Experimental Investigation of Various Physical Factors Affecting the Stability of Water-in-Oil Emulsions in Oil Production

by

Abdul Karim Mohammad Al-Jaziri

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

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EXPERIMENTAL INVESTIGATION OF VARIOUS PHYSICAL FACTORS AFFECTING THE STABILITY OF WATER-IN-OIL EMULSIONS IN OIL PRODUCTION

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This Thesis, written by Mr. Abdul Karim Mohammad Al-Jaziri under the direction of his thesis Advisor and approved by the Thesis Committee, has been presented to, and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the Master Degree in Petroleum Engineering.

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DEDICATION

This thesis is dedicated To my mother, my wife, my son , my daughter, my home land Saudi Arabia, and to its hard working people

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خلاصة الرسالة

اسم الطالب : عبدالكريم محمد عبدالعزيز الجزيري
عنوان الرسالة : دراسة عملية لتقصي مختلف العوامل الطبيعية المؤثرة على ثبات المستحلبات النفطية المنتجة مع البترول
التخصص : هندسة البترول
تاريخ الرسالة : يناير ١٩٩٥ م

إن النفط المنتج من بعض حقول البترول في المملكة العربية السعودية يبقى في حالة مستحلب متجانس عندما تنخفض درجة حرارته بشكل ملحوظ قبل أن يصل إلى معمل فرز الغاز عن الزيت ، وهذا يسبب عراقيل ينتج عنها مشاكل في عمليات الإنتاج ، والتي بدورها يتم وقف إنتاج الآلاف من براميل النفط يومياً .

الرسالة تشمل دراسة معملية لتقصي مختلف العوامل الطبيعية التي تؤثر على ثبات وتجانس المستحلبات المنتجة . لقد تم تصميم جهاز قادر على محاكاة مختلف أوجه جريان هذه المستحلبات بدءاً من فوهة البئر وحتى أن يصل إلى معمل الفرز . بواسطة هذا الجهاز تم اختبار فصل أطوار المستحلب ديناميكياً تحت ضغوط وحرارة مماثلة لما هي عليه في معمل الفرز ، كذلك تم اختبار مدى تأثير إضافة المواد الكيميائية والتسخين على تفكيك هذه المستحلبات وبالتالي فصلها تدريجياً إلى زيت وماء .

لقد أظهرت النتائج أن هذه المستحلبات غير ثابتة عند درجة حرارة مكمن النفط (٢٠٠ د.ف) وإنها تتكون أثناء جريان السائل من أنبوب بئر النفط ومن ثم في أنابيب الإنتاج المؤدية إلى معمل فرز الغاز عن الزيت . إن للحرارة دور كبير على تفكيك هذه المستحلبات حيث أن تسخينها يؤدي إلى تفكيكها إلى ماء وزيت . كذلك إن للمواد الكيميائية دور هام في منع استحلاب النفط المنتج وتفكيك المستحلبات النفطية. استخدمت أربع مواد كيميائية مختلفة لتفكيك المستحلبات النفطية وقد تبين أن المادة الكيميائية المعروفة بـ(شامبيون) هي الأقوى تأثيراً من بين الأربع مواد على تفكيك المستحلبات. أن الكمية اللازمة من هذه المادة الكيميائية لتفكيك المستحلبات المنتجة من الآبار المسببة لمشاكل في الإنتاج أكثر بكثير منها في الآبار غير المسببة .

من خلال هذه الدراسة تبين أنه من المهم جداً دراسة تفكيك المستحلبات النفطية تحت ظروف ديناميكية مشابهة لما هي عليه في حقول البترول ، فبعد المقارنة بين الحالتين – الساكنة والديناميكية – تبين أن كمية المواد الكيميائية اللازمة لتفكيك المستحلبات تحت ظروف ديناميكية أقل بكثير منها عند تفكيكها تحت ظروف ساكنة .

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THESIS ABSTRACT

STUDENT NAME : Abdulkarim Mohammad Al-Jaziri
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MAJOR FIELD : Petroleum Engineering
DATE OF DEGREE : January 1995

Produced fluids from some wells in certain Saudi Arabian oil fields remain in the form of a stable emulsion before entering the Gas Oil Separation Plant (GOSP). This causes significant problems for the smooth operation of the GOSP as a result thousands of barrels of oil per day can not be produced. A laboratory system ables to simulate various aspects of emulsion flow in the field was designed. Using this system we examined phase separation of field emulsions under dynamic conditions at temperatures and pressures similar to those existing at GOSPs in the oil fields under the influence of an electrostatic field. Also we examined the effectiveness of various demulsifying chemicals as well as the combined effects of temperature and demulsifier on breaking field emulsions. Finally an optimization study was done to find the optimum concentration of the best demulsifying chemicals.

