Treatment of Water in Heavy Crude Oil Emulsions with Innovative Microemulsion Fluids

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Abstract

In-situ formation of water-in-oil emulsions in crude oil is one of the severe problems encountered during the production phase of oil wells. These in-situ emulsions produce crude oil viscosities that are much higher than the viscosities of native crude oil. It is well known that these problems are frequently found in heavy and extra-heavy crude oils, because these oils have significant amounts of carboxylates and naphthenates, which are polar molecules that are excellent stabilizers of water-in-crude oil emulsions.

These in-situ emulsions form in the reservoir and in the near-wellbore regions. However, when the crude oil is produced to surface, they may also develop at various downstream locations such as at wellheads, pipelines, separation plants, and even at the refinery before processing. The major factors that determine the formation of in-situ emulsions are the crude oil/produced water ratio, properties and composition of the crude oil and connate water, and some reservoir properties such as temperature. Demulsifiers are traditionally used to prevent the formation of in-situ emulsions. These treatments are generally effective. In situations where the demulsifier chemistry cannot change the curvature of the oil/water interface, the emulsification problem persists, with inherent consequences such as loss of production, high-pressure drops in flow lines and increased operational costs.

A solution to treat these troublesome emulsions is to use microemulsion fluids technology. Microemulsion fluids typically have very low oil/water interfacial tension and can alter the interfacial curvature of the emulsion, producing coalescence and increasing water droplet size until the emulsion separates into water and crude oil.

This paper discusses the evaluation of microemulsion fluids as a treatment for emulsified heavy crude oil samples from oil fields. The evaluation includes crude oil characterization, interfacial tension, microscopy evaluation, fluids compatibility tests and treatment of the emulsion in an HPHT filtration cell.

Emulsion Problems in Heavy Crude oil

Impaired production from heavy crude oil reservoirs can be triggered by a variety of factors including the water composition, inherent high viscosity of the crude oil, composition of the crude oil, and the energy imparted during the pumping and flow through the equipment used during the wellbore construction process, as well as during the production phase of the wells. The emulsified water in the crude oil could

be production water, completion brine, drilling fluids, injection water or a combination of some or all of these.

The "heavy" nature of crude oil is primarily due to a relatively high proportion of complex, high molecular weight, aromatic and naphthenic compounds and a relatively low proportion of low carbon number compounds with low molecular weight (Alwadani 2009). It is known that the composition of the heavy crude oils includes asphaltenes, resins, naphthenates, mercaptans, and, in general, polar compounds such as carboxylates associated with these high molecular weight molecules. Such components have high interfacial activity and promote interaction between the crude oil and water phase that results in formation of water-in-crude oil emulsions.

Emulsions of water-in-crude oil or brine-in-crude oil could form either in the reservoir, near the wellbore or in downhole and surface facilities during the wellbore construction or during the production of the wells. In addition to the natural components with interfacial activity that are present in the crude oil, additives used in drilling, completion and hydraulic frac fluids such as emulsifiers, friction reducers, ROP enhancers, corrosion inhibitors, etc., could also potentially produce emulsions when they are in contact with some crude oils. The extent of damage while drilling is usually restricted to the near-wellbore region unless large volumes of drilling fluids have been lost to the reservoir. Emulsion problems could also result if high-rate acid stimulation treatments are pumped into a medium or heavy crude oil reservoir without the appropriate additives to prevent emulsion formation; that is, the mechanical energy and low pH of the stimulation fluid can create an ideal environment for generating unwanted viscous emulsions (Daaou and Bendedouch, 2012).

In thermal enhanced oil recovery (EOR) processes such as in-situ combustion and steam injection, emulsions are created through the addition of thermal energy that disperses water in crude oil. These emulsions are very stable and cause severe production problems (Bertness 1965). Cyclic Steam Stimulation (CSS) and Steam Assisted Gravity Drainage (SAGD) are effective methods for producing heavy oil. However, these processes can cause formation damage in the reservoir that can severely affect the performance of post-steam production. The formation damage primarily involves formation of stable in-situ emulsions, with the consequent reduction in oil production (Castro, 2001).

Other operations that could increase the possibility of water-in-crude oil emulsion formation include (1) water injection to maintain reservoir pressure; (2) casing leaks and perforated production pipe that can lead to the migration of water into an oil-producing zone; and (3) gas lift, where agitation in the produced liquid is introduced, favoring emulsification of water in the crude oil, etc. In all cases, mechanical energy is required to generate small emulsified water droplets in the presence of the two immiscible fluids (water and crude oil) and surface active agent molecules that act as emulsifiers, and are found either in the crude oil or in the fluids pumped into the wells (Nuraini 2011).

Depending on the amount of mechanical energy imparted and the strength of the added emulsifiers or natural surfactants inherent to the crude oil, the emulsion can have very strong or very weak stability. When a crude oil/water mixture passes through pumps, production tubing, safety valves, or other process equipment that produce high shear conditions, the result could be a very stable emulsion. In the case of crude oil/water systems that do not have molecules acting as emulsifiers, a dispersion of one liquid into the other phase is generated, but the dispersed droplets will coalesce and separate relatively easily after the shear condition terminates.

Heavy crude oil with stable emulsions not only create flow assurance issues, they also increases surface treatment costs for pipelines, separation facilities, and processing plants. The disposal of the water, salt, and residual oil separated from the crude oil before the refining process can be costly and affect the value of the operator's asset.

