ASPECTS OF OILY BRINE CLARIFICATION BY THE USE OF CHEMICAL ADDITIVES

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The presence of small amounts of free or emulsified oil or oil coated solids in produced brines can adversely affect the properties of that brine in waterflooding and enhanced oil recovery projects. Likewise, the disposal of such oily brines can present a problem if the brine is being injected into a tight formation or, in the case of offshore platforms, if the brine is being disposed of overboard. Even if no difficulties are encountered in the reinjection or disposal of oily produced brines, the economic advantage of recovering even several hundred parts per million of residual oil from the brine should be considered. In many cases, the cost of the water clarification chemical required to recover the residual oil is small when compared to savings realized by recovering the oil.

A large portion of the oil in oily produced brines is, in fact, emulsified into the water as a "reverse" emulsion. Such emulsions can be quite stable and require a long period of time to separate, due to stabilizing forces within the emulsion. Once recognized some of these forces can be neutralized by the addition of certain water soluble demulsifiers. A discussion of oily brine clarification, some theoretical considerations of emulsion technology, and a case history showing the economic advantage to residual oil recovery are included in this paper.

INTRODUCTION

The growing importance of water quality in oil production fields has become increasingly recognized in recent years Because most modern day oil fields are being waterflooded, and many are also being subjected to some additional form of enhanced oil recovery (EOR) technique requiring water, such as improved profile waterflooding, micellar polymer flooding, caustic/caustic silicate flooding or steam injection, the use of high quality water has become a prerequisite for efficient operation. The requirements for acceptable water quality vary from one geographic region to another and even from one formation to another within the same region, depending upon the permeability of the formation and the type of recovery process being employed. In general however, the presence of even small amounts of free or emulsified oil, or oil coated solids contained in the flooding water can cause operational difficulties which could influence the economic success of the recovery project.

Oil field brines which are not being reinjected as part of an enhanced oil recovery project are usually disposed of by reinjection into salt water disposal (SWD) wells, or in the case of offshore platforms, by overboard disposal. Brines containing residual oil or oil coated solids in any substantial concentrations can cause premature plugging of the disposal well, or in the case of overboard disposal, the formation of an oil slick.

If the disposal or injection of oily brines does not present a problem to the operator, due consideration should be given to the economic value of recovering the residual oil from the brine.

The cost of the water clarification chemical required to recover several hundred parts per million of oil is in many cases small when compared to the savings realized by recovering the saleable oil.

DISCUSSION

Waterflooding and Enhanced Oil Recovery Operations

The produced brine used in waterflooding projects must, in most cases, be conditioned to insure that no plugging of the formation will occur. This generally means that scale inhibitors may have to be added to prevent the deposition of mineral scales and microbiocides may have to be added to prevent bacterial growth and subsequent plugging problems. In addition, solids in the produced water, when present, need to be removed by settling. Solids sedimentation is sometimes enhanced by the addition of polyelectrolytes or surfactants if the solids are oil coated. Much information can be found in the literature describing and recommending solutions to the scale, bacteria and solids problems associated with waterflooding. Several of these papers are cited in the references.[1,2,3]

Many textbooks dealing with oil field waters have also been written devoting much attention to waterflooding problems In addition to the more classical problems of scale, bacteria and solids buildup, most operators are now concerned with the residual oil content (both emulsified and free oil) in the flooding water and some are imposing limits on the allowable residual oil content. The imposed limits depend of course, upon the characteristics of the formation into which injection is being performed. For example, one large operator in West Texas is attempting to maintain oil carryover levels below 50 ppm to insure good injectivity and oil recovery. A different operator in California requires that the residual oil be kept below 10 ppm Maintaining these low levels of residual hydrocarbon in the waterflood water reduces the chances of plugging and/or increased injection pressure caused by the "filtering out" of emulsified oil or oil coated solids on the formation face.

While it would be highly desirable in many cases to use only fresh water for EOR projects such as micellar polymer flooding, improved profile water flooding, caustic/caustic silicate flooding and steam injection, the constraints of fresh water availability do not always permit this. When this is the case, produced water is used alone or in combination with fresh water blended to specific ratios. In all cases, certain limits of total dissolved solids (TDS) content and/or hardness content must be observed. A recent survey of fourteen operating companies showed some differences in opinion regarding the maximum amount of total dissolved solids and hardness content allowable for several types of EOR operations. However, consensus values show that steam flooding requires the highest water quality (TDS less than 10,000 ppm, hardness less than 1 ppm), while micellar polymer flooding probably demands the least stringent restraints.[4] Another study, however, has shown that steam generator feed waters containing up to 22,500 ppm of TDS can be used successfully, if properly softened.[5]

If produced brine is used as a water source for any of these EOR methods, its residual oil content must be kept to a minimum, usually below 5 ppm. Residual oil content higher than this can cause fouling of the resin beads used in the softening equipment as well as other operational problems throughout the system.

