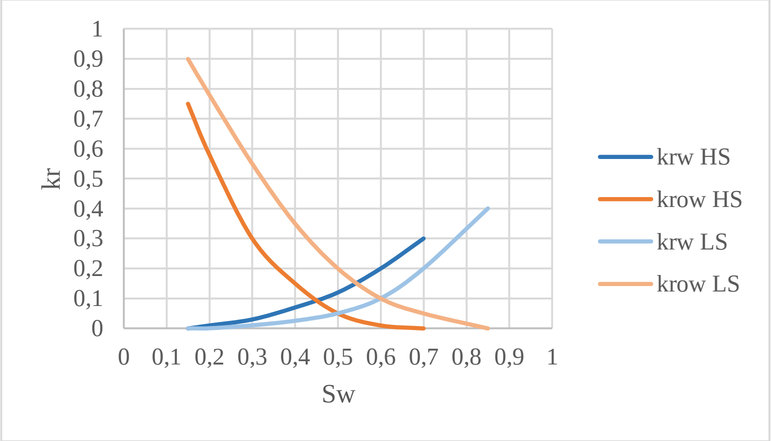


Fig18._ Relative permeability curves for water (krw) and oil (krow) in High Salinity (HS) and Low Salinity (LS) regimes as a function of water saturation (Sw).

The displacement in the curves leads to considerable changes in crude oil production. In HS water flooding the cumulative production in a lapse time of 15 years (from 2010 to 2025) would be around 21.5 million of barrels, while during the same time, in LS water flooding, the cumulative production would rise to 23 million of barrels (See Fig19).

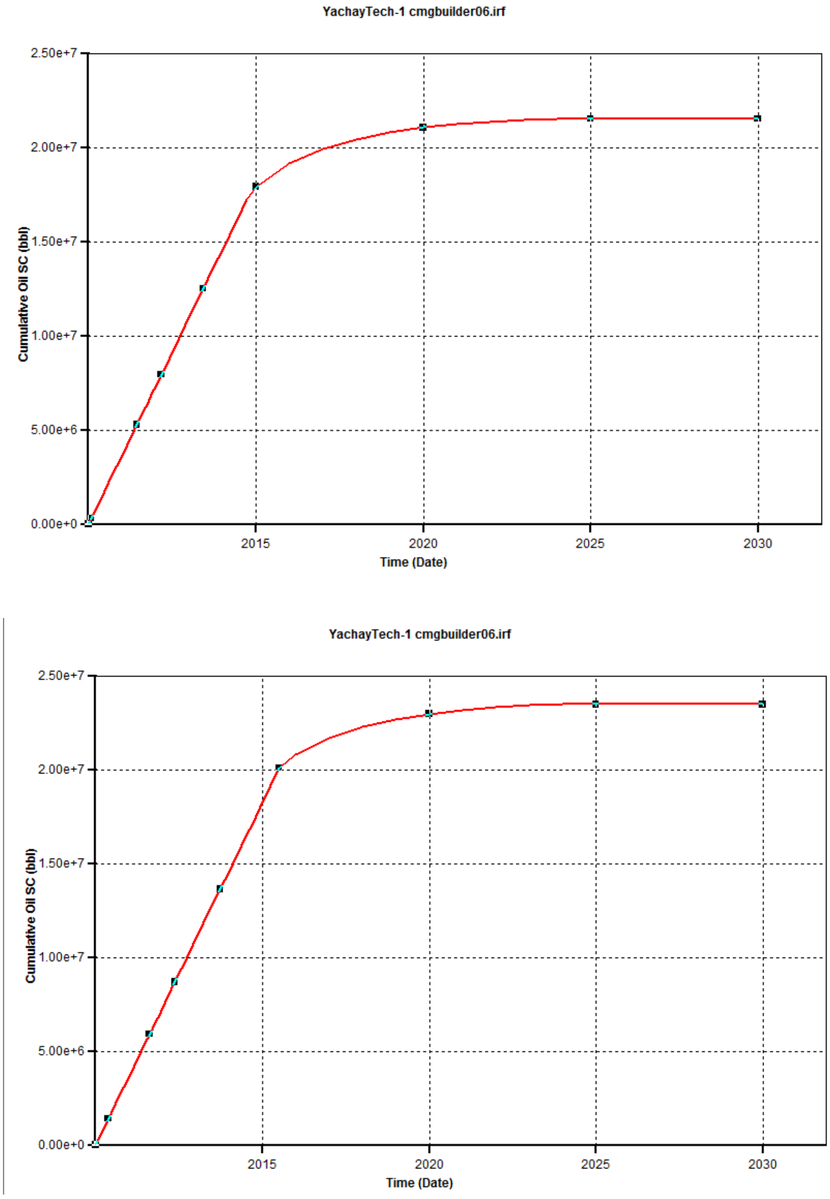


Fig 19._ HS (above) and LS (below) cumulative oil curves obtained from CMG.

The crude oil recovery is higher in LoSal water flooding since the first years of the application. The total increment in LoSal is around 7% higher than in normal secondary recovery, this increment can be considered meaningful for some projects, thence, the implementation of this type of EOR projects should be reinforced as soon as the additional crude oil recoveries allow to compensate the expenses associated with the injection of fresh water.

b) Evaluation of salinity shock on emulsion stability:

As mentioned before, crude oil and formation water are the components of emulsions considered in the present research. However, live crude oil obtaining is a difficult task because during normal production activities, cocktails of chemical products such as anti-scaling and corrosion inhibitor are injected in the wells, and these modify, at some extent, the chemistry of the original petroleum *in situ*. For this reason, prior to experimental set-up, measurements of interfacial tension (IFT) were made using the Du Nouy ring method, which consists on measuring the force applied on a ring for breaking the liquid layer. The results are shown in Fig20.

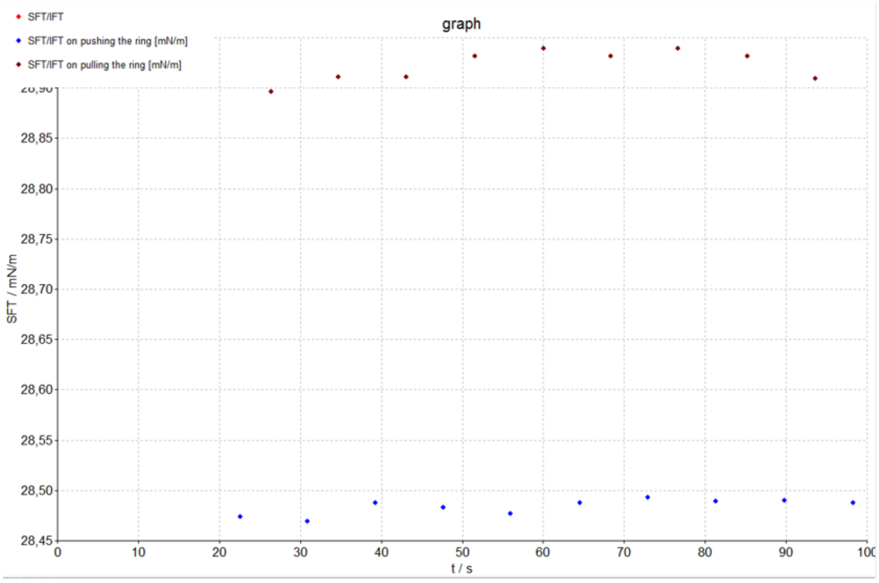


Fig 20._ IFT between crude oil and formation water measured by Du Nouy ring method.

It was considered that an IFT lower than 5 mN/m implies a significant influence of chemicals additives on natural surfactants. The IFT was calculated averaging the tensions for pushing the ring into water and pulling it back into crude oil, and the obtained value was 28.70 mN/m, evidencing that the crude oil sample is valid for the considered experiments.

Emulsions between crude oil and formation water were effectively created without external emulsifiers. It is due to the presence of natural surfactants, asphaltenes, resins and organics acids, present in the medium crude oil of Sacha oilfield (25.3 API). Also, when the salinity of formation water was reduced, ten and one hundred times, the emulsions were satisfactorily generated (See Fig21).

Fig 21._ Mixture of crude oil and formation water (left). Emulsions 31100, 31010, 31001, 21100, 21010, 21001 generated at 8000 rpm with a homogenizer (right). The first two numbers in the nomenclature refers to the volumetric ratio of crude oil and water and the other three to the volumetric percentage of formation water in the aqueous phase.

Initially, all the water get dispersed in the crude oil and the system looks like an apparent one phase. However, the separation of phases began after the first day. Because of the differences of density, crude oil remains in the upper part, the resolved water in the lower part and an emulsion layer, brown color and mayonnaise like consistency, is located between them. The width of emulsion layer is decreased as additional water gets resolved (See Fig22).

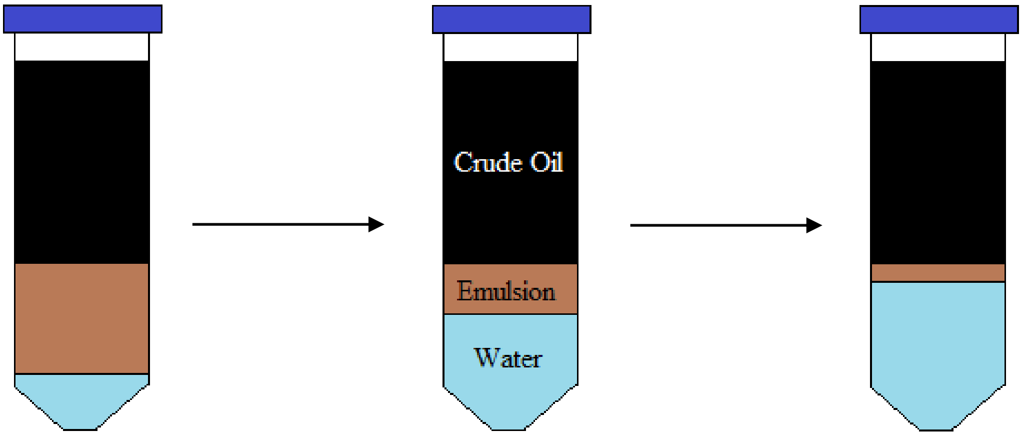


Fig 22._ Scheme of water separation seen in bottle tests.

In emulsions where crude oil and water volumetric relation is 3:1, such as 31100, 31010 and 31001, the stability was analyzed by centrifugal bottle tests and the results are shown in Fig23.

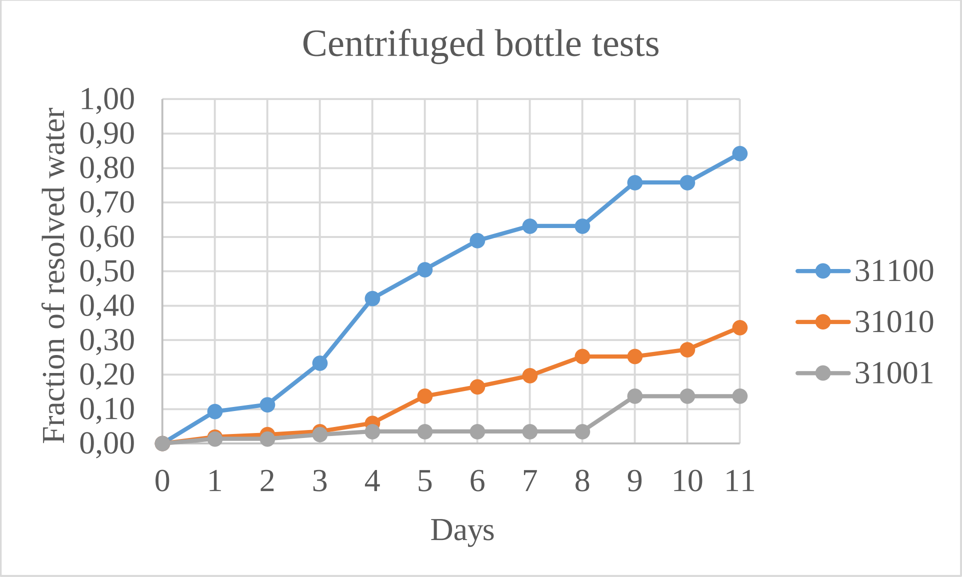


Fig23._ Fraction of resolved water as a function of time in centrifuged bottle tests at 25°C and 3000 rpm.