To select an efficient treatment for crude oil emulsions, it is important to understand where and how they are produced, their composition and the properties of the water-in-crude oil emulsions.
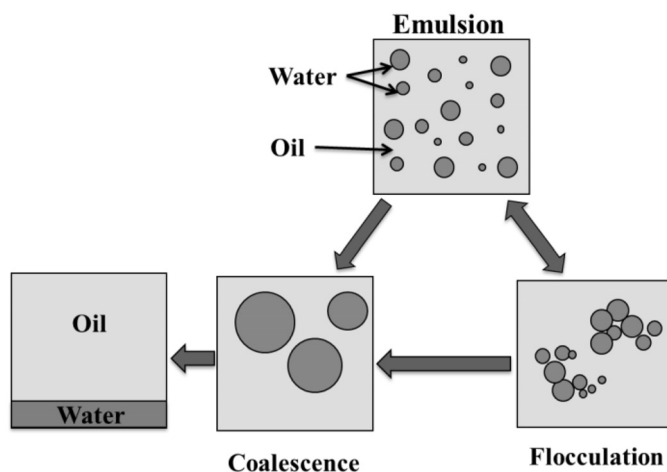
Figure 1—Schematic of flocculation and coalescence process.

Fundamentals of Emulsions

The properties of the emulsion, interfacial properties and the principle of the emulsion breaking using the concept of optimum formulation at hydrophilic lipophilic difference (HLD) zero are discussed in the next sections because these fundamental concepts are important in the selection of the treatment fluids of water-in-oil crude emulsions.

Definition and Properties of Emulsions

A water-in-oil emulsion is defined as a system of two immiscible liquids, one of which is dispersed as droplets (the dispersed or internal phase) throughout the other (the continuous or external phase). A third component present in the emulsion is the surface-active material that stabilizes the dispersed droplets (Becker 2001, Friberg and Larsson 1997). The emulsion droplet size, by definition, is greater than one micron. Many emulsion properties, such as stability and rheology, depend on average and distributions of their droplets size (Becker 2001, McClements 2005).

The high concentration of water droplets and smaller average size results in higher apparent viscosity of the crude oil, causing decreased flow rate and well productivity (Borges et al. 2009).

Emulsion stability is a property that requires some discussion. There is no standard way to estimate stability. This depends on the conditions under which the emulsion is handled. In many instances, the time required for a certain amount of emulsion to separate is a good indication of the stability.

Emulsion stability depends on many factors related to adsorbed molecules with surface activity called "surfactants" or natural surfactants. There are various emulsion breakdown processes (creaming, Ostwald ripening, flocculation and coalescence). The more important processes in crude oil emulsions are flocculation and coalescence. Fig. 1 shows a schematic of these breakdown processes.

The flocculation process refers to aggregation of the droplets, without any change in the primary droplet size. Flocculation is the result of the van der Waals attraction forces that are universal in all dispersed systems. Flocculation may be prevented by steric stabilization; using non-ionic surfactants or polymers that form a thick layer at the liquid/liquid interface.

Coalescence occurs when two or more droplets come in contact. Thinning and disruption of the liquid film can occur, resulting in a rupture and the droplets joining each other. Coalescence is an irreversible phenomenon. In some emulsions, the dispersed droplets can become close to each other but they do not coalesce, due to electrical repulsion or the steric stabilization of the interfacial film surrounding each droplet.

Optimum Formulation and Emulsion Breaking

The principle of emulsion breaking using the concept of optimum formulation at HLD was discussed by Rondon et al. 2006. Equations 1 and 2 show the HLD empirical correlations for anionic and non-ionic surfactants, respectively. The optimum formulation at HLD = 0 presents no difference between the hydrophilic and lipophilic interaction energies of the surface active molecules in the emulsion system. This formulation condition is associated with very low interfacial tension and minimal emulsion stability, which is the desired situation for emulsion breaking (Salager et al. 1990). Fig. 2 shows a schematic of the emulsion stability variation with the HLD.
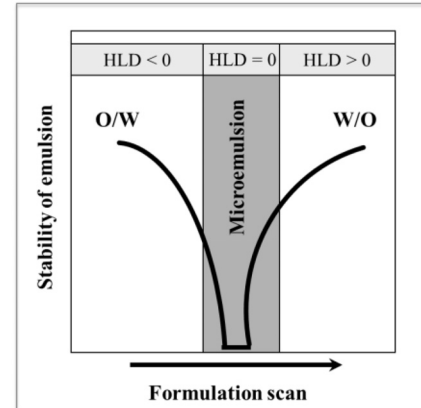

Figure 2—Emulsion stability variation with the HLD.

Fig. 2 shows that the stability decreases when the optimum formulation is approaches from either side. This facilitates the drop-breaking process and results in smaller droplet size. When the formulation comes very close to the optimum formulation the coalescence rate increases considerably. This increase in coalescence rate and the increase in drop-breaking rate are desirable conditions to eliminate emulsions formed in crude oils.

Even if the water-in-crude oil (W/O) emulsions are stabilized by natural surfactants present in the crude oil or other additives from the fluids used in the operations performed in the well, these emulsions are located on the region of HLD > 0.

$$HLD = \ln S - k \times ACN - f(A) + \sigma - a_T \times (\Delta T) \tag{1}$$

$$HLD = SAD / RT = \alpha - EON + b \times S - k \times (ACN) - \phi(A) + c_T \times (\Delta T) \tag{2}$$

where,

S is the optimum salinity of the microemulsion system, expressed in wt. % NaCl with respect to the aqueous phase

K is a constant for a given surfactant that depends on the type of surfactant head group

ACN is the linear alkane carbon number of the oil (for a non-linear hydrocarbon oil or for a non-hydrocarbon oil it becomes EACN, equivalent alkane carbon number)

$f(A)$ and $\varphi(A)$ are functions of the alcohol/co-surfactant type and concentration

σ and α are parameters that are functions of surfactant structure

a_T is a constant (~0.01 when temperature is in Celsius)

T is the temperature of evaluation

T_{ref} is a reference temperature

EON is the average number of ethylene oxide group per molecule of nonionic surfactant.

b, k, a_T and c_T are empirical constants that depend on the type of system.

The concept of HLD is also used to formulate microemulsion fluids because at the optimum formulation or HLD zero the systems reach ultra-low interfacial tension, and high solubilization. At this condition, the surfactants have the same affinity for the water and the oil phases and the interfacial free energy of the system is near zero, producing a maximum solubilization of the oil.