Brine Disposal

Oil fields that are not being waterflooded present a problem of produced brine disposal. Since produced brines can contain from 5,000 to 180,000 ppm of chloride ion (mostly due to the high concentration of dissolved sodium chloride) special disposal techniques are required to insure that these brines do not contaminate fresh water aquifers used to supply drinking water or sensitive surface waters such as lakes and streams.[6] Most producing companies now use subsurface injection as the preferred method of brine disposal. However, in some cases, the salt water disposal wells are drilled into low permeability formations. If this condition exists, free or emulsified oil and oil coated solids carried over into the injection wells can cause increased injection pressures and eventual well plugging. Since the drilling or servicing of a SWD well is an expense which has no return on investment, the longevity of a SWD well is of primary concern.

Many offshore oil production platforms discharge produced brines into the surrounding surface waters. For this reason, it is imperative that the level of residual oil in the produced brine be as low as possible since a relatively small amount of oil can cause a "slick." It has been shown that as little as 50 gallons of oil on the surface of a square mile of water will cause a silvery sheen.[7] In addition to the aesthetic value of maintaining low levels of residual oil in overboard water, several governmental regulatory agencies have imposed limits on the oil content of the produced brines which are discharged. The U.S. Environmental Protection Agency has established a limit of 72 mg/l for most federal waters, but other federal, state or local agencies may impose more strict limits and hence all agencies having jurisdiction should be consulted to determine the applicable limits.[8] A recent study conducted on ten Louisiana production platforms showed variation in the performance of different designs of water clarification equipment systems used on these platforms, and hence, variation in the amount of oil carryover in the water being discharged overboard.[9]

The Economic Aspects Of Residual Oil Recovery

If the adverse effects of injection well plugging (in the case of SWD wells or waterflooding operations) or governmental regulations (in the case of offshore overboard brine dispose) are not applicable to a particular oil field, the economic operation of that oil field is always of concern. Residual oil emulsified into the brine and reinjected with the injection water accounts for a significant loss of saleable oil, in many cases enough to fully cover the cost of the water clarification chemical required to recover the emulsified oil. An example of this is shown in the Appendix where an actual case history involving a large West Texas producing field is detailed.

THE OCCURRENCE OF EMULSIONS IN THE OIL FIELD

Since formation water is usually produced with crude oil, the application of one or more separation techniques is usually required. The objective of these separation techniques is twofold:

1. To recover as much clean, dry hydrocarbon as possible, for sale and;
2. To remove the residual hydrocarbon (free and emulsified) and solids from the water to expedite disposal or reinjection of the water.

Both mechanical and chemical techniques are applied to effect this separation. Figure I shows a simplified separation system, some common separation vessels, and typical chemical injection points.

Water and oil which are not tied up in an emulsion generally require only a small amount of settling time to separate. However, if the water and oil are emulsified, the application of heat, chemical demulsifiers, and long retention times may be required to break the emulsion.

An emulsion can be defined as "A stable mixture of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers."[10]

Oil field emulsions are either "regular" (water-in-oil) emulsions or "reverse" (oil-in-water) emulsions. The first type, the water-in-oil (w/o) emulsion has water as the dispersed phase and oil as the continuous phase. The water content of a regular emulsion is usually considered to be about 25 per cent and the droplet size of the emulsified water ranges from 2 to 100 microns. Regular emulsions are believed to be stabilized by emulsifying agents which concentrate at the interface of the water droplet and form a physical barrier.[11]

The second type of emulsion found in oil production is the oil-in-water (o/w) emulsion and is the type of emulsion discussed in this paper. In this type of emulsion the oil is the dispersed phase and the water is the continuous phase. These emulsions contain only small concentrations of oil typically less than 2,000 ppm, and appear as brownish "dirty" water. Figure II shows a reverse emulsion from a large West Texas oil field. Figure III shows, diagrammatically, the difference between a regular and a reverse emulsion.

The typical droplet size found in a reverse emulsion is about 10 to 40 microns.[12]

Demulsifiers which are designed to break water-in-oil emulsions are necessarily different in chemical structure and in mechanism of operation from those demulsifiers designed to break oil-in-water emulsions. The table below shows a functional comparison of the two types.

A Comparison of Regular and Reverse Demulsifiers (Water Clarifiers)

	Regular Demulsifiers:	Reverse Demulsifiers
1.	Are added to break w/o emulsions	Are added to break o/w emulsions
2.	Are soluble in oil	Are soluble in water
3.	Migrate through the oil to the oil/water interface	Migrate through the water to the water/oil interface.
4.	Control solids at the interface	Control solids at the interface
5.	Are composed of polymers of alkyl phenols, polyols blended into hydrocarbon solvents	Are composed of polymers of amines and carboxylic acids blended into water - sometimes combined with inorganic salts.
6.	Are nonionic or anionic	Are cationic or anionic

Reverse demulsifiers function by promoting coagulation, flocculation and coalescence of the dispersed phase. Coagulation can be described as the neutralization of the charge surrounding the oil droplet to cause a reduction in the repulsion between the droplets.[13] Flocculation occurs when the neutralized oil droplets begin to collide and grow in size to form an aggregate, but the droplets have not completely lost their identity. This process is considered reversible. Coalescence is the combining of each aggregate to form a single drop. This step is considered irreversible.[14]

FACTORS WHICH STABILIZE REVERSE EMULSIONS

Emulsions are very complex systems and many factors affect emulsion stability. For instance, it has been shown that the presence of finely divided solids such as calcium carbonate, iron hydroxides and common clays at the water/oil interface can act as emulsifying agents in o/w emulsions.[15] Temperature also has a profound effect on emulsion stability. Three of the most fundamental factors contributing to reverse emulsion stability, however, are the oil droplet size, the interfacial tension between the oil droplet and the brine, and the electrical charge on the droplet.