From Fig23, it is evident that reductions in the salinity of the water, from 31100 (the most concentrated) to 31001 (the most diluted), generated stronger emulsions so, the quantity of resolved water was lower for the emulsion with the least saline aqueous phase.

In addition, the stability of emulsions, where crude oil and water volumetric ratio is 2:1, such as 21100, 21010 and 21001, was analyzed by centrifugal bottle tests and the results are shown in Fig24.

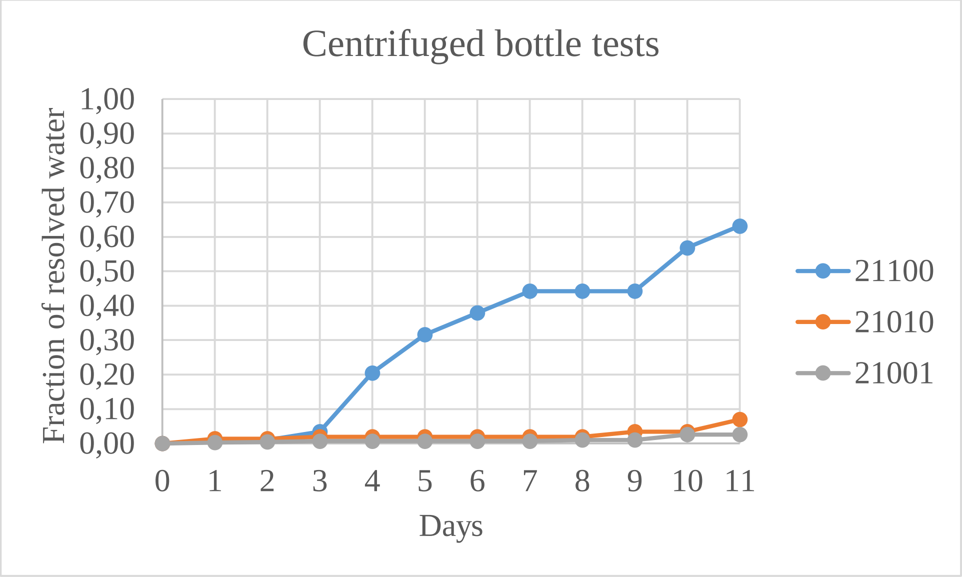


Fig24._ Fraction of resolved water as a function of time in centrifuged bottle tests at 25°C and 3,000 rpm.

The latter emulsions exhibits the same pattern than the former ones, that is, a decrease of aqueous phase salinity produced stronger emulsions (See Fig 25).

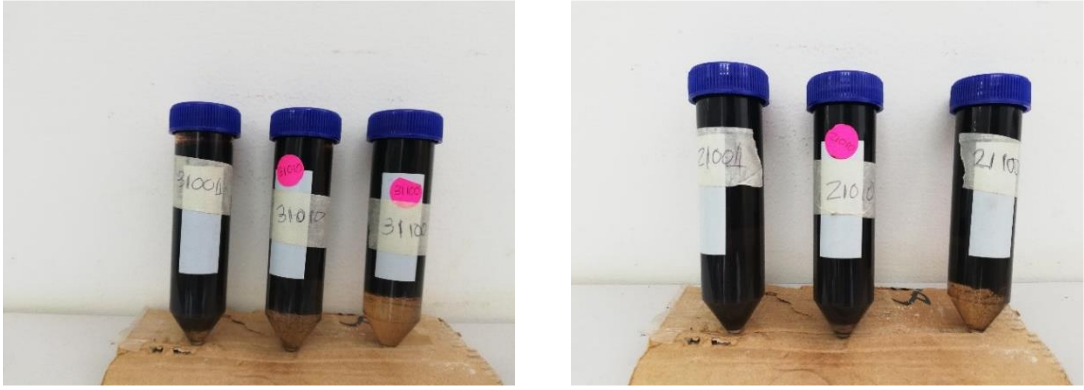


Fig25._ Emulsions 31001, 31010, 31100 (left) and 21001, 21010, 21100 (right) after centrifugations.

However, the fraction of resolved water is considerable lower for emulsions where the ratio of phases is 2:1, giving the idea that these emulsions are stronger than the former ones. This fact could sound contradictory, taking into account that a higher amount of dispersed phase must produce less stable emulsions because droplets have a higher probability of encounter and experience one of the demulsification steps. Nevertheless, higher amounts of water generated a thicker emulsion layer, probably because of a higher migration of emulsifiers toward interface (See Fig26).

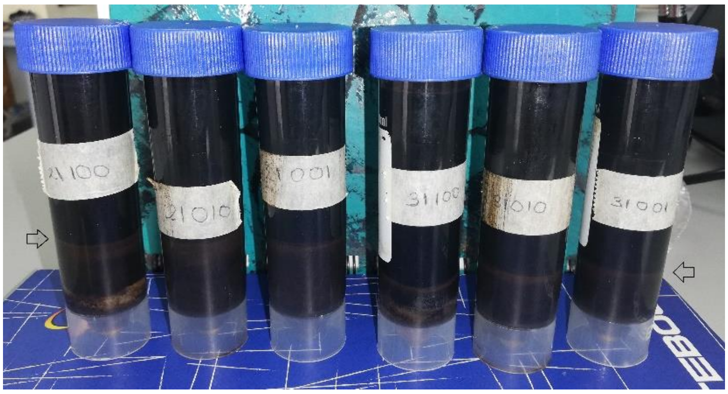


Fig26._ Emulsions 21YYY (left) and 31YYY (right) after centrifugations. Narrows indicate the upper level of emulsion layer.

c) Evaluation of cation type on emulsion stability:

Synthetic brine with monovalent cations exhibits the same tendency than formation water, i.e. a decrease in the ionic concentration favor the formation of more stable emulsions (See Fig 27).

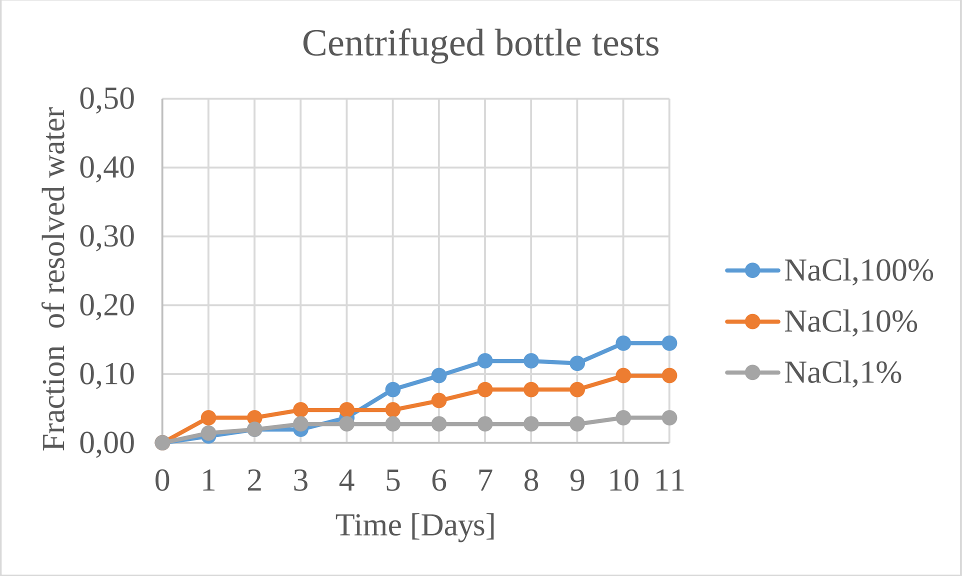


Fig 27._ Fraction of resolved water as a function of time in centrifuged bottle tests at 25°C and 4000 rpm. In nomenclature, the last number represent the percentage of monovalent synthetic brine in aqueous phase.

It can be due to the fact that, most of the cations present in formation water are monovalent, and so, formation water and synthetic brine of monovalent cation exhibit the same behavior.

On the other hand, emulsions with divalent cations does not necessarily exhibit the same pattern than emulsions with formation water. In fact, increments of calcium cations produce more stable emulsions (See Fig28). This fact is in agreement with some studies stating that divalent cations can strength emulsion layer.

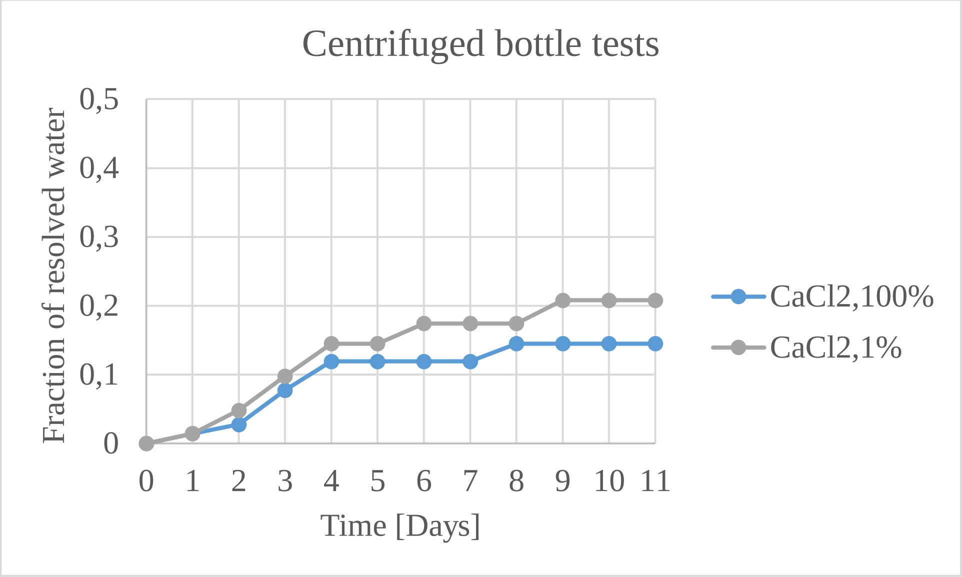
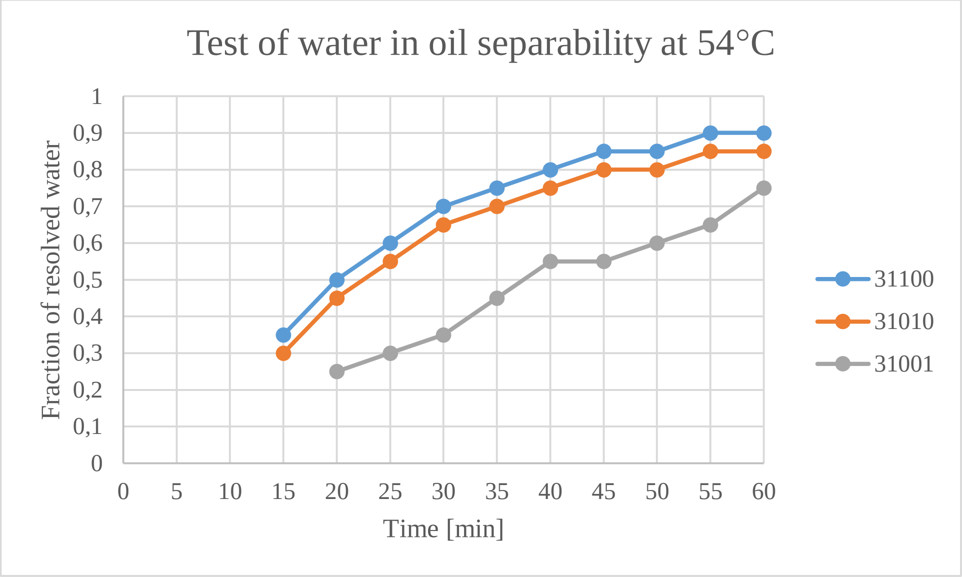