Interfacial Properties and Other Considerations in Water-in-Crude Oil

Detailed properties of the emulsion film, together with a fundamental knowledge of the chemistry of the interfacially-active components in the crude oil, are key factors that need to be understood in order to be able to properly select solutions to treat or prevent the crude oil emulsions.

Interfacial properties and other considerations that have a considerable effect on the emulsified fluids as listed below:

- Reduction of interfacial tension decreases average droplet size.
- Emulsions with small droplets with less than 10 microns are very stable emulsions.
- High acid number indicates the presence of components with interfacial activity in the crude oil, and these will activate as natural surfactants when contacted with acid or base. Therefore, the pH affects the droplet size and emulsion formation.
- Acid treatments could lead to precipitation of asphaltenes and resins, completely altering the droplet film and stabilizing the emulsions.
- High interfacial viscosity and resistance of the emulsifier film to be deformed reduces the coalescence of water droplets in the emulsion. Low pH values in the aqueous phase can lead to high interfacial viscosity and a viscoelastic film that produces a mechanical barrier to droplet coalescence.
- High viscosities of external phase crude oils decrease the coefficient of diffusion and decrease the droplet collision frequency, increasing the stability of emulsions.
- Divalent cationic molecules, such as calcium and magnesium, tend to produce a very compact film around the droplets due to electrostatic effects.

Microemulsion Treatment

Mobilization of high-viscosity crude oil emulsions from the formation rock to the surface facilities is not an easy task, especially at low temperatures. To restore the native viscosity of the crude oil and increase its mobilization and production, a fluid with low viscosity and interfacial properties that destabilizes or breaks the emulsions should be used for wellbore clean-up or displacement of fluids. In these scenarios, a custom-designed, downhole or surface microemulsion treatment to demulsify the crude oil and promote flow may be beneficial and extend the production life of the well.

Microemulsions are single-phase bicontinuous systems, in which the oil and water coexist separated by an interfacial film of surfactant molecules. They are thermodynamically-stable systems composed of a solvent or oil, brine, surfactants and optional co-surfactants and linker molecules. In general, single-phase systems such as microemulsions are less viscous than multiphase systems, e.g., drilling fluids and emulsified crude oils. These microemulsions could be produced at the surface or inside the well by pumping surfactant in solution packages.

To predict the behavior of the microemulsion when it contacts crude oil emulsions, the important tests that need to be evaluated for each particular crude oil system are the emulsion breaking and sludge destruction, without adding mixing energy (diffusion process) to the microemulsion/crude oil emulsion system.

Microemulsions are promising fluids that have been used to clean up near-wellbore damage (Quintero et al. 2011). They are chosen over traditional organic solvent systems because they can solubilize polar components, e.g., salts, non-polar solvents, and slurrify the precipitated materials from crude oil, e.g., wax and asphaltenes particles. They exhibit low viscosity and intensify the surfactant action by decreasing the interfacial tension, altering wettability, and increasing solubility of oil (Paul and Moulik 2001).

A good microemulsion formulation should be able to resist changes in salinity, temperature, and type of oil to which it is exposed. The insensitivity of the system to these variables is formulated to meet application requirements, using the most-compatible solvents and the best surfactant package. The
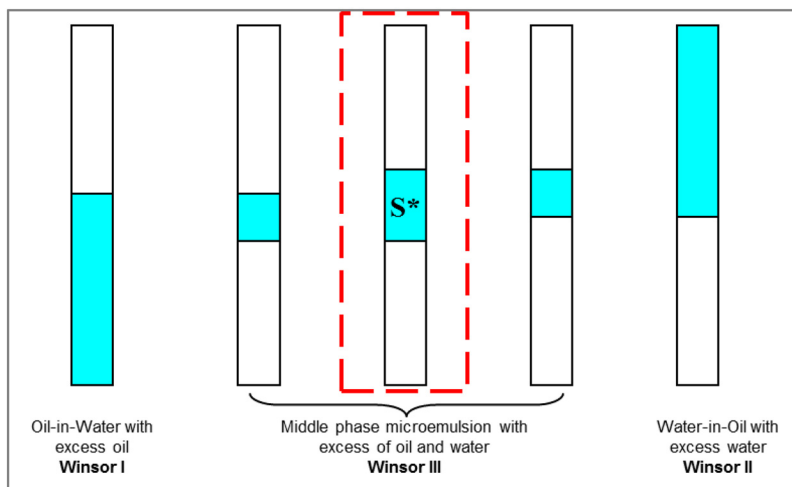
Figure 3—Winsor behavior and optimum formulation point (S*).

surfactants are chosen based on the application and type of solvents used or type of oil to be contacted. Anton et al. 1992 demonstrated how to blend different surfactants to form insensitive microemulsions.

Generally, two-phase behavior is observed at low surfactant concentration. If the surfactant concentration is increased, one-, two-, or three-phase behavior patterns can be observed. A two-phase behavior system is formed when the surfactant has a distinctive preference for the water in the system. This is a Winsor I (W I) system, defined as an oil-in-water (O/W) emulsion in equilibrium with excess oil. If the surfactant preference is for the oil, the result is a Winsor II (W II) system, whereby excess water coexists with a water-in-oil (W/O) emulsion. If the surfactant has equal affinity for the water and the oil, the system is called Winsor III (W III), in which a microemulsion coexists with an excess of water and oil. Winsor IV (W IV) systems are defined as a single-phase microemulsion in which the concentration of surfactant is high enough for the microemulsion to solubilize all the water and oil present in the system. Fig. 3 shows the Winsor phase behavior. The optimum formulation point (S*) is defined as the point at which the middle phase is a microemulsion. In the S* zone, the mutual solvency between water and oil is maximized and the interfacial tension is minimized (near zero). The behavior is a W III and the excess of water and oil are equal. If the surfactant concentration is increased at this point, Winsor IV behavior is easily attained.