Droplet Size - The oil droplet size in a reverse emulsion affects the stability of that emulsion. "Tight" emulsions having small droplets are as a rule more stable and more difficult to break. This behavior is predicted by Stoke's Law, given in useful terms as follows:[16]

$$V_T = \frac{g\,(P - p)D^2}{18\,u}$$

Where D = droplet diameter
g = acceleration due to gravity
P = density of the water
p = density of the droplet
u = viscosity of the water
V_T = rate of rise of the droplet.

A large D^2 term would cause a large V_T term (rapid rate of rise). It can be seen from Stoke's Law that the droplet size is an important factor and any measures which would promote the formation of a larger droplet from several smaller ones would promote emulsion destabilization. These measures in the oil field involve both mechanical and chemical techniques. The mechanical techniques include the use of wash tanks and holding tanks, skim tanks, separators, and other gravity separation equipment. The chemical techniques involve the use of the water soluble demulsifiers previously described.

Interfacial Tension - Interfacial tension exists at the interface formed by the combination of two immiscible liquids. Interfacial tension is caused by an imbalance of forces on the molecules near the interface in contrast to the molecules in the bulk of the solution.[17] Figure IV shows, diagrammatically, this imbalance of molecular forces on an oil droplet in a brine. The lower the interfacial tension existing between two immiscible liquids, the greater the tendency is for the liquids to emulsify.

For example, the interfacial tension existing between a mixture of hexane and water is 51.1 dynes/cm, while the interfacial tension is only 15.59 dynes/cm for an oleic acid/water system. Hence, water would tend to form an emulsion with oleic acid much more readily than with hexane. This is relevant to the oil field in that reverse emulsions containing crude oil droplets which have a high content of carboxylic acids (such as naphthenic acid) or other polar species such as amines, esters or ketones would have a low interfacial tension at the oil/water interface and would tend to emulsify readily. More paraffinic crudes would mimic the water/hexane system and show less of a tendency to form a stable emulsion.

Surface Charge- The surface charge is another important factor affecting emulsion stability since coagulation (neutralization of the surface charge) is the first step in breaking an emulsion. Emulsion stability depends to a great extent upon the ability of the oil droplets to repel each other and keep from colliding. The charge on an oil droplet, usually considered to be negative, must first be neutralized to reduce this repulsion and allow the random collisions to occur.

Typically the charge on the oil droplet is caused by naturally occurring carboxylic acids and other anionic species in the oil phase. Most reverse emulsion breakers contain polymers and inorganic salts which act as neutralizing agents to aid in coagulation. Figure V illustrates the repulsive forces between oil droplets.

Although the three factors previously mentioned contribute to emulsion stability, not all three factors can be manipulated to induce emulsion instability. While interfacial tension can be lowered by the use of surfactant type materials (thus promoting emulsion formation) it cannot be practically raised. The droplet size and charge can, however, be modified by the use of chemical demulsifiers. In fact, most reverse demulsifiers function by mechanisms which include:

1) neutralizing the charge on the droplet with polyelectrolytes or inorganic salts to cause coagulation and

2) "bridging" the droplets with polyelectrolytes to effectively increase the droplet size, causing flocculation.

Chemical formulations are developed and tested to optimize the factors causing destabilization of reverse emulsions.

EVALUATION OF WATER CLARIFICATION FORMULATIONS

The evaluation of formulations used in oily brine clarification is best accomplished by testing in the field. Bottle testing is a commonly used tool which is useful in simulating a particular formulation's performance in settling tanks and other oil/water separation vessels. In the bottle test, a series of prescription bottles is treated with varying amounts (in the parts per million range) of the formulation to be evaluated, the oily brine is added to the bottle, and the bottles are shaken vigorously for a designated period. The best water clarification formulation for that system will show the clearest water and the best interface at the lowest concentration after settling for a specified period of time. This formulation is then retested several times at different concentrations to optimize the treating range.

When gas flotation cells are used in the system to remove residual oil, the best flotation aids can be picked by screening with a portable bench-top flotation simulator. This type of testing equipment allows the operator to vary the air pressure and volume, as well as the testing time to simulate the actual flotation unit in the field, thus enabling a cost effective formulation to be selected.

Once the best chemical for a particular location has been selected and the treating rate tentatively established by bottle or flotation simulator testing, a plant test is usually conducted to pinpoint the optimum treating rate in the system under operating conditions. Following a successful plant test and the commencement of actual treatment of the system an effective monitoring program is needed..

Such a program should include routine determinations of oil carryover at key points in the system as well as membrane filtration rate determinations and solids analysis. Monitoring of these factors will assure the continuance of a cost effective chemical treatment program.