Based on the results obtained it is concluded that at reservoir temperatures of about 220 ^{O}F emulsions are unstable and are mostly formed after fluids enter the wellbore and during their flow into the GOSPs. The temperature plays a critical role on the stability of emulsions since heating these emulsions helps in breaking them into two phases, oil and water. Also addition of demulsifiers reduces emulsification tedency of produced oil extensively. It is found that, among the four commercially available demulsifiers used in this study, Champion demulsifier is the most effective one in resolving tight emulsions. The concentrations of this demulsifier needed to resolve tight emulsions from problem wells are over 10 folds greater than that of non-problem important to study the demulsification process under dynamic condition which represents the condition that exists in the oil fields since the amount of demulsifier needed to resolve tight emulsions under dynamic condition is three to four times less than that needed under static condition.

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CHAPTER 1

INTRODUCTION

Emulsions are mixtures of two immiscible liquids [1] such as oil and water where one liquid is dispersed in the other. Emulsions are inherently unstable and will eventually break down to form two phases [2]. However the nature of the interfacial film and its strength is an important parameter in the stability of an emulsion and therefore the rate of phase separation[3]. Normally an emulsion system is stabilized by one or more emulsifying agents.

Emulsions are one of the many problems which are associated with both upstream and downstream operations in the petroleum industry. In each case the presence and nature of emulsions can determine both the economic and technical successes of the industrial process concerned. Emulsions must be resolved to have a marketable oil product or to conduct the refining processes effectively. The nature of these emulsions varies from one crude to another. This is because crude oils are different in their chemical compositions (such as their content of asphaltene, other polar molecules, and associated impurities such as clays and other fines, etc.) and their geological history.[4,5]

In addition, the chemical and physical properties of produced water (associated with oil production) has also an impact on the characteristics of produced emulsions. This differs from one reservoir to another and will also change during the life of oil wells depending on recovery methods applied in oil production.[5,6]

Produced oil must meet or exceed specifications required by refineries, shipping, and pipeline operations. In general the marketable oil may not contain more than 0.5 percent basic sediments and water (BS&W) as determined by a standard ASTM D96 test (or a variation of it). Failure by the oil producers to meet these specifications for any extended period of time will cause a penalty payment imposed by transportation and shipping companies and/or by downstream operations, and may even result in the refused pipeline companies to accept produced oil as the excessive water content can create significant operation problems as well as corrosion problems in pipelines.[4]

Therefore oil producers all over the world are forced to ensure that emulsions are resolved properly in order to reduce the BS&W content to an acceptable level. In addition, the higher is the BS&W content of oil, the higher is the cost of transportation of the produced oil to markets. Moreover there is a significant cost associated with the treatment and disposal of the associated water in downstream operations. Therefore it is important that the BS&W content of oil be reduced below 0.5% as described above. Producers use a desalting process to reduce soluble inorganic chloride salts content of the oil which are produced in formation water alone with produced oil. The salt removal process is accomplished by addition of relatively fresh water (wash water) into the produced fluids at oil water separator inlet lines (or crude-oil charge line in refinery operations) to extract the salt or "wash" the oil.[7]

Desalting also removes most of the harmful contaminants from crude, improves corrosion control in transportation and processing units of a given crude oil, reduces the requirements of corrosion control chemicals, improves waste water management in downstream operations, smoothes out process variations and eliminates system upsets.

1.1 Factors Influencing the Stability of Water-in-Oil Emulsions and their Phase Separation

Some of the physical factors influencing the petroleum water-in-oil emulsions, their phase separation and settling rates are understood through Stokes's law which describes the separation of two immiscible liquids as shown by the equation (1.1) below. It gives the rate of fall or rise of a small sphere through a viscous fluid. This equation which is derived from Stokes's law states that spheres under the influence of gravity attain a constant settling velocity given by the following equation[8]:

$$v = \frac{2gr_d^2(\rho_d - \rho_c)}{9\mu_c} \qquad (1.1)$$

where: v= settling velocity of the dispersed droplet in cm/s ; r_d= radius of dispersed droplet in cm;ρ_d= density of dispersed phase in g/cc; ρ_c= density of continuous phase in g/cc; μ_c = viscosity in poises of the continuous phase at the settling temperature; and g= 980 cm/sec^2 (gravitational acceleration).

Examination of the above equation shows the following three factors which influence the settling velocity of the water droplets in a water-in-oil system.

(a) The settling velocity is higher when a larger density difference between two phases (oil and water) exists. This may be achieved by heating the emulsion or heating a low density hydrocarbon liquids (to decrease the density of oil phase). This is especially important for low API crudes.

(b) Viscosity: The higher is the viscosity of oil, the more stable is the emulsion. This is due to the fact that oils with high viscosities have the ability to hold up a large number of droplets as well as larger droplets than oils with lower viscosities. Again application of heat and addition of a diluent will decrease the viscosity significantly (especially in heavy oils). This will have a positive impact on the settling velocity of water droplets.