The system is considered in an optimum formulation at S* condition. When HLD values are greater than zero (positive), the affinity for the oil increases and system will evolve from WI → WIII →WII. On the other hand, if the value is less than zero, i.e., negative, the affinity for the water will increase and the system evolves from WII → WIII → WI (Salager et al. 2001).

Laboratory Tests and Results

Sample Characterization

Samples of crude oil and formation water from offshore California USA were characterized and used to evaluate microemulsions for breaking emulsions. The samples of the formation water and crude oil are shown in Fig. 4.

The crude oil sample exhibited high viscosity and very low pourability properties. Several tests were performed with the sample to determine the cause of the high viscosity. The properties measured were API degree, viscosity, solids content, water composition, and resin/asphaltenes ratio.

A hydrometer was used to determine the crude oil density at 60°F. The °API of the crude oil sample was calculated using the standard equation of °API (ASTM D 1298 – 85) and the SG of the crude oil. The
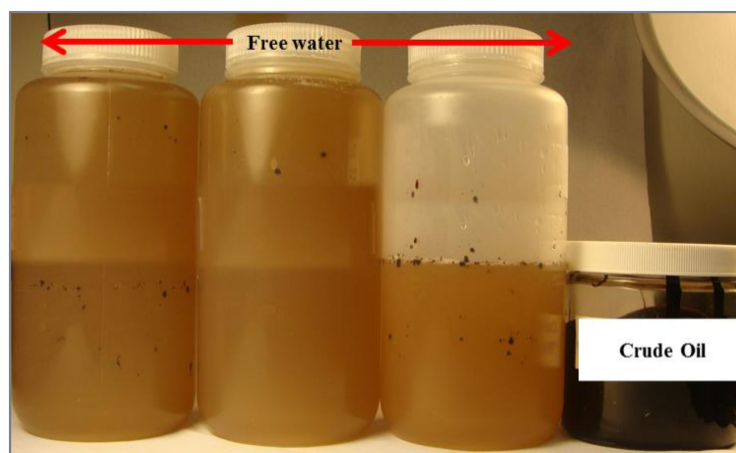
Figure 4—Samples of production water and emulsified crude oil.

test results indicate that the crude oil sample had a 21.3°API. According to the American Petroleum Institute (API) classification system, this sample was a heavy crude oil (ASTM D 1298–85).

The asphaltenes and resin content were measured using the ASTM D6560-00 methods described by Kim et al. 1996. For this particular crude oil, the resin/asphaltenes ratio was equal to 4.6. Values greater than the range of 2.5 – 3.0 indicated the resin content was usually sufficient to prevent the asphaltenes precipitation.

Table 1—Crude oil sample properties.

Properties of crude oil sample	Values
°API at 60 °F	21.3
Asphaltenes, wt%	11.16
Resin, wt%	51.25
Percentage of water and solids, %	29.2
Solids content, vol%	10.00
Chlorides in production water, mg/L	18,000

Table 1 summarizes the California crude oil properties. Following the guidelines described in the ASTM D4007 – "Standard Method for Water and Sediment in Crude Oil by Centrifuge Method", the water and sediments content from the crude oil sample was determined to be 29.2 vol%, where 11% were solids. The results were corroborated by performing a standard retort test described in the API 13B-2 to determine oil, water, and solids concentration. The retort test resulted in a measurement of 10 vol% solids. These results indicated the sample had fine solids that could act as a mechanical stabilizer of oil droplets in crude oil emulsions. The fine solids were smaller than the emulsion droplets. They precipitated at the oil/water interface and were wetted by both oil and water. The effectiveness of these fine particles on stabilizing the emulsion depends on many factors, such as particle size, particle interactions, and wettability of the particles. Some common solids present in crude oils are clays, sand, scales, asphaltic products, corrosion products, and drilling fluid solids (Kokal 2002).

The production water was analyzed using ion chromatography and the results showed the presence of chlorides in a concentration of 18,000 mg/L. Bromides were present at a low concentration (200 mg/L).

Moradi et al. 2011 studied the effect of the salinity on W/O emulsions in crude oils with different synthetic production water salinities, showing low stability at higher concentrations. A value of 18,000 mg/L of chloride ions is considered a low value, thus the internal aqueous phase stability in the 21.3 °API California crude oil may be due the low salinity of the emulsified production water.

Characterization by Microscopy

Optical microscopy was used to determine the presence of water-in-crude oil emulsion in the California crude oil sample. Fig. 5 shows images of the crude oil and the clearly visible tiny water droplets in oil in the range of 1 to 2 microns. The droplets at the edge of the capillary tube are the easiest to see because they are in the thinnest layer of sample.
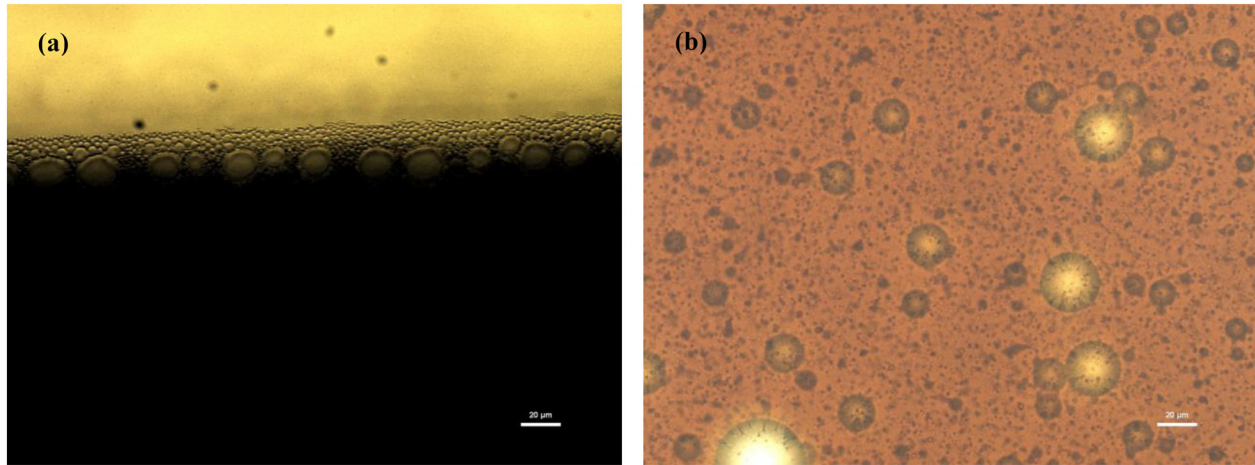
Figure 5—Water droplets present in the crude oil sample.