Fig28._ Fraction of resolved water as a function of time in centrifuged bottle tests at 25°C and 4000 rpm. In nomenclature, the last number represent the percentage of divalent synthetic brine in aqueous phase.

d) Evaluation of temperature on emulsion stability:

This experiment was carried out under the norm ASTM D1401-02, according to which the number of revolutions for homogenization was considerable lower (~5 times) than the one used for the previous experiments. This considerable difference produced weak emulsions, probably because the dispersed phase drops were bigger and more heterogeneously dispersed in the continuous phase. Emulsions created under this shear agitation, resolved an amount of water smaller than the minimum division mark of the cylinders after 1 hour of test at 25°C, for that reason results at this temperature were not reported.

With increments of temperature, the kinetic of demulsification becomes considerable faster as a result of the reduction on the viscosity of the continuous phase and the increase in the energy of the system that increase the probability of collision between dispersed phase drops (See Fig 30).



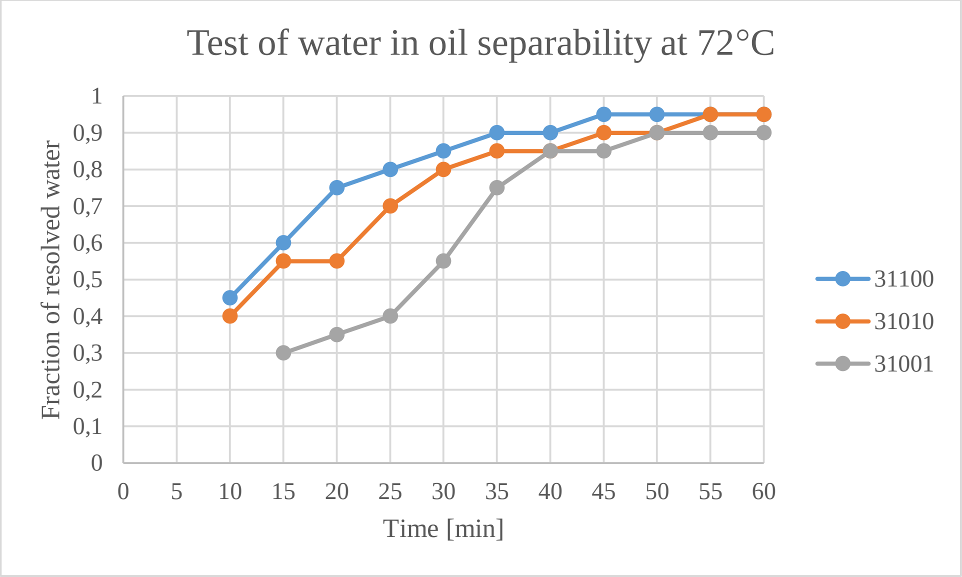


Fig 30._ Test of water and oil separability. Agitation was set at 1500 rpm and temperatures were 54°C (above) and 72°C (below).

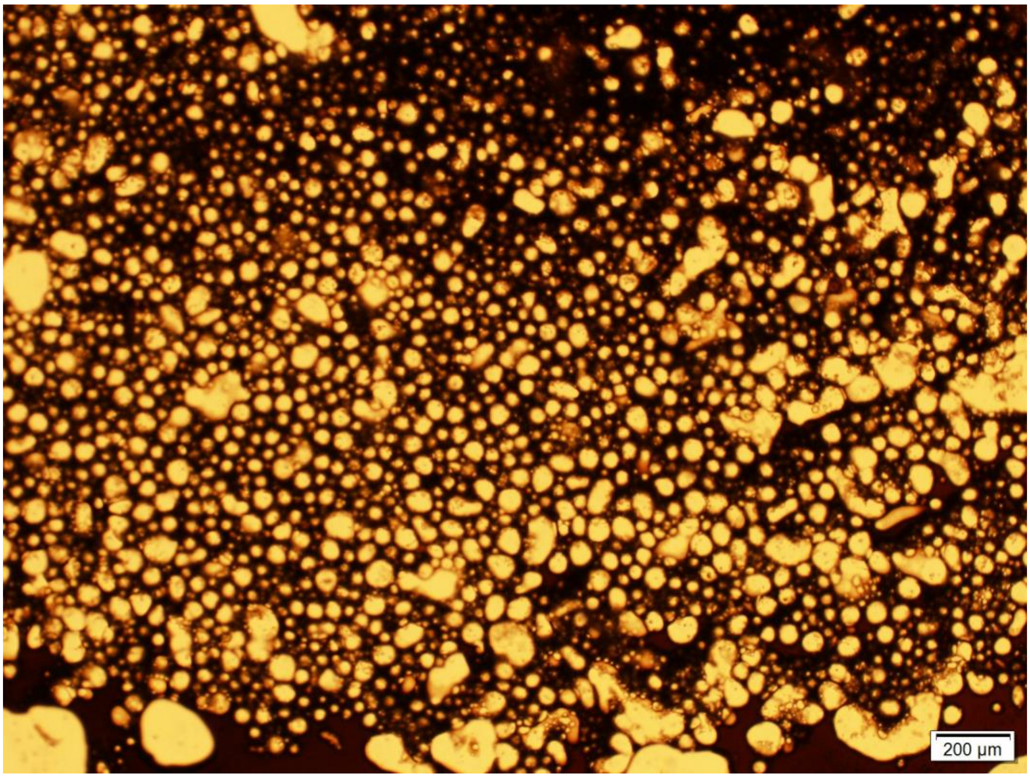
At the end of the tests, not all the water was resolved. It implies a limitation of this norm on crude oils because extended periods of time could conduct to a total separation of phases.

Agitation and temperature are parameters that strongly influence the stability of emulsions. If agitation from pumps is not high enough, the resulting emulsions are weak, even to prevail at ambient conditions. On the other hand, high temperatures, as the ones occurring deep on the reservoirs, weaken emulsions to the point that these emulsions could not prevail enough time for being mobility control agents.

Additional tests must be carried out at high shear rates, high temperatures and during prolonged periods of time, in order to effectively demonstrate if emulsions generated by LoSal could resist the harsh conditions on reservoirs. Nevertheless, following the purpose of the present research, it was shown that at low temperatures, when the kinetic of demulsification is slow enough to make comparisons statistically meaningful, LoSal conditions strengthen emulsions stability in Amazonian-Ecuadorian crude oils from Campo Sacha.

e) Analysis of water in oil emulsion morphology:

Micrographies can be used to make inferences about emulsion stability. Since the transmission of light is higher in the dispersed phase, the resulting emulsions are w/o emulsions. A microphotography of the emulsions 31001, 31010 and 31100 is shown in Fig31.