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APPENDIX

A CASE HISTORY OF OILY BRINE CLARIFICATION

SUMMARY

A major oil company in West Texas, producing 85,000 bwpd and 7000 bopd from the San Andres formation, was experiencing water injection well plugging with a high total suspended solids water. A high percentage of the analyzed total suspended solids was entrained oil in the form of a "reverse" emulsion. A water clarifier was selected to enhance the separation of the oil without utilizing additional expensive surface equipment. The recovery of this oil from the produced water has saved $232,687.00 per year.

Discussion

Field testing consisted of bottle tests with various water clarifiers, flotation tests with a portable benchtop flotation simulator, and flotation tests with a portable benchtop flotation simulator in coapplication with water clarifiers to the test fluids. The flotation simulator required the addition of chemical to recover the same amount of oil as did the application of chemicals to the test fluids in the bottle tests.

The operator had adequate storage facilities for oil recovery. Simple piping modifications increased the retention time of the tanks. An injection point upstream of the existing free-water knockout was selected as the treating point for the water clarifier. Some water wetting properties were observed with this product and the solids could be more readily removed from the system in the free-water knockout than in the water storage tanks.

Before the application of the water clarifier, the produced water carried a high content of suspended solids.

Total Suspended Solids = 100.0 mg/1
Oil Soluble Solids = 31 3 mg/1
Acid Soluble Solids = 66.4 mg/1
Inert Solids = 2 3 mg/1

Total Injected Suspended Solids = 2975 lbs. in 85,000 barrels of water.

After the application of the water clarifier and the slight mechanical alterations, the produced water had 13.1 mg/1 of total suspended solids.

Total Suspended Solids = 13.1 mg/1
Oil Soluble Solids = 5.1 mg/1
Acid Soluble Solids = 6.3 mg/1
Inert Solids = 1.7 mg/1

Total Injected Suspended Solids = 389 lbs. in 85,000 barrels of water.

The oil carryover averaged 300 ppm out of the system before the application of the water clarifier. The oil carryover could be reduced to near 1 ppm with the water clarifier, but the economic treatment justification occurred at 50 ppm. The program was established and monitored weekly and adjusted seasonally to assure maximum recovery of oil on a cost effective basis. The yearly treatments varied from 7 ppm in the summer to 14 ppm in the winter. The average amount of free oil recovered for sale was 21.5 barrels per day. This equals 7,756 barrels recovered annually At $30 per barrel, this is a recovered earnings of $232,687 per year.

A typical water analysis from this location is shown below.

TYPICAL WATER ANALYSIS*

Calcium	2,320
Magnesium	146
Iron	0
Barium	0
Sodium	14,812
Chloride	21,000
Sulfate	3,750
Carbonate	0
Bicarbonate	1,488
Hydroxide	0
Sulfide	1,250
Total Dissolved Solids	44,766
pH	6.8

* All values are in parts per million, except pH.

Photomicrographs of the oil in water emulsion discussed in this case history are illustrated in Figure VI.

Actual data showing the oil carryover (vol./vol.) in the treated produced water prior to injection are illustrated in Figure VII. This case history encompasses four (4) years of field monitoring.

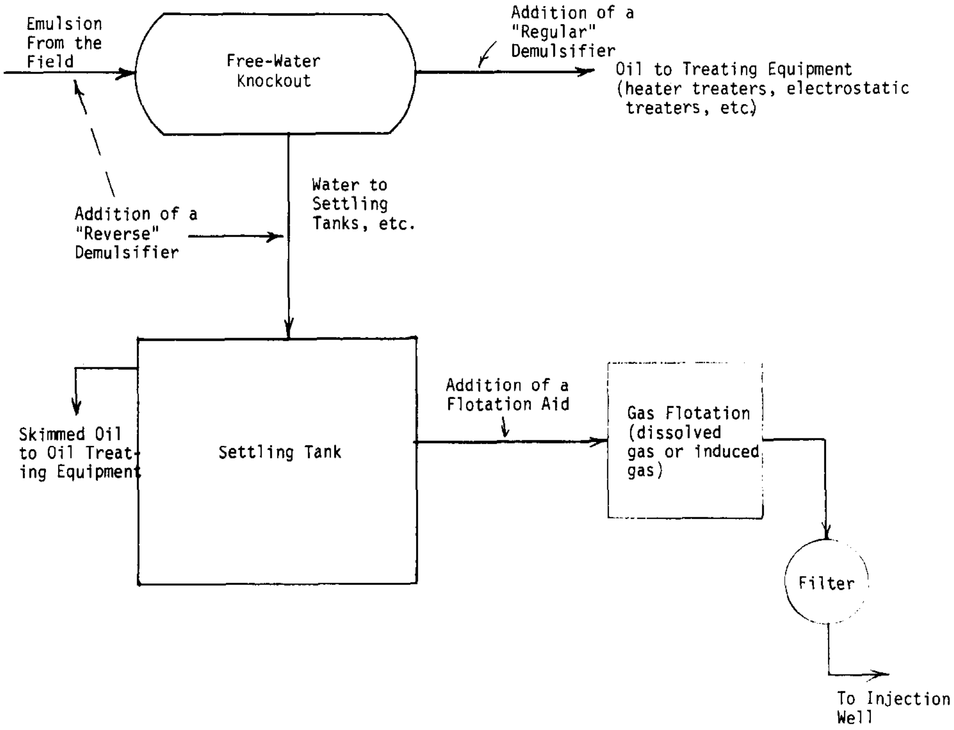
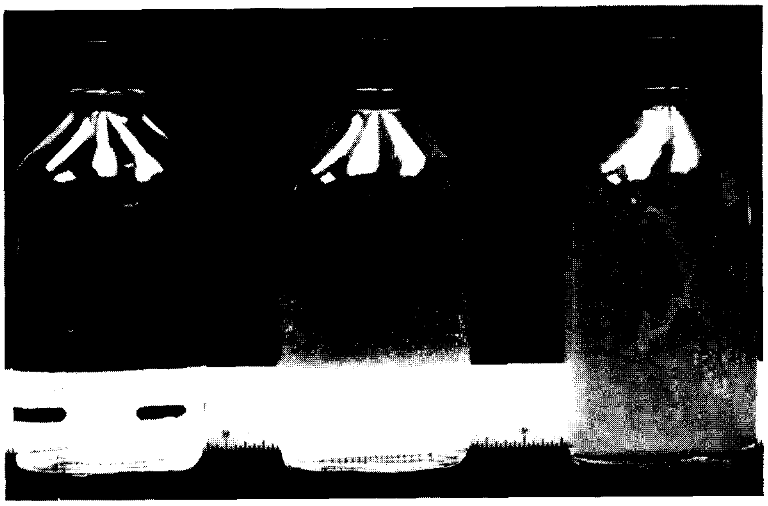