Due to the nature of tight emulsion droplets in a crude oil sample, it is often difficult to observe them under a microscope. A standard glass slide made it difficult to observe the internal emulsions without dilution because the crude oil was dark in color and a thick layer of oil filtered out most of the transmitted light. Fig. 5a shows a sample without dilution in a thin/flat glass capillary with the ends of the capillary sealed to minimize sample movement within the capillary space. Fig. 5b shows the microscopy image of the sample diluted with xylene.

In general, microscopy is a well-known technique used to determine the particle or droplet size in emulsified fluids. The typical information found in images is sample state, geometry, dispersity, etc. For an emulsion, the most important finding is the droplet size, concentration, and distribution.

The samples must have certain optical properties, because the technique relies on reflection, refraction, scattering, and absorption of radiation. To study emulsions under the microscope, they must be transparent and the external and internal phases must have different refractive indices, different color. The resolution limit of the equipment must be taken into account; additional errors could be added to the measurement (Sjöblom et al. 2003).

As with most techniques, proper sampling is critical. The most common sampling is performed by deploying the sample droplet between an object slide and a cover slide. Often, some form of sample cell may have optical advantages, for example hollow – flat microcapillaries. Inside a capillary, the sample will remain protected against evaporation, movement can be avoided, and the emulsion can be seen without altering the size and/or distribution internal phase. Capillary tubes are often used to study stable systems.

Viscosity Evaluation

Fig. 6a presents the viscosity of the neat crude oil sample (without emulsified water) measured at various temperatures. The viscosity decreased with increase temperature, which is a typical behavior encountered in crude oils. The sample of the same crude oil with 29.2% water and sediments has much higher viscosity. The viscosity measured at 75 °F increased from about 100 cP to about 42,000 cP by having 29.2% internal phase. Fig. 6a shows that the apparent viscosity increased with a noticeable jump of up to several orders of magnitude as the emulsified water cut approached the limit of high concentration internal phase.

The increase of the emulsified internal phase or water cut in the crude oil resulted in an increased viscosity, especially at low shear rates. Fig. 6b is a schematic of typical behavior of the changes in relative viscosity of crude oil with the increase of emulsified water cut and various values of average droplet size. A transition occurred because the spherical drops reached the state of close packing, leading to changes in the rheological behavior of emulsions (Derkach 2009, Adb et al. 2014).
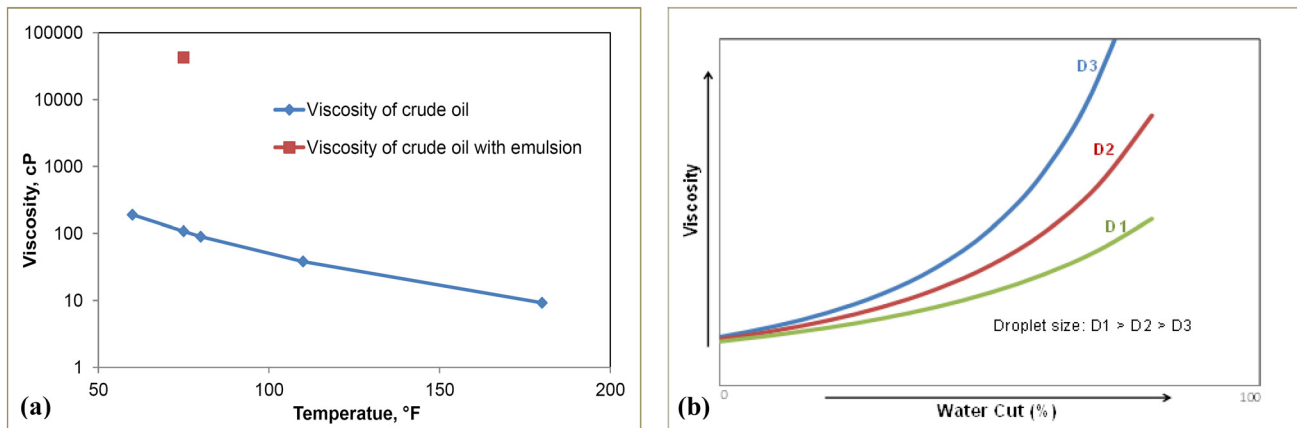
Figure 6—Apparent viscosity of (a) crude oil sample from California, (b) schematic of viscosity of the crude oil with increase of emulsified water cut
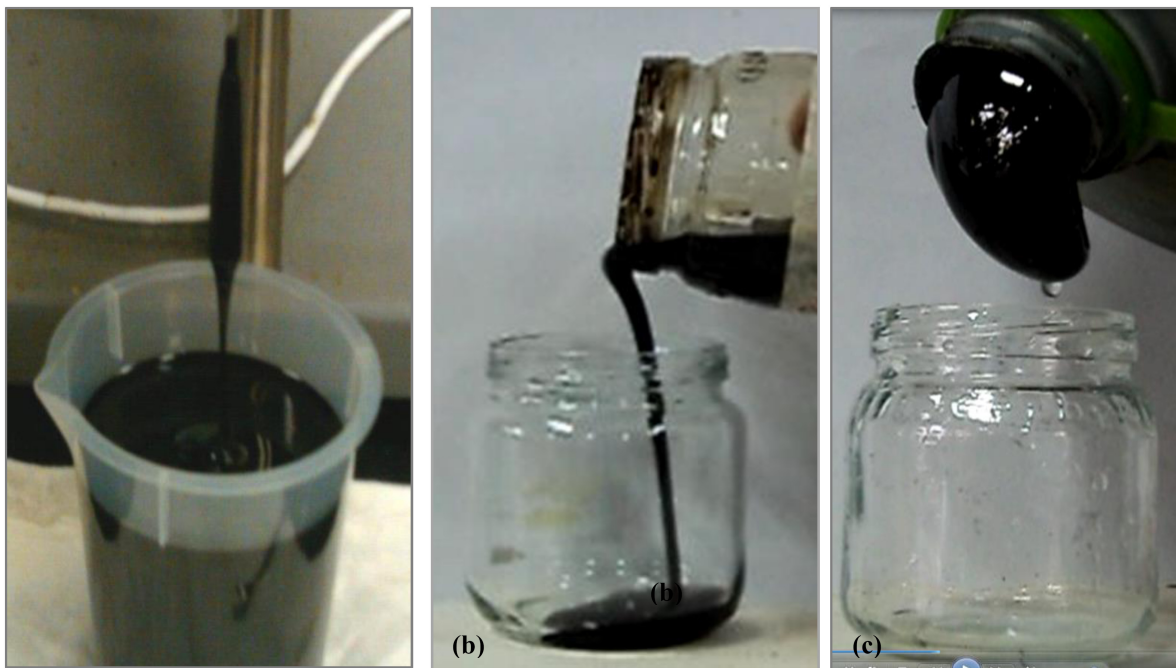