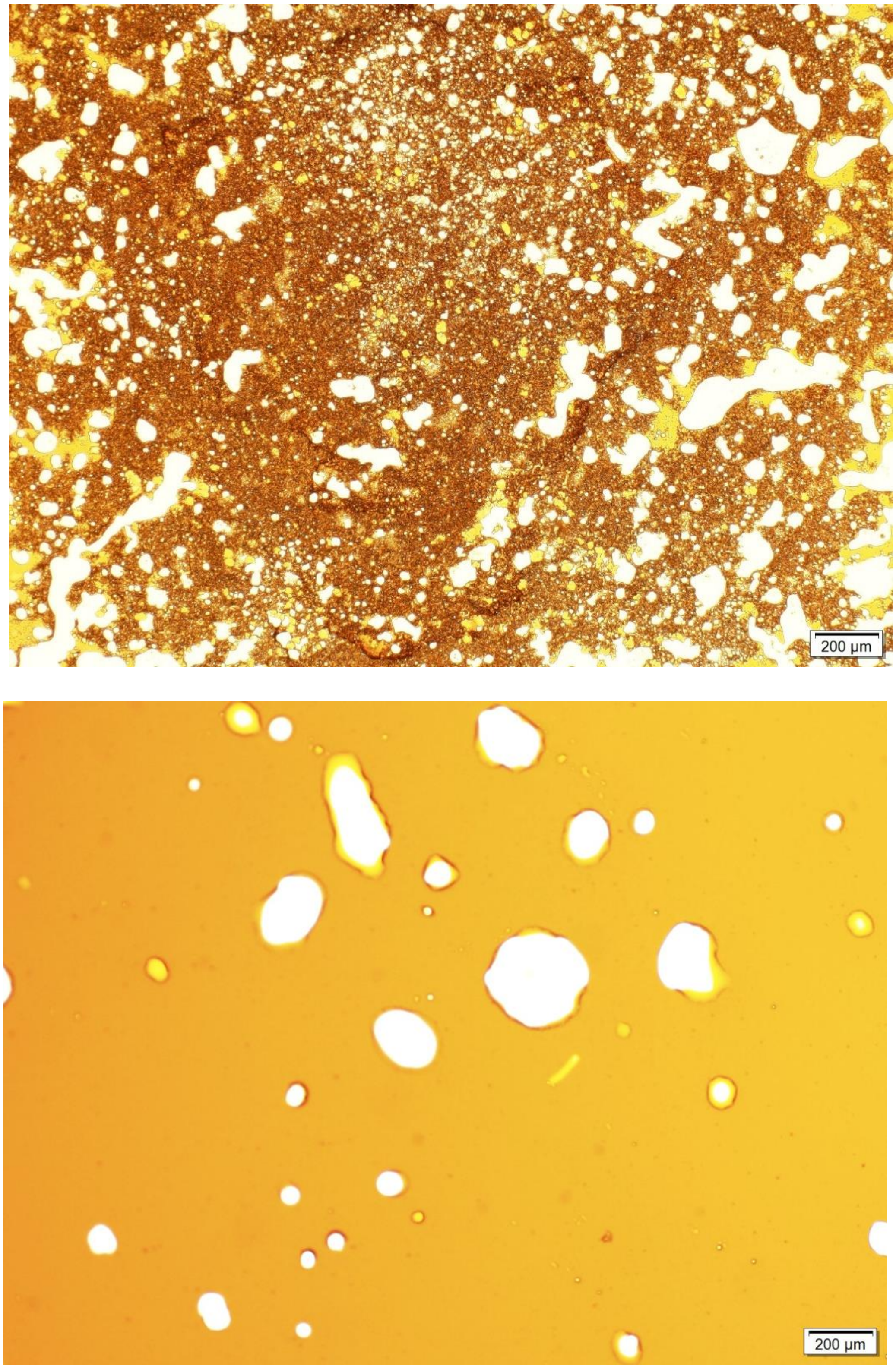


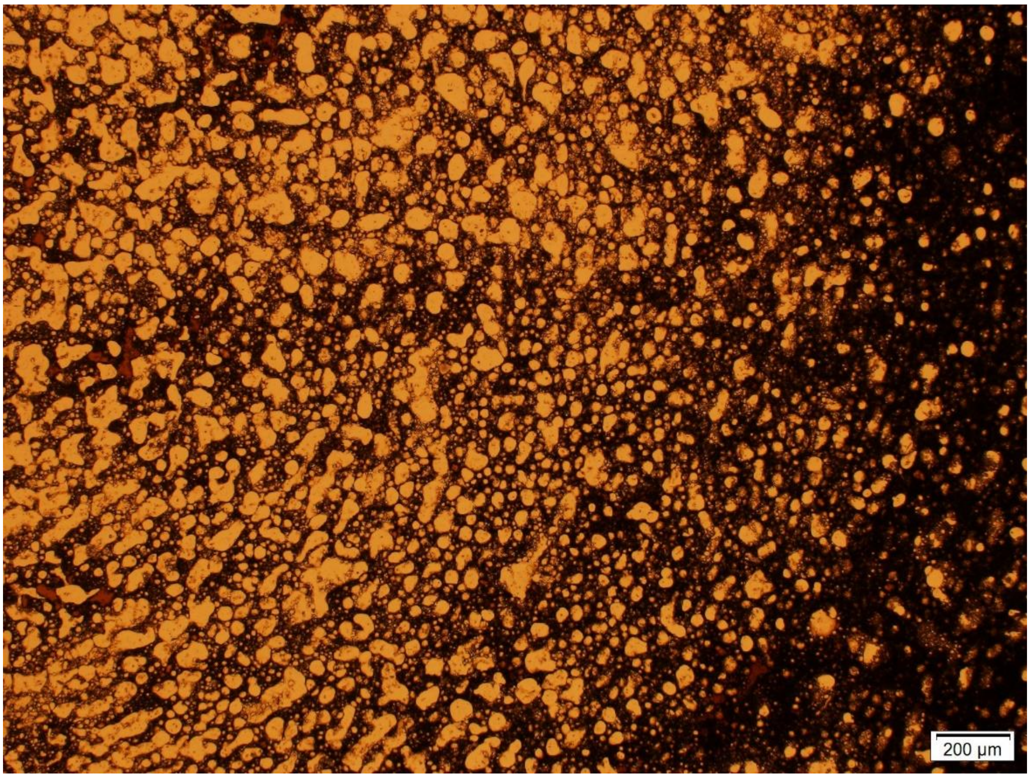
Fig 31._ Microphotography of emulsion 31001 (top), 31010 (medium) and 31100 (bottom) taken with a 4x zoom in the objective. Dispersed phase is water and the continuous phase is crude oil.

Emulsion 31001 shows a good dispersion of one phase into the other. The dispersed phase droplets with an average size around 28 µm are homogeneously distributed and the occurrence of coalescence is not significant.

In emulsion 31010, the dispersed phase drops have a heterogeneous distribution and these droplets are significantly deformed, evidencing a high occurrence of coalescence. Also, the mean drop diameter is 38 µm, which means that the drops are slightly bigger than drops in emulsion 31001.

In emulsion 31100, the dispersion is not good and the coalescence is high with formation of drops with an average size of 92 µm. Hence, the dilution in the formation water conducted to emulsions with small dispersed phase drops where the coalescence was diminished resulting in stable emulsions. This observation is in agreement with the results of bottle tests.

A microphotography of emulsions created with synthetic brines of monovalent cations is shown in Fig 32.



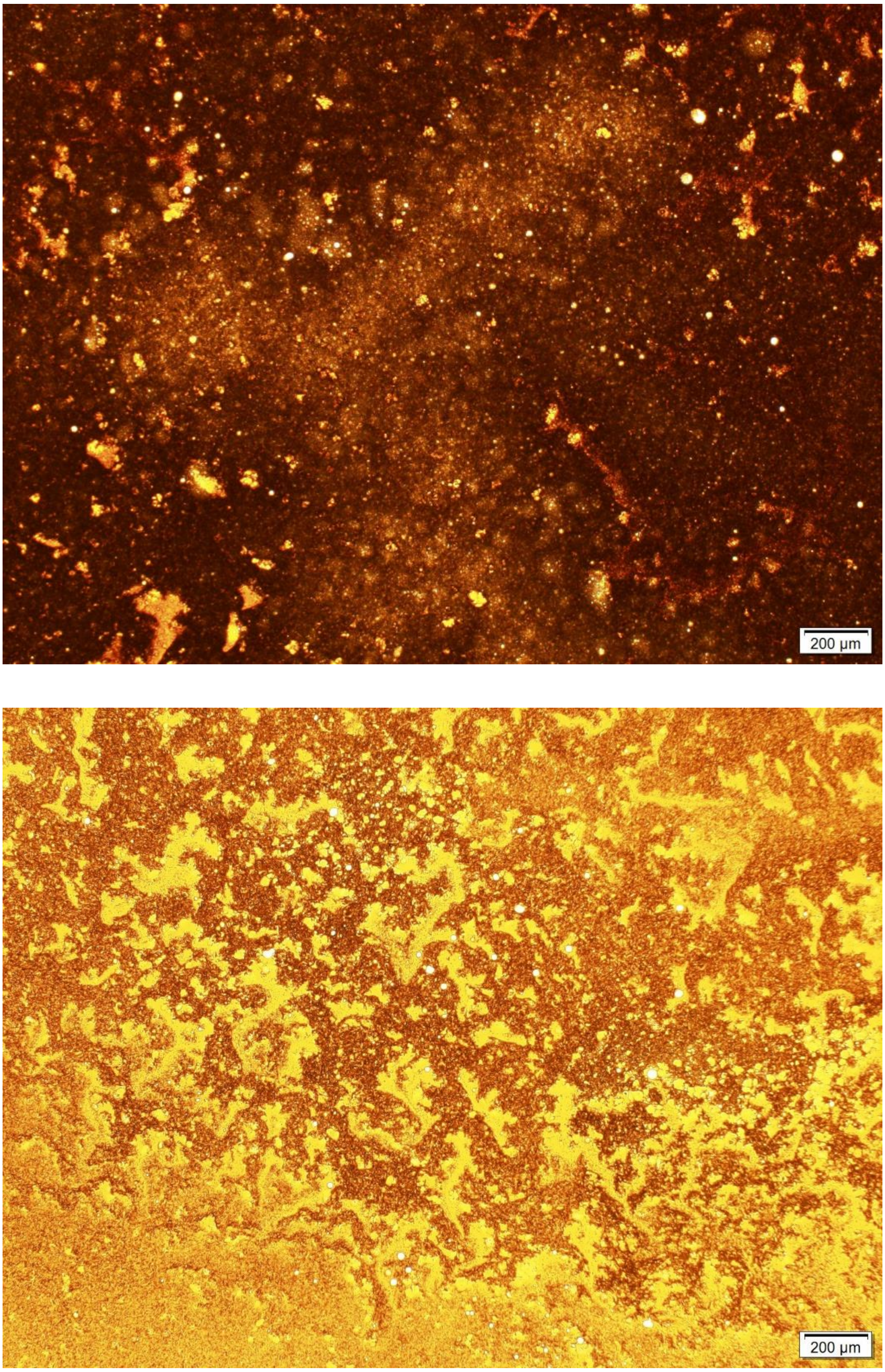
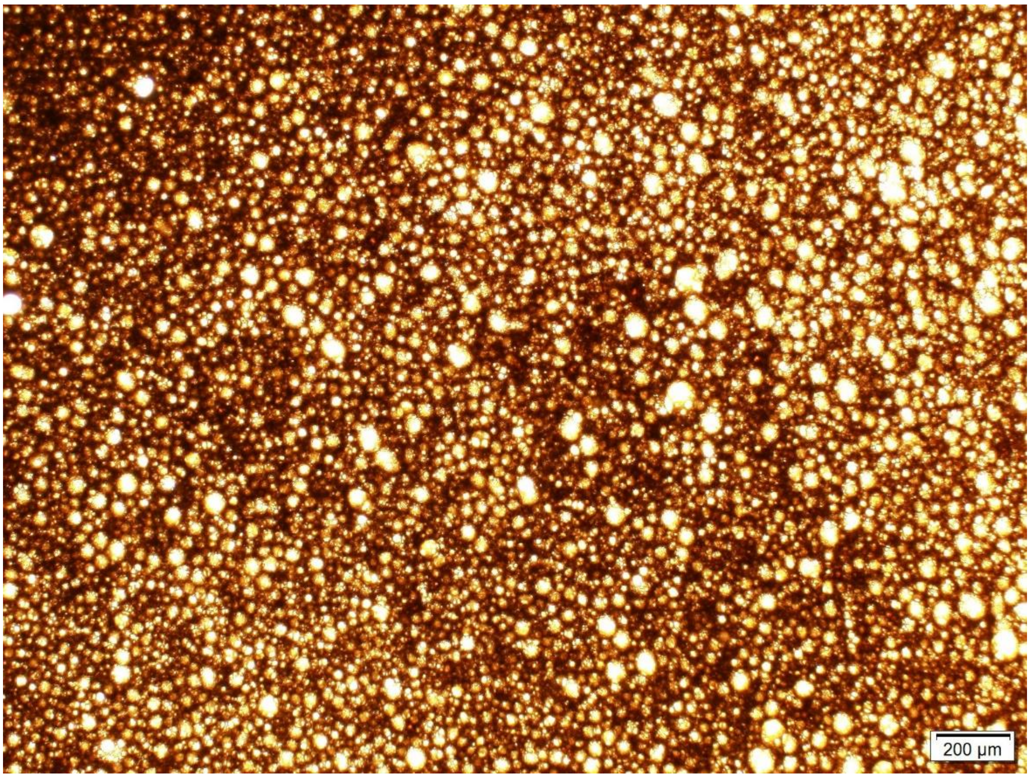


Fig 32._ Microphotography of emulsion prepared with synthetic brines of monovalent cations of NaCl, 1% (top), NaCl, 10% (medium) and NaCl, 100% (bottom) taken with a 4x zoom in the objective.

Only the emulsions prepared with the most diluted brine of monovalent cations created a good distribution of dispersed phase drops with an average size of 35 µm, while in emulsions prepared with more concentrated brines the formation of drops is not clear. For that reason, emulsions generated with diluted brine are the most stable, similarly to emulsions generated with formation water.

On the other hand, emulsions prepared with synthetic brines of divalent cations does not necessarily shows the same tendency described before. A microphotography of emulsions prepared with synthetic brines of $CaCl_2$ is shown in Fig 33.