Figure 1 - A simplified oil field separation system



Note: The bottle on the left contains distilled water. The bottle in the middle contains treated produced water prior to injection. The bottle on the right contains untreated produced water. See the Appendix for more information on the water quality at this location.

Figure 2 - An oil field oil/water emulsion.

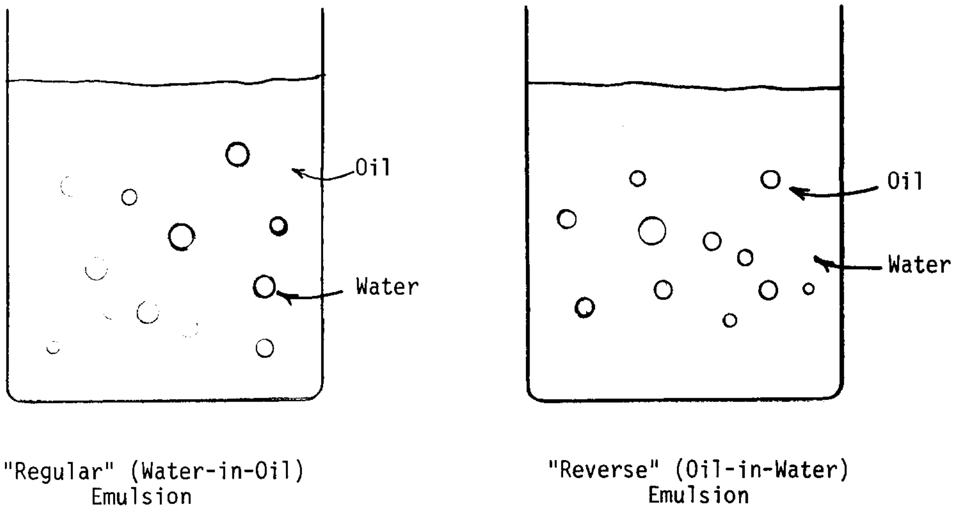


Figure 3 - Two types of emulsions

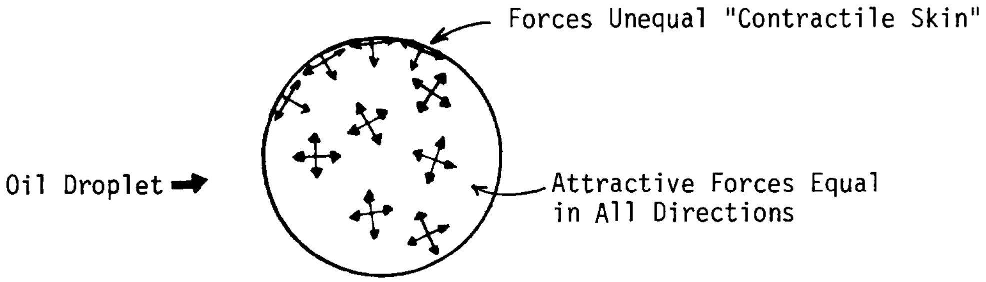


Figure 4 - The imbalance of forces at the oil droplet/water interface