Figure 7—Apparent viscosity of the crude oil sample and comparison with other crude oils: (a) crude oil sample from California (21.6°API), (b)Venezuelan crude oil (22°API), and (c) Venezuelan crude oil (12.8°API) at about 68 °F.

Such change in viscosity behavior is more significant when the average size of water droplets is very small (Alboudwarej, et al. 2007). The droplet size influences the volume-to-surface area ratio, leading to a more pronounced increase of viscosity with the decreased of average droplet size.

Fig. 7a shows a sample of the heavy crude oil from California used in the tests discussed in this paper. The sample appears very viscous and has limited pourability. Fig. 7b is a picture of a typical crude oil from Venezuela having about 22 °API. The difference in appearance between the samples of Fig. 7a and 7b is that the crude oil samples of Fig. 7b do not have a large volume of water emulsified; consequently, it flowed easily from the sample container. Fig. 7c shows a picture of a very heavy crude oil as a reference. This highly viscous crude oil would not flow without applying an initial shear to the sample. When the California crude oil, with the stable water-in-oil emulsion, was tested with a Brookfield Viscometer, high viscosity values were observed, showing a behavior similar to 11 °API crude oil, despite being a 21.3 °API crude oil.

Microemulsion Fluid Formulation

Treatments using solvents, or solvent/co-solvent mixtures were screened to determine the most suitable treatment for the viscous crude oil sample containing emulsion. To achieve improved flow properties, the solvent must be almost completely miscible with all components of the crude mixture.

Fig. 8 is a photograph of the crude oil sample evaluated with two different solvents: (1) xylene and (2) a solvent/co-solvent blend.

Xylene, used in the test shown in Fig. 8a, offered only a limited dilution of the crude oil. Furthermore, the emulsified water droplets inside the crude oil were completely immiscible after the treatment as observed in Fig. 8a. Thus, the flow profile was marginally improved. On the other hand, the solvent/co-solvent mixture (Fig. 8b) offered complete miscibility of the emulsified crude oil. This solvent/co-solvent mixture reduced the crude oil viscosity and significantly improved its mobility across the glass surface of the bottle test. This type of solvent/co-solvent mixture in a microemulsion treatment fluid can be expected to destroy emulsions and increase the flow rate of viscous crude oils.

The nature of the solvent and co-solvent must be taken into account because they can be incompatible and cause separation, depending on their chemical structure and affinity.

The solvent/co-solvent mixture that produced good miscibility with the crude oil (see Fig. 8b) was used to formulate the microemulsion to treat the sample of crude oil. To design a robust microemulsion treatment fluid, it is necessary to select a combination of ionic and nonionic surfactants capable of efficiently microemulsifying the solvent/co-solvent oily phase.

Lipophilic and hydrophilic linkers were added to the system to make a stable microemulsion (Pietrangeli and Quintero 2013). The microemulsion formulation was based on Winsor phase behavior, where Winsor IV is the desired behavior in which the fluid will have low interfacial tension, high oil solubilization, produce coalescence of emulsified water droplets, and high oil recovery efficiency. Table 2 shows a generic formulation of the microemulsion fluid formulated to treat the crude oil used in this study.

Figure 8—Crude oil sample mixed with different solvents at 25°C – (a) Xylene and (b) solvent/co-solvent mixture.

Table 2—Composition of a generic microemulsion.

Components	Composition, Vol %
Solvent/co-solvent	3.0 – 6.0
Surfactant/co-surfactant	5.0 – 15.0
Linkers	0.1 – 1.0
Brine	50.0 – 80.0
Acid	0.0 – 5.0
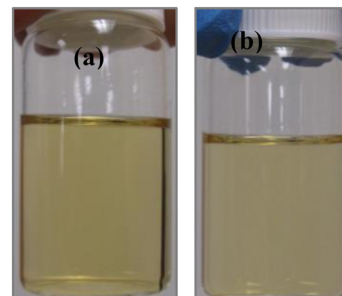
Figure 9—Microemulsion stability test (a) at 77°F, (b) at 150°F after 24 hours.

Stability Bottle Test

Phase stability is evaluated by conducting a simple bottle test. A microemulsion treatment fluid must maintain single-phase stability at different temperatures or be insensitive to temperature changes.