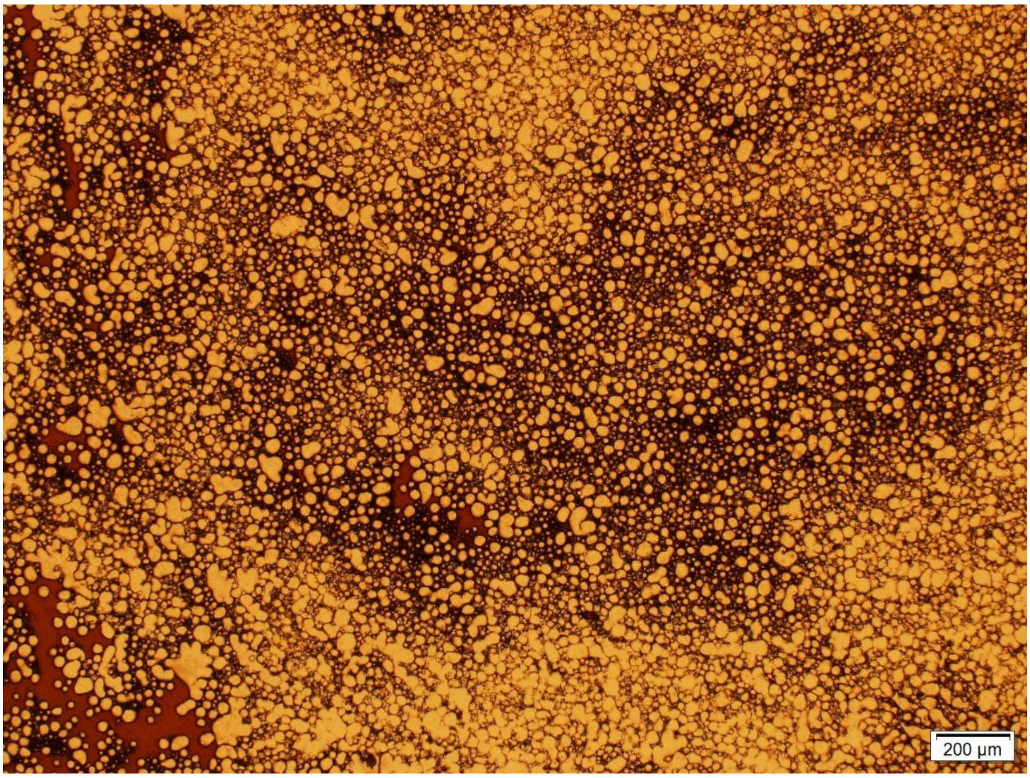


Fig 33._ Microphotography of emulsion made of synthetic brine full-of $CaCl_2$ diluted one hundred times (above) and without dilution (below) with a 4x zoom in the objective.

Emulsions prepared with synthetic brines of divalent cations exhibit a good distribution of dispersed phase drops of small size, 25 µm when diluted and 19 µm without dilution.

In this case, the tendency is inverted because the increments in the calcium concentration originated emulsions slightly more stable. Nevertheless, the difference is small and it is preferred to interpret that small quantities of divalent cation can favor the formation of stable emulsions.

Formation water is a mixture of different salts with a predominance of monovalent cations. It can explain why the behavior of emulsions prepared with synthetic brines made of monovalent cations behave similar to emulsions prepared with formation water. In addition, divalent cations have a different effect on emulsion stability which can be proved both by bottle tests and micrographs observations.

Chapter 5: Conclusions

When mixed with low salinity water, crude oil from Campo Sacha can form emulsions without the addition of external emulsifiers. This can be attributed to the presence of natural surfactants in its composition. Micrograph observations show that the generated emulsions correspond to macroemulsions and that their characteristics depend on the aqueous phase composition.

At laboratory temperatures (~20°C), it was corroborated that LoSal water flooding working conditions, such as salinity shock and the presence of divalent cations, favor the stability of emulsions. Emulsions prepared with diluted formation water are more stable than emulsions prepared with formation water. In addition, emulsions prepared with synthetic brines made of divalent cations (Ca^{2+}) exhibited a different behavior than emulsions prepared with formation water or synthetic brines made of monovalent cations (Na^{+}), because increments in divalent cations created slightly more stable emulsions.

Agitation and temperature are crucial factors in the stability of emulsions. On one side, emulsions created at low agitation were considerably weaker than emulsions generated at high agitations, to the point that they could be separated at environmental temperatures. On the other hand, increments of temperature weaken the stability of emulsions considerably, enabling an almost complete resolution of water in a short time.

LoSal water flooding is a simple and low cost EOR method, provided the existence of secondary recovery installations in the oilfields, and can lead to considerable increments in crude oil recovery. In our considered simulation case, the changes in permeability curves associated to LoSal water flooding conducted to an additional recovery of 7% in comparison to secondary recovery made with high salinity water.

The present study also points out that LoSal EOR method can be applied in some reservoirs of similar crude oil and formation water characteristics that the one used in the experimental set-up. The Cuenca Oriente in Ecuador fulfill the above mentioned characteristics such as connate water with divalent cations and polar compounds in crude oil.

It is recommended to carry out tests with Pickering emulsions stabilized with kaolinite and illite for evaluating the effect of these clays on emulsion stability. Also, rheological tests and experiments with emulsions generated at high agitations maintaining high temperatures could complement the present research.

Finally, it must be mentioned that this study faced a three-component problem (crude oil, water and substrate) with just two of these parameters, whereby it is necessary to implement this technique in core floods tests for estimating the crude oil recovery associated to this technique and the effective participation of the macroemulsions generated in its EOR action.

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Annexes

A. Data for simulation in CMG-IMEX

- Reservoir

Grid	
Grid type	Cartesian
K direction	Down
Number of grid blocks	i=11
	j=11
	k=3
Block widths	i=11*500
	j=11*500

Array properties	
Grid top	Layer 1= 8 000 ft
Grid thickness	Layer 1= 25 ft
	Layer 2= 75 ft
	Layer 3= 50 ft
Porosity	Whole grid= 0.2
Permeability	Layer 1 (i,j,k)= 277 md
	Layer 2 (i,j,k)= 1120 md
	Layer 3 (i,j,k)= 700 md
Rock compressibility	4x10-6 1/psi

- Components

Components (Quick BlackOil Model)	
Reservoir Temperature	200 F
Generate data upto	3 000 psi
Bubble Point Pressure	3 000 psi
Oil density	49 lb/ft3
Gas density (Air=1)	0.792
Reference pressure	14.696 psi
Water salinity	10 000 ppm

- Rock-fluid

<table>
<tr><td colspan="3">High Salinity</td></tr>
<tr><td colspan="3">Relative permeability: Water-Oil Table</td></tr>
<tr><td>Sw</td><td>krw</td><td>krow</td></tr>
<tr><td>0.15</td><td>0</td><td>0.75</td></tr>
<tr><td>0.2</td><td>0.01</td><td>0.58</td></tr>
<tr><td>0.3</td><td>0.03</td><td>0.3</td></tr>
<tr><td>0.4</td><td>0.07</td><td>0.15</td></tr>
<tr><td>0.5</td><td>0.12</td><td>0.05</td></tr>
<tr><td>0.6</td><td>0.2</td><td>0.01</td></tr>
<tr><td>0.7</td><td>0.3</td><td>0</td></tr>
<tr><td colspan="3">Relative permeability: Liquid-Gas</td></tr>
<tr><td>Sg</td><td>krg</td><td>krog</td></tr>
<tr><td>0</td><td>0</td><td>0.75</td></tr>
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<table>
<tr><td colspan="3">Low Salinity</td></tr>
<tr><td colspan="3">Relative permeability: Water-Oil Table</td></tr>
<tr><td>Sw</td><td>krw</td><td>krow</td></tr>
<tr><td>0.15</td><td>0</td><td>0.9</td></tr>
<tr><td>0.2</td><td>0</td><td>0.78</td></tr>
<tr><td>0.3</td><td>0.01</td><td>0.55</td></tr>
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<tr><td colspan="3">Relative permeability: Liquid-Gas</td></tr>
<tr><td>Sg</td><td>krg</td><td>krog</td></tr>
<tr><td>0</td><td>0</td><td>0.9</td></tr>
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</table>

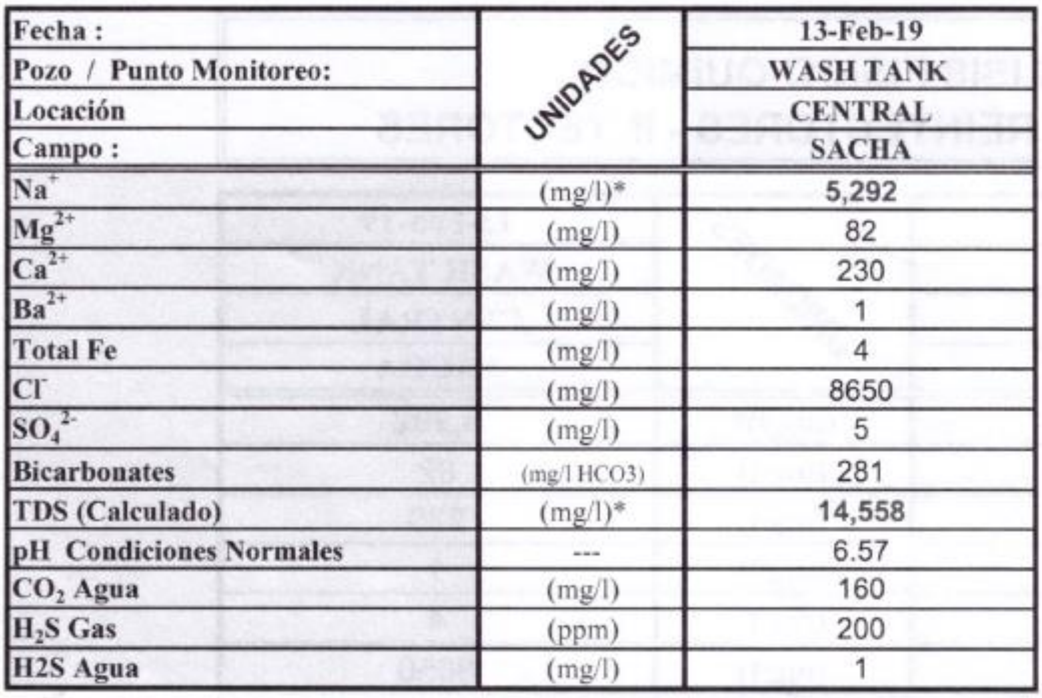
- Initial Conditions

Initial Conditions	
Pressure	4 500 psi
Depth	8 000 ft
Phase contact depth	8 151 ft
Bubble point pressure	3 000 psi