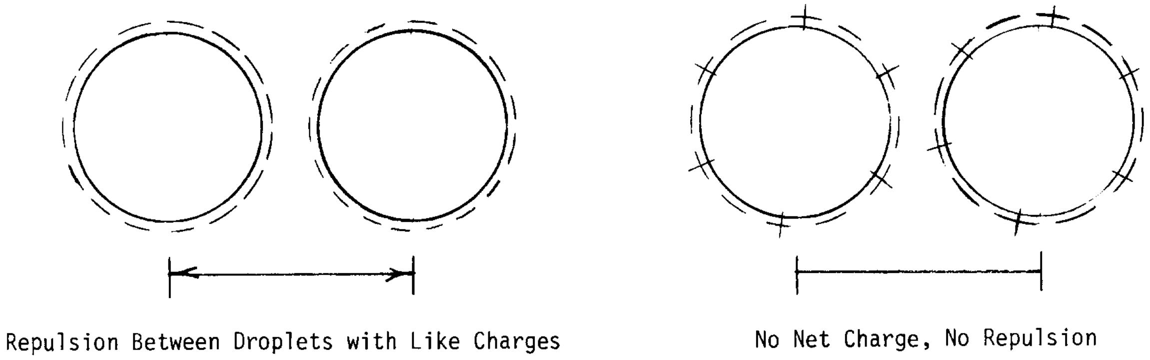
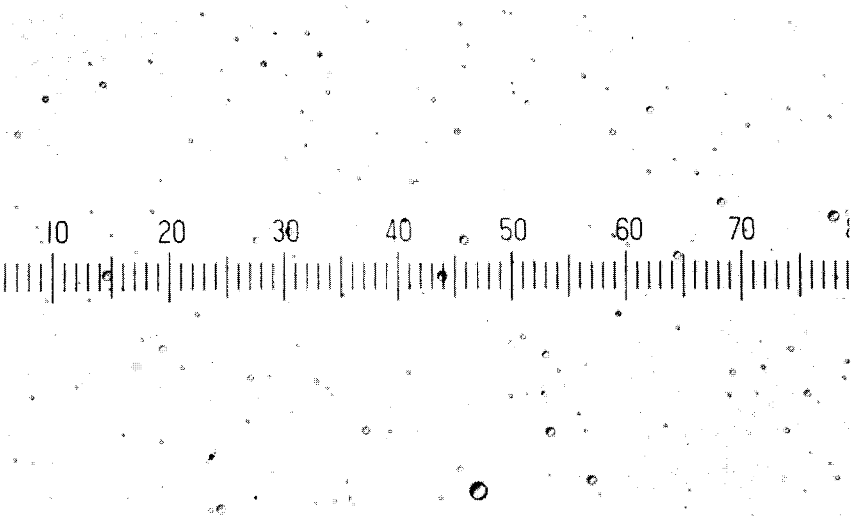
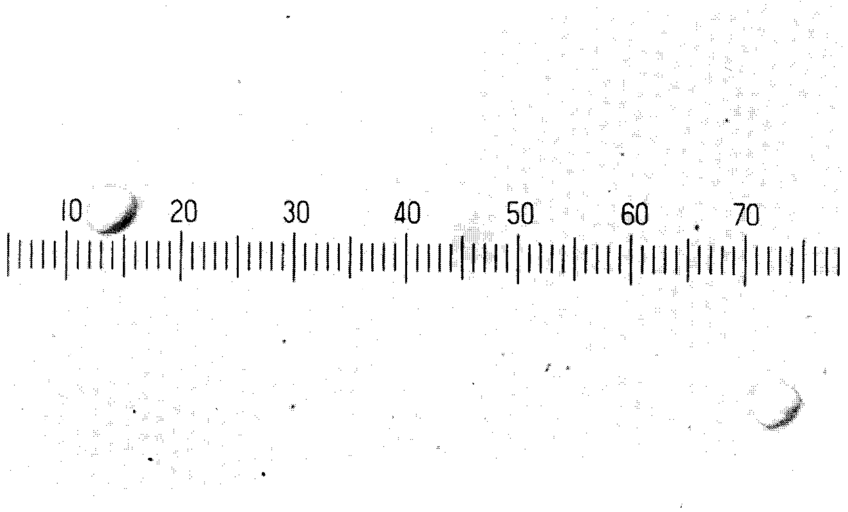


Figure 5 - The surface charge on oil droplets



A. Oil-in-water emulsion influent to the treating vessel (untreated fluid). Scale units equal 2.7 microns



B. Oil-in-water emulsion effluent from the treating vessel (treated fluid). Scale units equal 2.7 microns

Figure 6 - Photomicrographs (500x) of the oil-in-water emulsion from the San Andres production in West Texas