The test consists of adding 10 mL aliquots of the treatment fluid into small vials and placing them at controlled temperature environments. Fig. 9 shows microemulsion stability test at 77°F (a) and 150°F (b) over a 24-hour period. By remaining in a single-phase over the temperature range between 77°F and 150°F, the microemulsion blended in each vial showed good phase stability.

Detergency Bottle Test

The detergency bottle test is a simple test to deter-mine the ability of the treatment fluid to solubilize oil and mobilize crude oil emulsions. First, the crude oil and the microemulsion treatment fluid are pre–heated at 150°F. After adding 1mL of crude oil to a glass vial and spreading it across the bottom, 10 mL of microemulsion fluid is added, ensuring the treatment fluid covers all the crude oil. The bottle lid is then replaced. The vial is placed in an oven at 150°F and visually inspected at pre-determined in-

Figure 10—Detergency test (a) at 150°F and 0 minutes, and (b) at 150°F and 10 minutes.

tervals. Fig. 10a is a photo of the system at the beginning of the test. The ability of the fluid to clean the California crude oil from the bottom of the vial is observed in Fig. 10b. The crude oil is completely displaced from the bottom of the vial within 10 minutes after contacting the microemulsion, without generating any additional emulsification.
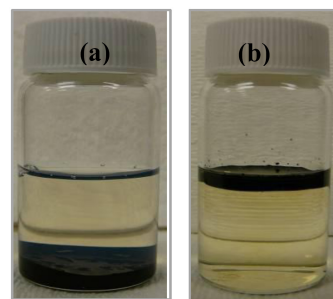
Successful near-wellbore clean-up applications requires a treatment fluids with high oil solubility potential, ultra-low interfacial tension, and low inherent viscosity to effectively solubilize oil and mobilize crude oil with tightly bound water-in-oil emulsions. A fluid with these characteristics is capable of mobilizing a viscous sludge and hydrocarbon deposits effectively without creating additional emulsification problems.

Dynamic Interfacial Tension (IFT)

The IFT between crude oil and the microemulsion fluid is evaluated using a Dataphysics Model SVT20 Spinning Drop Tensiometer. IFT is measured as function of time when two immiscible fluids are in contact and one of them contains surface active agents.

In the tests performed using California crude oil, the interfacial tensions were measured until equilibrium was attained or until the drop of crude oil was completely solubilized by the microemulsion fluid. The test was performed at 80°C (176°F) and lasted for 100 minutes. The crude oil was pre–heated at 80°C (176°F) and then injected into the microemulsion that was already in the capillary at the same temperature. As soon as the samples were in contact, the first measurement was performed. The initial interfacial tension measured between the two fluids was 1.0 mN/m. After a few minutes in contact, the interfacial tension between the liquids dropped dramatically (Fig. 11). After 20 minutes, the IFT decreased 80%, and at 100 minutes the system reached 0.1 mN/m. After the 100-minute interval, the system turned very dark with no distinctive interface, making it impossible to record further measurements.

Sludge Filter Cake Clean-up

A modified HPHT filtration test was performed to evaluate the effectiveness of the microemulsion treatment on the viscous crude oil sludge. The test is based on the API 13B-2. The aim of the test was to evaluate the efficiency of a fluid to clean-up the sludge and decrease viscous emulsions under wellbore conditions. The sludge was made by mixing 75 vol% California crude oil with 25 vol% of water-based drilling fluid (WBM).

Table 3 shows the composition of the water-based drilling fluid mixed with the crude oil.

For the tests discussed in this paper, a 40-micron ceramic disk was used. The cleaning test procedure began with the sludge deposition. A sludge mud-off was performed for 2 hours at 500 psi and 150°F. Then, the drilling fluid/California crude oil sludge in the cell was replaced with the microemulsion treatment fluid and 100 psi differential pressure was applied to the cell. When the cell reached 150°F, the bottom stem of the HPHT cell was carefully opened and the breakthrough time for the treatment fluid to pass through the sludge cake was recorded. It was previously established that the high viscosity of the California crude oil was due to tightly-emulsified water droplets. Fig. 12 shows the weight of filtrate
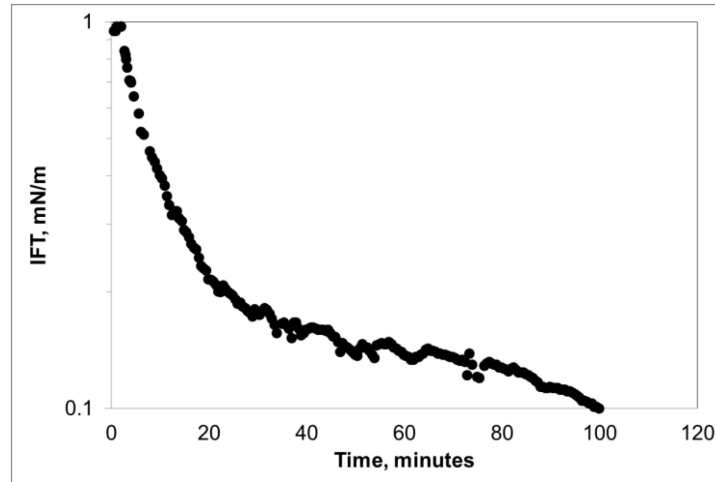
Figure 11—Dynamic Interfacial Tension values over time for the California crude oil and the microemulsion treatment at 176°F.

Table 3—Composition of water-based drilling fluid.