- Well & Recurrent Data

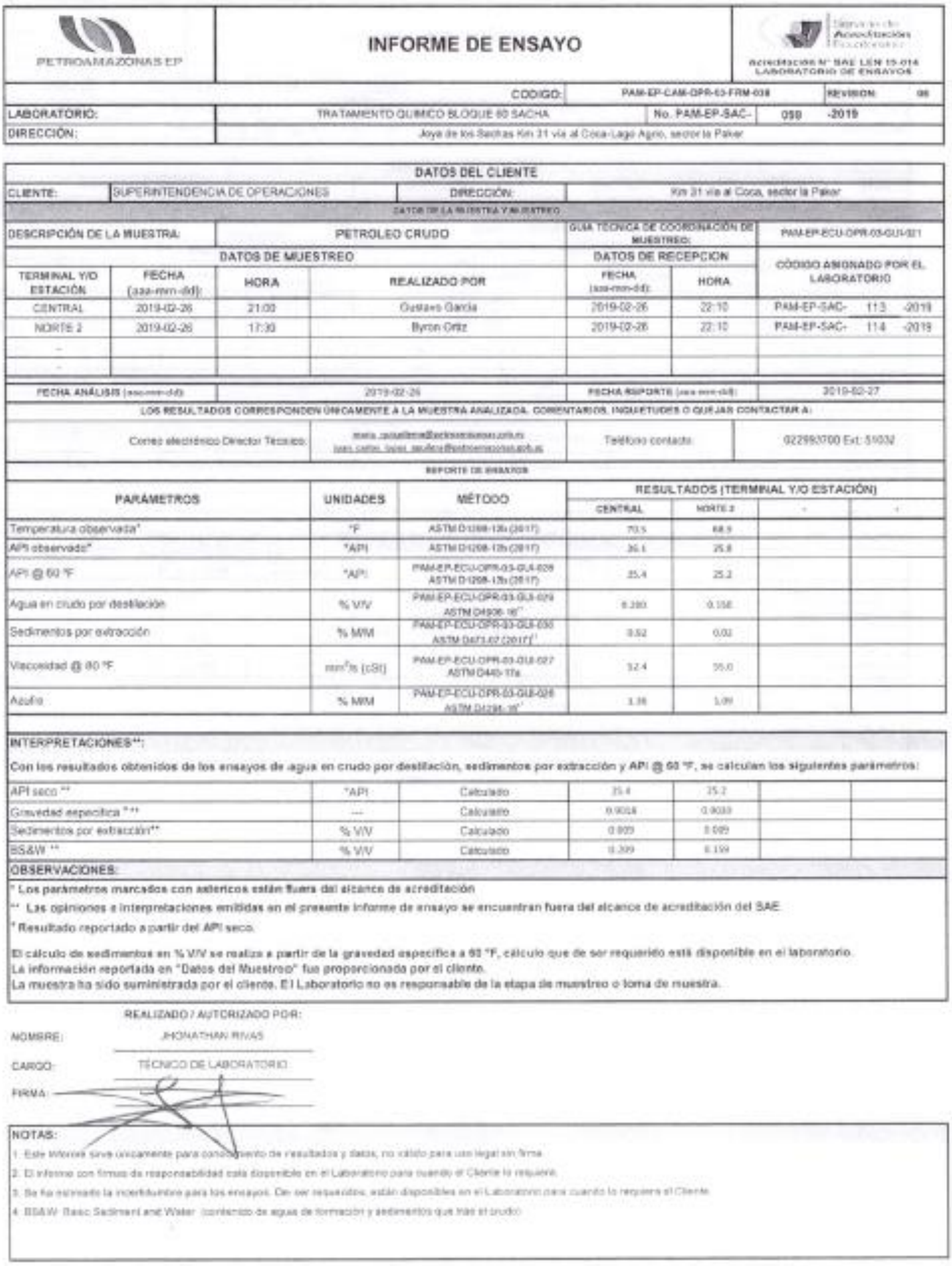
Well & Recurrent Data			
Well Type		Producer	
Constraints	Parameter	STO surface oil rate	
	Limit/mode	Max	
	Value	10 000 bbl/day	
	Action	Continuous	
Well Completion Data		1 11 1	
Dates (yearly)		From	1/1/2010
		To	1/1/2030

B. Physical-chemistry analysis of formation water in Campo Sacha



Fecha :	UNIDADES	**13-Feb-19**
Pozo / Punto Monitoreo:		**WASH TANK**
Locación		**CENTRAL**
Campo :		**SACHA**
Na$^+$	(mg/l)*	**5,292**
Mg^{2+}	(mg/l)	82
Ca^{2+}	(mg/l)	230
Ba^{2+}	(mg/l)	1
Total Fe	(mg/l)	4
Cl$^-$	(mg/l)	8650
SO$_4^{2-}$	(mg/l)	5
Bicarbonates	(mg/l HCO3)	281
TDS (Calculado)	(mg/l)*	**14,558**
pH Condiciones Normales	---	6.57
CO$_2$ Agua	(mg/l)	160
H$_2$S Gas	(ppm)	200
H2S Agua	(mg/l)	1

C. Characterization of crude oil of Campo Sacha



PETROAMAZONAS EP

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CODIGO:	PAM-EP-CAM-OPR-03-FRM-038	REVISION:	06
LABORATORIO:	TRATAMIENTO QUIMICO BLOQUE 60 SACHA	No. PAM-EP-SAC-	050 -2019
DIRECCIÓN:	Joya de los Sachas Km 31 vía al Coca-Lago Agrio, sector la Palmar		

DATOS DEL CLIENTE

CLIENTE:	SUPERINTENDENCIA DE OPERACIONES	DIRECCIÓN:	Km 31 vía al Coca, sector la Palmar

DATOS DE LA MUESTRA Y MUESTREO

DESCRIPCIÓN DE LA MUESTRA:	PETROLEO CRUDO	GUIA TECNICA DE COORDINACIÓN DE MUESTREO:	PAM-EP-ECU-OPR-03-GUI-021

DATOS DE MUESTREO				DATOS DE RECEPCION		CÓDIGO ASIGNADO POR EL LABORATORIO
TERMINAL Y/O ESTACIÓN	FECHA (aaa-mm-dd):	HORA	REALIZADO POR	FECHA (aaa-mm-dd):	HORA	
CENTRAL	2019-02-26	21:00	Gustavo Garcia	2019-02-26	22:10	PAM-EP-SAC- 113 -2019
NORTE 2	2019-02-26	17:30	Byron Ortiz	2019-02-26	22:10	PAM-EP-SAC- 114 -2019
-						
-						

FECHA ANÁLISIS (aaa-mm-dd):	2019-02-26	FECHA REPORTE (aaa-mm-dd):	2019-02-27

LOS RESULTADOS CORRESPONDEN ÚNICAMENTE A LA MUESTRA ANALIZADA. COMENTARIOS, INQUIETUDES O QUEJAS CONTACTAR A:

Correo electrónico Director Técnico:	[illegible] [illegible]	Teléfono contacto:	022993700 Ext: 51032

REPORTE DE ENSAYOS

PARÁMETROS	UNIDADES	MÉTODO	RESULTADOS (TERMINAL Y/O ESTACIÓN)			
			CENTRAL	NORTE 2	-	-
Temperatura observada*	°F	ASTM D1298-12b (2017)	70.5	68.9		
API observado*	°API	ASTM D1298-12b (2017)	26.1	25.8		
API @ 60 °F	°API	PAM-EP-ECU-OPR-03-GUI-028 ASTM D1298-12b (2017)	25.4	25.2		
Agua en crudo por destilación	% V/V	PAM-EP-ECU-OPR-03-GUI-029 ASTM D4006-16^{e1}	0.200	0.150		
Sedimentos por extracción	% M/M	PAM-EP-ECU-OPR-03-GUI-030 ASTM D473-07 (2017)^{e1}	0.01	0.01		
Viscosidad @ 80 °F	mm²/s (cSt)	PAM-EP-ECU-OPR-03-GUI-027 ASTM D445-17a	52.4	55.0		
Azufre	% M/M	PAM-EP-ECU-OPR-03-GUI-026 ASTM D4294-16^{e1}	1.16	1.09		

INTERPRETACIONES:**

Con los resultados obtenidos de los ensayos de agua en crudo por destilación, sedimentos por extracción y API @ 60 °F, se calculan los siguientes parámetros:

API seco **	°API	Calculado	25.4	25.2		
Gravedad específica ⁺**	---	Calculado	0.9018	0.9030		
Sedimentos por extracción**	% V/V	Calculado	0.009	0.009		
BS&W **	% V/V	Calculado	0.209	0.159		

OBSERVACIONES:

* Los parámetros marcados con asteriscos están fuera del alcance de acreditación

** Las opiniones e interpretaciones emitidas en el presente informe de ensayo se encuentran fuera del alcance de acreditación del SAE

⁺ Resultado reportado a partir del API seco.

El cálculo de sedimentos en % V/V se realiza a partir de la gravedad específica a 60 °F, cálculo que de ser requerido está disponible en el laboratorio.
La información reportada en "Datos del Muestreo" fue proporcionada por el cliente.
La muestra ha sido suministrada por el cliente. El Laboratorio no es responsable de la etapa de muestreo o toma de muestra.

REALIZADO / AUTORIZADO POR:

NOMBRE: JHONATHAN RIVAS

CARGO: TÉCNICO DE LABORATORIO

FIRMA:

NOTAS:

1. Este informe sirve únicamente para conocimiento de resultados y datos, no válido para uso legal sin firma.
2. El informe con firmas de responsabilidad está disponible en el Laboratorio para cuando el Cliente lo requiera.
3. Se ha estimado la incertidumbre para los ensayos. De ser requeridos, están disponibles en el Laboratorio para cuando lo requiera el Cliente.
4. BS&W: Basic Sediment and Water (contenido de agua de formación y sedimentos que trae el crudo)

D. Stoichiometric calculation for synthetic brines preparation.

By considering that the most representative salts present in formation water are NaCl, $CaCl_2$, $MgCl_2$, $NaHCO_3$, and that the concentrations of salts in formation water are in ppm (w/v). Then:

$$230\ \frac{\text{mg Ca}}{\text{L}}\text{x}\frac{110.98\ \text{mg CaCl}_2}{40.08\ \text{mg Ca}} = 636.86\ \frac{\text{mg CaCl}_2}{\text{L}}$$

$$82\ \frac{\text{mg Mg}}{\text{L}}\text{x}\frac{95.205\ \text{mg MgCl}_2}{24.305\ \text{mg Mg}} = 321.2\ \frac{\text{mg MgCl}_2}{\text{L}}$$

$$8003.94\ \frac{\text{mg Cl}}{\text{L}}\text{x}\frac{58.44\ \text{mg NaCl}}{35.45\ \text{mg Cl}} = 13\ 194.65\ \frac{\text{mg NaCl}}{\text{L}}$$