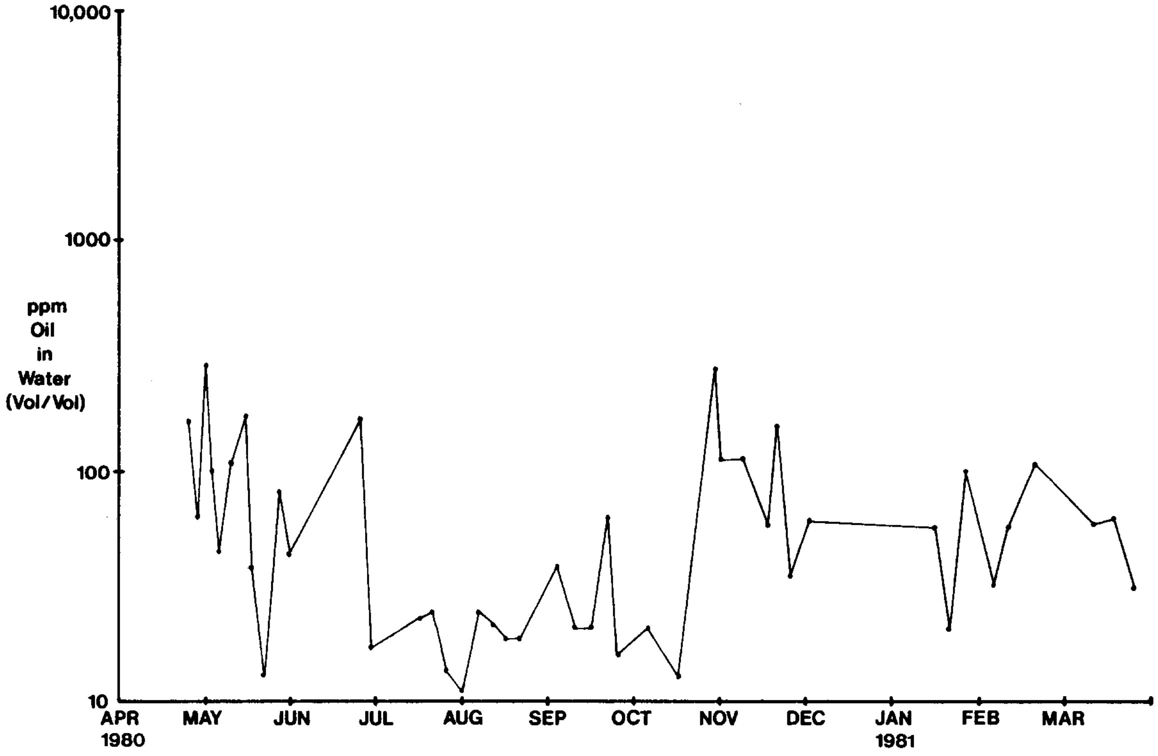


Figure 7A - Oil carryover -- 10,000 barrel tank effluent

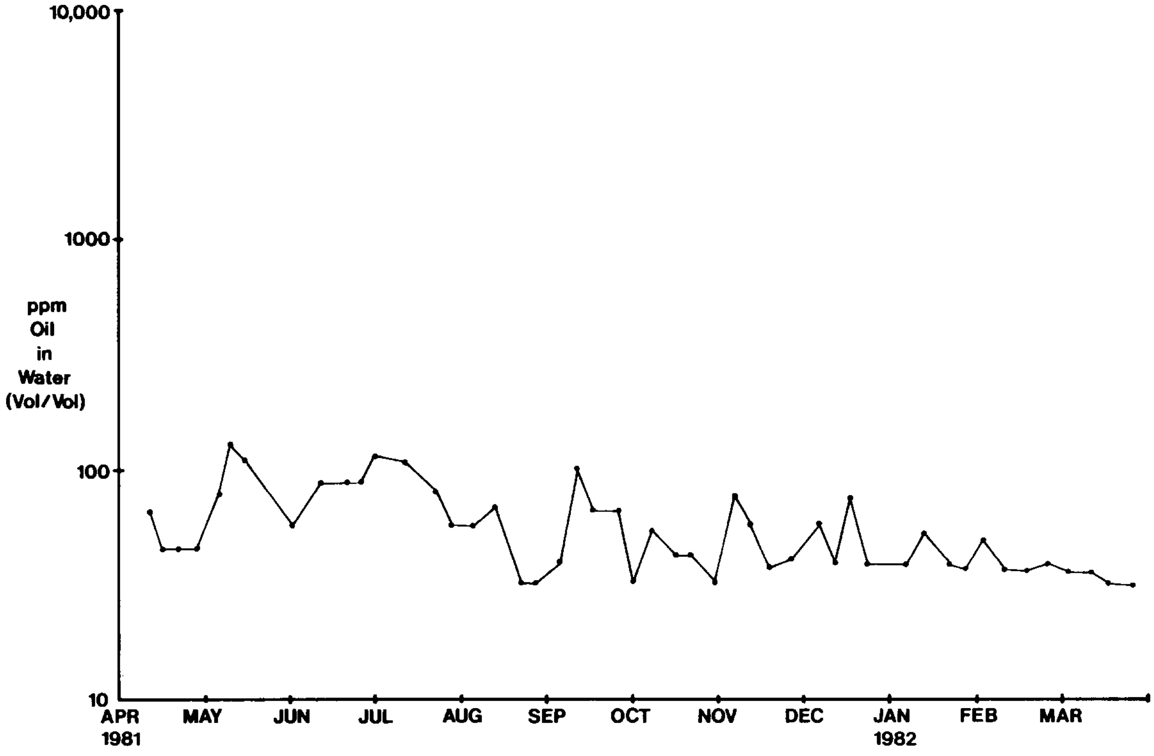


Figure 7B - Oil carryover -- 10,000 barrel tank effluent