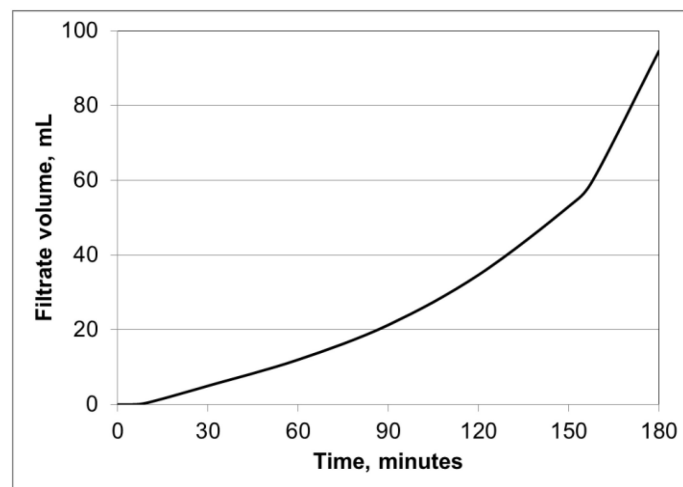| Products	Composition
Water, bbl	0.8317
Bentonite, lb	12
Polyanionic cellulose, lb	0.5
Calcium Carbonate, lb	50
Barite, lb	149.9
Density, lb/gal	12.0

Figure 12—Breakthrough filtrate volume over time at 150°F.

collected as a function of time. The viscosity of the emulsified crude oil delayed the breakthrough time. The graphic shows a moderate but exponential increase in filtrate collected over a three-hour period.

From previous studies, drilling fluids mixed with non-emulsified crude oils produce sludges that are relatively easy to break. Their graphics show a rapidly exponential growth and the filtrate is collected within a few minutes.

After all the filtrate was collected and recorded, the bottom stem of the HPHT cell was closed and the pressure was released.
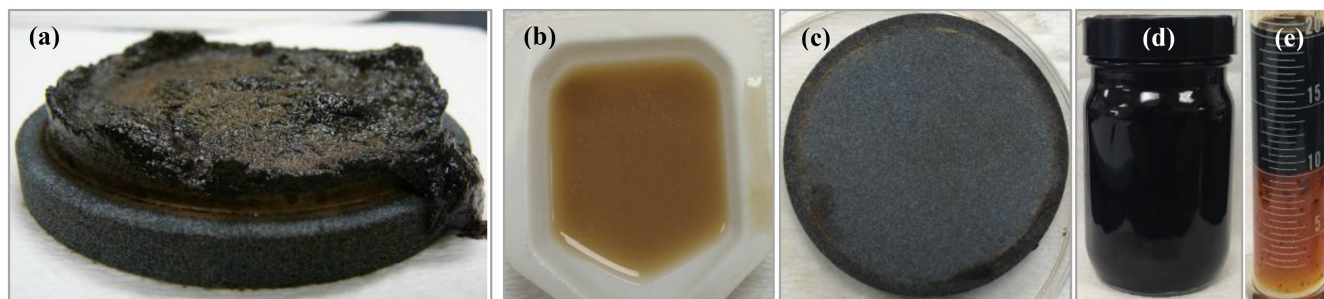
Figure 13—Sludge filter cake clean-up: (a) filter cake after treatment with microemulsion fluid, (b) solids dispersion in water, (c) aloxite disc after rinsing with fresh water, (d) filtrate collected during the test, and (d) filtrate separation after 1 hour.

The aloxite disk was removed from the cell to evaluate the characteristics of the residual cake (Fig. 13a). The untreated sludge has an oily appearance, and is compact and black. The treated sludge lost most of its black color, while the drilling fluid color remained light brown.

The residual solids on the filter cake were assessed for water-wetness and dispersability (Fig. 13b). A portion of the residual solids were submerged in fresh water. The photo shows that the filter cake solids remaining on the disc were water-wet and easily dispersed in water.

Fig. 13c shows the aloxite disc after being rinsed with fresh water. All solids are easily removable, leaving the disc completely clean, indicating that the microemulsion fluid effectively solubilized the crude oil and changed the wettability of the solids from oil-wet to water-wet. Fig. 13d shows the filtrate that was collected during the soak-and-filtrate collection period. The filtrate was a mixture of the crude oil and the microemulsion treatment fluid. Over time, the crude oil separated from the treatment fluid due to the ultra-low interfacial tension (**Fig. 14c**).

Conclusions

1. Microemulsion treatment reduced interfacial tension, thus capillary forces were reduced and the oil-in-crude oil emulsion was broken, allowing better mobility of the crude oil.
2. A single-phase microemulsion, using the non-aromatic solvent/co-solvent mixture as the oil phase, successfully treated the emulsified crude oil, exhibiting ultra-low interfacial tensions and high solubility.
3. Deep understanding of microemulsions and surfactant technology can be used to systematically develop a custom solution depending on the well requirements and crude oil characteristics.
4. Viscosity measurements and microscopy techniques were used to confirm the water-in-oil emulsion.
5. A non-aromatic solvent/co-solvent mixture was miscible in all proportions with the California crude oil and effectively reduced its apparent viscosity.
6. Low salinity and possible completion/remediation processes generate tight water emulsions inside the California crude oil.

Acknowledgments:

Nomenclatures

°API	API degree
API	American Petroleum Institute
ASTM	America Society for Testing and Materials

EOR   Enhanced Oil Recovery
HLD   Hydrophilic Lipophilic Difference
HPHT   High Pressure High Temperature
IFT   Interfacial Tension
O/W   Oil in Water
R/A   Resins/Asphaltenes
S*   Optimum formulation
SG   Specific Gravity
W/O   Water in Oil
WBM   Water Based Mud
W I   Winsor I
W II   Winsor II
W III   Winsor III
W IV   Winsor IV

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SI Metric Conversion Factors

°API	141.5/(131.5+°API)	= g/cm^3
°F	$\times$ (°F – 32)/1.8	= °C
cP	$\times$ 1.0 E-03	= Pa.s
hours	$\times$ 2.8 E-04	= s
mN/m	$\times$ 1.0 E+03	= kg/s^2
minutes	$\times$ 1.7 E-02	= s
mg/L	$\times$ 1.0 E-03	= kg/m^3
mL	$\times$ 1.0 E 00	= cm^3
μm	$\times$ 1.0 E-06	= m