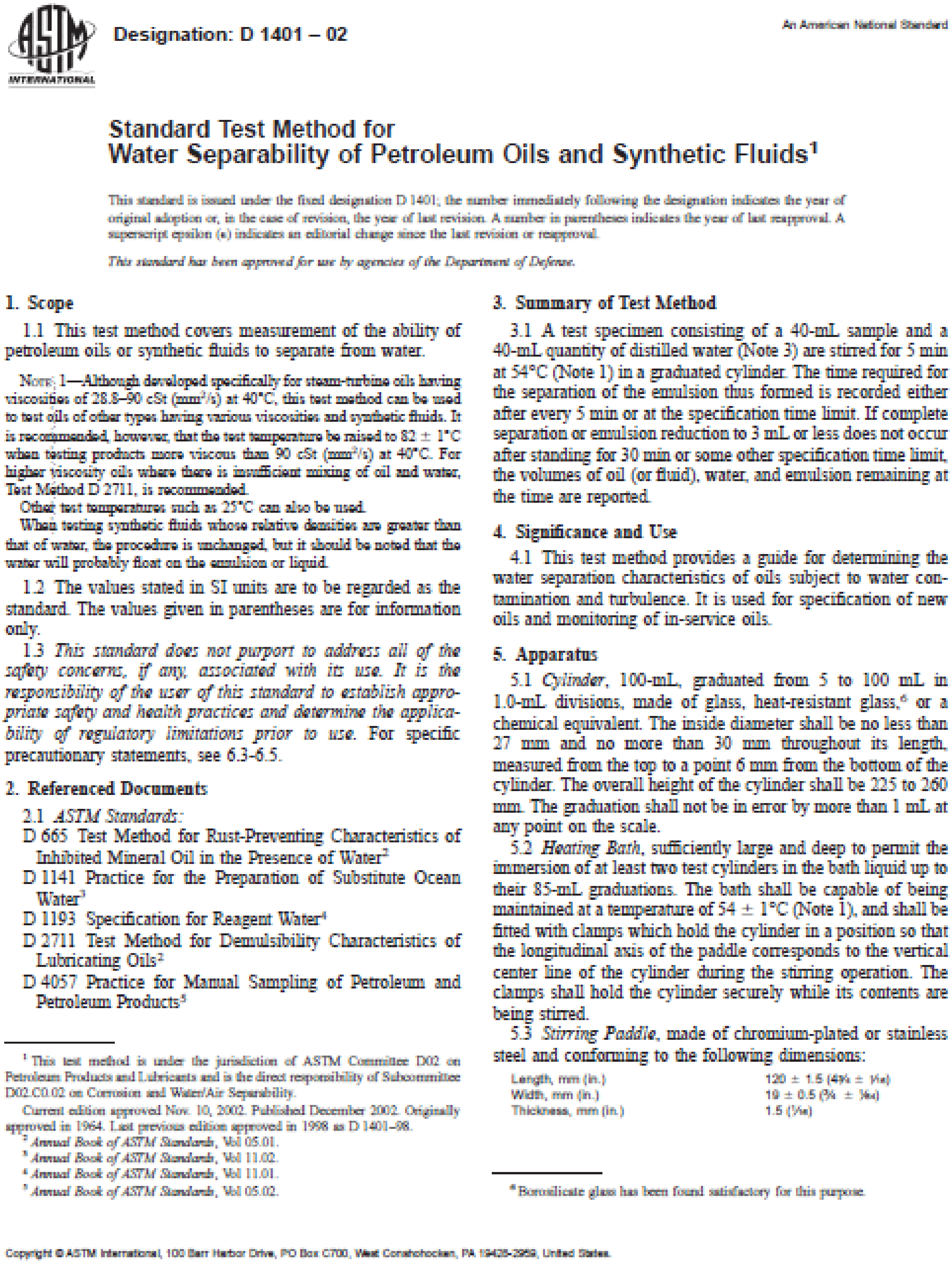
$$101.3\ \frac{\text{mg Na}}{\text{L}}\text{x}\frac{83.97\ \text{mg NaHCO}_3}{22.99\ \text{mg Na}} = 370\ \frac{\text{mg NaHCO}_3}{\text{L}}$$

In the case of samples with kaolinite, the clay was added depending on the mass of the crude oil-water mix.

$$\text{For 100 ppm: } \frac{\text{x}}{91.24\ \text{g} + \text{x}} = 0.0001 \rightarrow \text{x} = \frac{91.24\ \text{g}(0.0001)}{1 - 0.0001} = 0.00912\ \text{g} = 9\ \text{mg}$$

$$\text{For 1000 ppm: } \frac{\text{x}}{90.14\ \text{g} + \text{x}} = 0.001 \rightarrow \text{x} = \frac{90.14\ \text{g}(0.001)}{1 - 0.001} = 0.0902\ \text{g} = 90\ \text{mg}$$

E. ASTM D1401-02



Designation: D 1401 – 02

An American National Standard

Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids[1]

This standard is issued under the fixed designation D 1401; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers measurement of the ability of petroleum oils or synthetic fluids to separate from water.

NOTE 1—Although developed specifically for steam-turbine oils having viscosities of 28.8–90 cSt (mm²/s) at 40°C, this test method can be used to test oils of other types having various viscosities and synthetic fluids. It is recommended, however, that the test temperature be raised to 82 ± 1°C when testing products more viscous than 90 cSt (mm²/s) at 40°C. For higher viscosity oils where there is insufficient mixing of oil and water, Test Method D 2711, is recommended.

Other test temperatures such as 25°C can also be used.

When testing synthetic fluids whose relative densities are greater than that of water, the procedure is unchanged, but it should be noted that the water will probably float on the emulsion or liquid.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 6.3-6.5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water[2]

D 1141 Practice for the Preparation of Substitute Ocean Water[3]

D 1193 Specification for Reagent Water[4]

D 2711 Test Method for Demulsibility Characteristics of Lubricating Oils[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[5]

3. Summary of Test Method

3.1 A test specimen consisting of a 40-mL sample and a 40-mL quantity of distilled water (Note 3) are stirred for 5 min at 54°C (Note 1) in a graduated cylinder. The time required for the separation of the emulsion thus formed is recorded either after every 5 min or at the specification time limit. If complete separation or emulsion reduction to 3 mL or less does not occur after standing for 30 min or some other specification time limit, the volumes of oil (or fluid), water, and emulsion remaining at the time are reported.

4. Significance and Use

4.1 This test method provides a guide for determining the water separation characteristics of oils subject to water contamination and turbulence. It is used for specification of new oils and monitoring of in-service oils.

5. Apparatus

5.1 *Cylinder*, 100-mL, graduated from 5 to 100 mL in 1.0-mL divisions, made of glass, heat-resistant glass,[6] or a chemical equivalent. The inside diameter shall be no less than 27 mm and no more than 30 mm throughout its length, measured from the top to a point 6 mm from the bottom of the cylinder. The overall height of the cylinder shall be 225 to 260 mm. The graduation shall not be in error by more than 1 mL at any point on the scale.

5.2 *Heating Bath*, sufficiently large and deep to permit the immersion of at least two test cylinders in the bath liquid up to their 85-mL graduations. The bath shall be capable of being maintained at a temperature of 54 ± 1°C (Note 1), and shall be fitted with clamps which hold the cylinder in a position so that the longitudinal axis of the paddle corresponds to the vertical center line of the cylinder during the stirring operation. The clamps shall hold the cylinder securely while its contents are being stirred.

5.3 *Stirring Paddle*, made of chromium-plated or stainless steel and conforming to the following dimensions:

Length, mm (in.)	120 ± 1.5 (4 23/32 ± 1/16)
Width, mm (in.)	19 ± 0.5 (3/4 ± 1/64)
Thickness, mm (in.)	1.5 (1/16)

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.C0.02 on Corrosion and Water/Air Separability.

Current edition approved Nov. 10, 2002. Published December 2002. Originally approved in 1964. Last previous edition approved in 1998 as D 1401–98.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 05.02.

[6] Borosilicate glass has been found satisfactory for this purpose.

It is mounted on a vertical shaft of similar metal, approximately 6 mm (¼ in.) in diameter, connected to a drive mechanism which rotates the paddle on its longitudinal axis at 1500 ± 15 rpm. The apparatus is of such design that, when the cylinder is clamped in position and the paddle assembly is lowered into the cylinder, a positive stop engages and holds the assembly when the lower edge of the paddle is 6 mm from the bottom of the cylinder. During the operation of the stirrer, the center of the bottom edge of the paddle shall not deviate more than 1 mm from the axis of rotation. When not in operation, the paddle assembly can be lifted vertically to clear the top of the graduated cylinder.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II in Specification D 1193.

6.3 *Cleaning Solvents, Light-Hydrocarbon*, such as precipitation naphtha (**Warning**—Health hazard) for petroleum oils. Use other appropriate solvents for dissolving synthetic fluids.

6.4 *Acetone*, (**Warning**—Health hazard, Flammable.)

6.5 *Cleaning Reagent*, Cleaning by either hot NOCHROMIX[8] (**Warning**—Corrosive. Health hazard oxidizer), or a 24-h soak at room temperature in MICRO[9] solution gave acceptable, statistically equivalent results in round-robin testing.

7. Sampling

7.1 The test is very sensitive to small amounts of contamination. Take samples in accordance with Practice D 4057.

8. Preparation of Apparatus

8.1 Clean the graduated cylinder by removing any film of oil (or fluid) with cleaning solvent followed by a wash first with acetone and then with tap water. The glassware shall be further cleaned with a suitable cleaning reagent. Rinse thoroughly with tap water and then with reagent water. Inspect the cylinders for any residue or water droplets adhering to the inside walls. Both conditions indicate a need for additional cleaning.

8.2 Clean the stirring paddle and shaft with absorbent cotton or tissue wet with cleaning solvent and air dry. Care must be taken not to bend or misalign the paddle assembly during the cleaning operation.

9. Procedure

9.1 Heat the bath liquid to 54 ± 1°C (Note 1) and maintain it at that temperature throughout the test. Add reagent water (Note 2 and Note 3) to the graduated cylinder up to the 40-mL mark and then add to the same cylinder a representative sample of the oil (or fluid) under test until the top level of the oil reaches the 80-mL mark on the cylinder. Place the cylinder in the bath and allow the contents to reach bath temperature. Heating time may vary with type of equipment and can reach up to 30 min.

NOTE 2—If initial volumetric measurements are made at room temperature, expansion occurring at the elevated test temperature will have to be considered. For example, there will be a total volumetric expansion of about 2 to 3 mL at 82°C. Corrections to each volume reading at 82°C, therefore, should be made so that the total of the volume readings made for oils (or fluid), water, and emulsion does not exceed 80 mL. An alternative procedure which would avoid the corrections is to make the initial volumetric measurements at the test temperature.

NOTE 3—A 1 % sodium chloride (NaCl) solution or synthetic sea water, as described in Practice D 1141 or Test Method D 665, can be used in place of distilled water when testing certain oils or fuels used in marine applications.

9.2 Clamp the cylinder in place directly under the stirring paddle. Lower the paddle into the cylinder until the stop engages at the required depth. Start the stirrer and a stop watch simultaneously and adjust the stirrer, as required, to a speed of 1500 ± 15 rpm. At the end of 5 min, stop the stirrer and raise the stirring assembly until it is just clear of the graduate. Wipe the paddle with a policeman (Note 4), allowing the liquid thus removed to drop back into the cylinder. Remove the cylinder from the retaining clamps and transfer it carefully to another section of the bath. At 5-min intervals, or at the specification time limit identified for the product being tested, lift the cylinder out of the bath (see Note 5), inspect, and record the volumes of the oil (or fluid), water, and emulsion layers.

NOTE 4—The policeman should be made of material resistant to the oil or fluid.

NOTE 5—It is not necessary to lift the cylinders out of the bath for inspection if the heating bath is constructed with at least one transparent side that allows for clear visual inspection of the oil (fluid), water, and emulsion layer volumes while the cylinder remains immersed in the bath.

10. Report

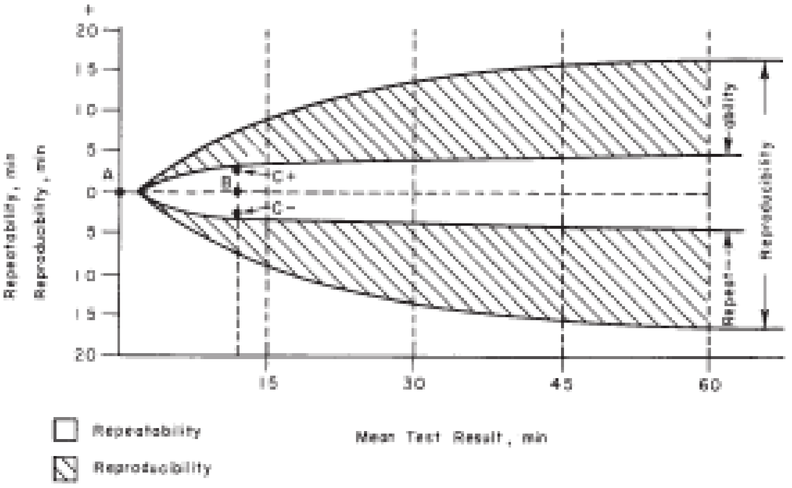
10.1 *Recording Measurements at 5–min Intervals*—Record the time until either (*1*) the product passes the water separability requirements it is being tested against, or (*2*) the test limit for water separability is exceeded (usually 3-mL emulsion or less for 30 min at 54°C and 60 min at 82°C). The maximum volume to be reported as the *oil layer* is 43 mL (see Note 6). For uniformity, test results may be reported in the manner shown in the following examples:

---

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[8] The sole source of supply of NOCHROMIX known to the committee at this time is Godax Laboratories Inc., 720–B Erie Ave., Takoma Park, MD 20912. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

[9] The sole source of supply of MICRO known to the committee at this time is International Products Corp., P.O. Box 70, Burlington, NJ 08016. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.