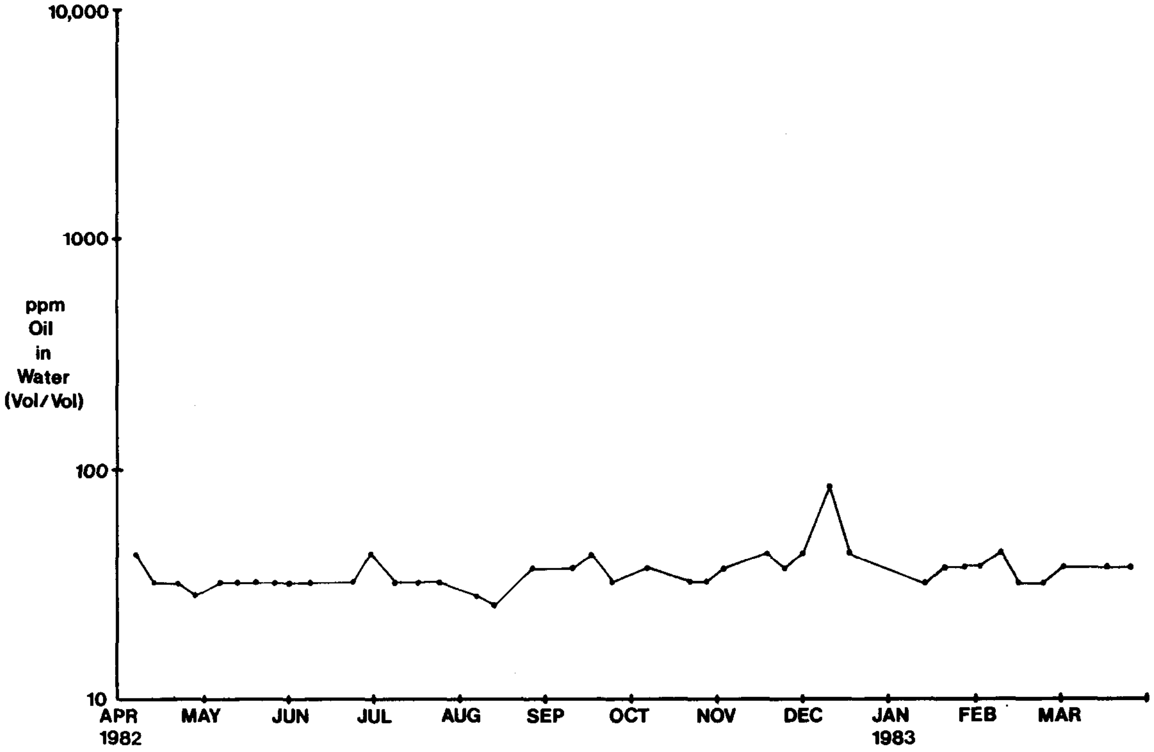


Figure 7C - Oil carryover – 10,000 barrel tank effluent

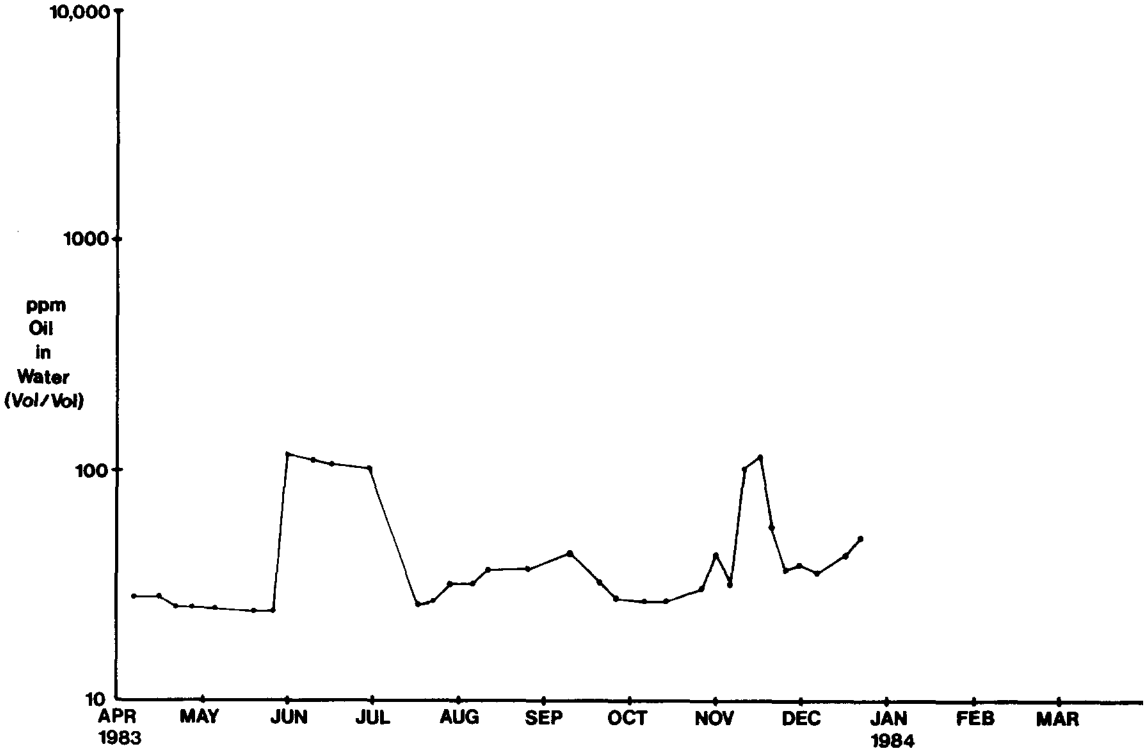


Figure 7D - Oil carryover – 10,000 barrel tank effluent