Use of Chart—Calculate the mean test result in minutes. Enter chart at the zero point, *A*, on the ordinate and move to the right on the abscissa to point *B*. Compute and locate the deviation points *C+* and *C−*, from the mean test result. If the deviation points fall within the repeatability area, then the results are within the precision of the test.

Example—An oil has emulsion of 40-40-0 (10 min) and 40-40-0 (15 min). The mean test result is 12.5 min (*B*) and the deviation from the mean is +2.5 (*C+*) and −2.5 (*C−*).

These points fall within the repeatability area.

Use this graph similarly for the reproducibility of means of different laboratories.

FIG. 1 Chart for Determining Test Precision

40-40-0 (20)	Complete separation occurred in 20 min. More than 3 mL of emulsion had remained at 15 min.
39-38-3 (20)	Complete separation had not occurred, but the emulsion reduced to 3 mL so the test was ended.
39-35-6 (60)	More than 3 mL of emulsion remained after 60 min—39 mL of oil, 35 mL of water, and 6 mL of emulsion.
41-37-2 (20)	Complete separation had not occurred but the emulsion layer reduced to 3 mL or less after 20 min.
43-37-0 (30)	The emulsion layer reduced to 3 mL or less after 30 min. The emulsion layer at 25 min exceeded 3 mL, for example, 0-36-44 or 43-33-4.

10.1.1 *Recording Measurements at the Specification Time Requirement Only*—Record the volumes for oil (or fluid), water, and emulsion layers at the specification time limit and determine whether (*1*) the product passes the water separability requirements it is being tested against, or (*2*) the test limit for water separability is exceeded (usually 3-mL emulsion or less for 30 min at 54°C and 60 min at 82°C). The maximum volume to be reported as the *oil layer* is 43 mL (see Note 6). For uniformity, test results may be reported in the manner shown in the examples provided in 10.1.

10.2 The appearance of each layer may be described in the following terms:

10.2.1 *Oil (or Oil Rich) Layer:*

10.2.1.1 Clear.

10.2.1.2 Hazy (Note 7).

10.2.1.3 Cloudy (or milky) (Note 7).

10.2.1.4 Combinations of 10.2.1.1-10.2.1.3.

10.2.2 *Water or Water-Rich Layer:*

10.2.2.1 Clear.

10.2.2.2 Lacy or bubbles present, or both.

10.2.2.3 Hazy (Note 7).

10.2.2.4 Cloudy (or milky) (Note 7).

10.2.2.5 Combinations of 10.2.2.1-10.2.2.4.

10.2.3 *Emulsion:*

10.2.3.1 Loose and lacy.

10.2.3.2 Cloudy (or milky) (Note 8).

10.2.3.3 Creamy (like mayonnaise) (Note 8).

10.2.3.4 Combinations of 10.2.3.1-10.2.3.3.

NOTE 6—Certain oils may produce a hazy oil layer. In situations where the measurement of the oil and water layer indicates essentially complete separation, the upper layer should be reported as oil. If there are two layers and if the upper layer is more than 43 mL, this layer should be considered the emulsion layer.

NOTE 7—A hazy layer is defined as being translucent and a cloudy layer opaque.

NOTE 8—The principal difference between cloudy and creamy emulsions is that the former is quite fluid and probably unstable while the latter has a thick consistency and is probably stable. A cloudy emulsion will readily flow from an inclined graduate while a creamy emulsion will not.

10.3 The appearance of the oil/emulsion and water/emulsion interfaces may be described in the following terms:

10.3.1 Well-defined, sharp.

10.3.2 Ill-defined, bubbles.

10.3.3 Ill-defined, lace.

10.4 Report the test temperature if other than 54°C and the aqueous medium if other than distilled water.

11. Precision and Bias

11.1 *Precision*—The precision of this test method was obtained on steam-turbine oils having viscosities of 28.8 to 90 cSt (mm^2/s) at 40°C and using time to 3 mL or less emulsion as the test completion. This precision is expressed graphically in Fig. 1. The graph shows the maximum allowable deviation in minutes for repeatability and reproducibility (95 % confidence) from mean emulsion test results for these oils. It may not be applicable to other oils or fluids.

11.2 *Bias*—The procedure in this test method for measuring water separability has no bias because the value for water separability is defined only in terms of the test method.

12. Keywords

12.1 emulsion; petroleum oils; steam-turbine oils; synthetic fluids; water separability

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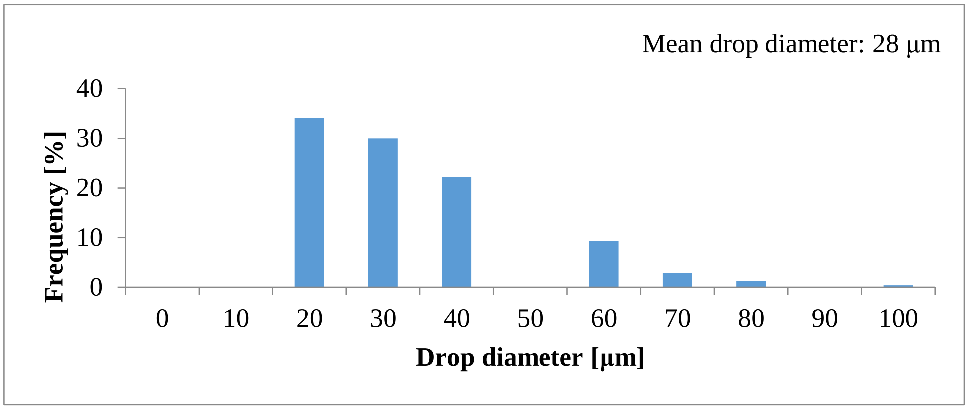
F. Drop size distributions in emulsions

- 31001



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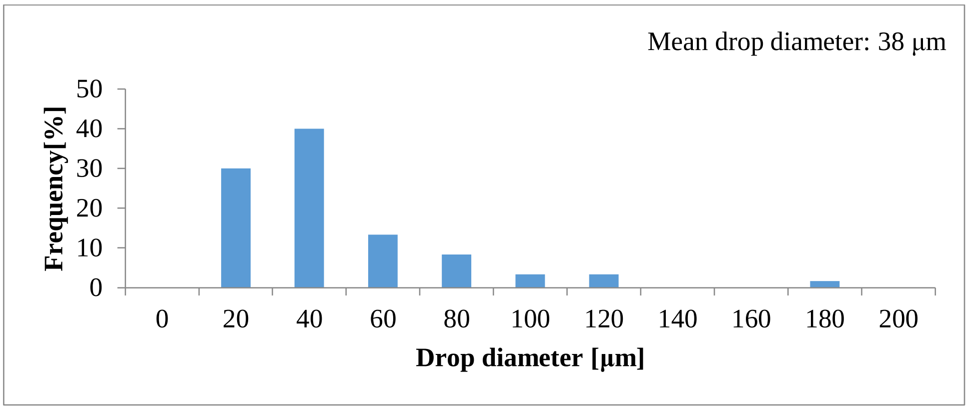

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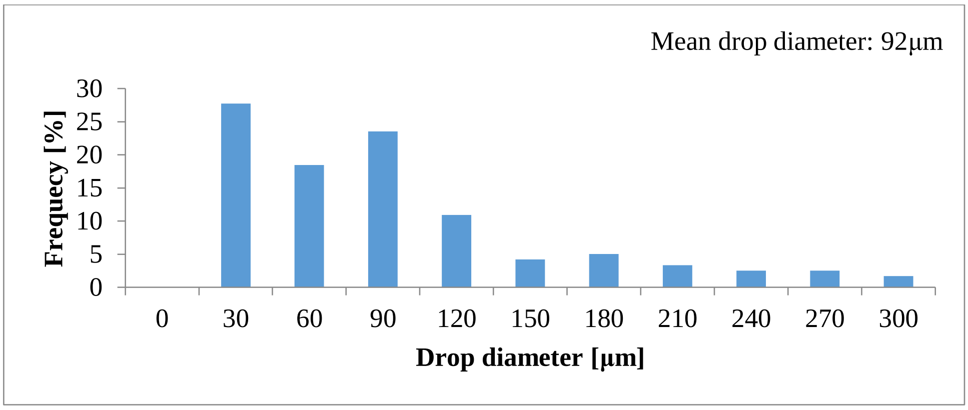
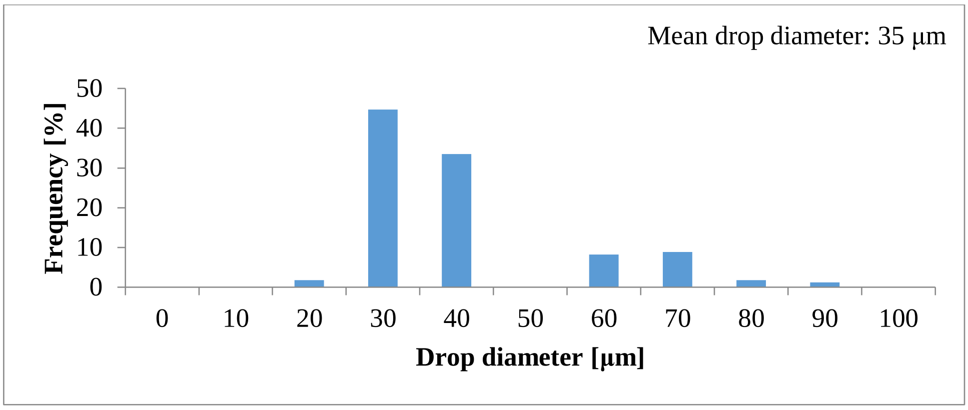
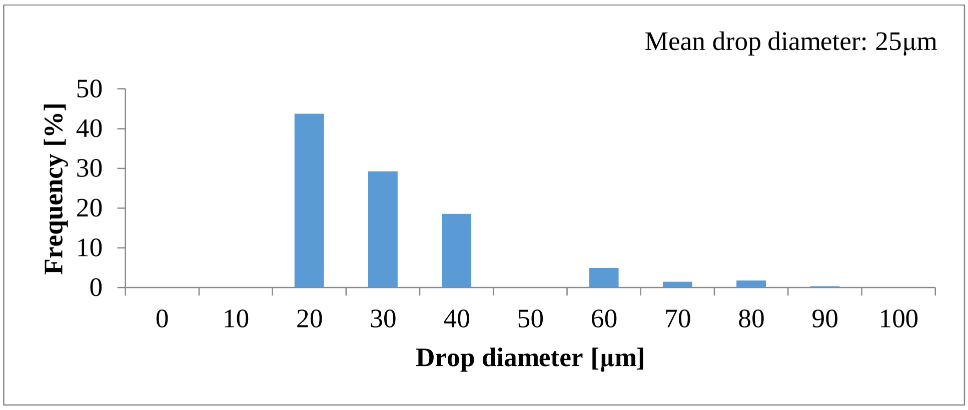


- NaCl, 1%



- $CaCl_2$, 1%



- $CaCl_2$, 100%