(c) Droplet size: Droplet size or the radius of dispersed phase (water) has the largest influence on settling rate of water droplets because it is not only squared but it can be also increased considerably by coalescence. The larger the droplets of the dispersed phase (internal phase) of an emulsion are, the greater is the tendency to coalesce and further increase the droplet size, and further destabilize the emulsion and enhance the phase separation. Therefore anything which increases the droplet size of the dispersed phase will increase the phase separation rate drastically. For example: subjecting the droplet to the influence of high voltage will cause the droplets to coalesce and form larger droplets[9] and enhance the demulsification process drastically (electrically enhanced coalescence).

Other physical factors which will aid the coalescence process thereby causing a rapid phase separation are:

(1) Equation 1.1 describes static systems. In oil field treating vessels there are vertical and horizontal movements that enhance coalescence of droplets thereby increasing the settling velocity.

(2) Produced fluids are generally introduced below the water/oil interface into the water leg within the treaters. This process helps to retain free water associated with produced oil as well as aids coalescence and therefore increases droplet size.

(3) The relative proportion of oil and water also affects the emulsion stability. In emulsions with a lower water content, water droplets have smaller chance of colliding with each other and coalescing than emulsion with a larger number of dispersed water droplets. Increasing the fresh water content of emulsion can destroy its stability. This is one of the reasons that the addition of wash water can help the oil water separation process in oil water separators and this is commonly practiced in the oil industry.

1.2 Effect of Emulsifying Agents on the Stability of Water-in-Oil Emulsions

Various naturally occurring polar molecules and surface active materials indigenous to crude oil (such as asphaltenes, resins, porphyrin complexes, paraffin particles, clay, and sand) [4] as well as some other polar molecules which are produced as a result of the recovery methods applied in oil production (such as fire flooding) can adsorb at oil-water interface and act as chemical emulsifying agents which stabilize water-in-oil emulsions.

More stable emulsions are formed when stronger emulsifying agents are present. Asphaltene molecules, paraffins particles, clay and sand have a greater influence on the stability of the emulsion as they are adsorbed at the surface where they can form a skin layer around dispersed water droplets which in turn reduces the interfacial tension between oil and water and increases the interfacial viscosity hence enhancing emulsion stability. The composition of the formation water can also be an important factor in the stabilization of crude oil emulsions. Bivalent ions like Ca^{2+} and Mg^{2+} present in the formation water may form soaps with organic acids of the oil phase (e.g. naphthenic acid). These soaps form stable films on the interface. Bicarbonate ions (HCO_3^-) in the formation water can also be introduced at the interface and contribute to the increase of film stability [3-10]. This will slow down the separation of the two phases. Therefore any chemical process which can eliminate, alter or neutralize these layers will assist oil-water phase separation [11] and therefore the demulsification process or can prevent the formation of tight emulsions. Also sometimes the use of higher amounts of chemicals or use of mixtures of chemicals may increase the interaction between droplets and can improve the coalescence process, however the adverse effects [12] of higher concentrations of chemicals and the economics favor the use of demulsifying agents at low concentrations.

1.3 Demulsification of Water-in-Oil Emulsions

Emulsions must be broken cost effectively to achieve the required parameters for oil and water as described above. Breaking emulsions implies rupturing and modifying the emulsifying films at oil-water interfaces as stability of emulsions depends on the interfacial film present between continuous phase and dispersed phase[13], so that coalescing and gravitational settling can take place. The breaking of emulsions consists of two steps that may occur separately or simultaneously. First, it is necessary to devise some means of bringing the dispersed droplets into contact with each other, and then some ways to allow the droplets to coalesce so that the second phase can be separated. One of the most common ways of bringing the droplets together is to allow the emulsion to stand undisturbed for a period of time. The dispersed phase either settles to the bottom or rises to the top of the vessel, and in this concentrated layer the droplets are brought into contact. However, when forced into contact, the droplets may not coalesce rapidly if their surfaces are highly charged or they are coated with a film of surface- active material.

The charge on the droplets may be removed by adding a neutralizing material which can be an inorganic acid or base. Considerable work has been done in studying the charges on dispersed solids or liquid particles. [14]

If an emulsion is stabilized by a film-forming surfactant, it is necessary somehow to drive this material away from the interface. This can be done either by chemically reacting with the material or by changing its solubility in one or more of the liquid phases. For instance, most materials are more soluble when they are hot rather than when they are cold. Therefore emulsions can be broken in some cases simply by applying heat to them. When the emulsion is heated, the materials in the surface film become more soluble in the external liquid phase and therefore tend to migrate away from the interface allowing the droplets to coalesce. At the same time the increased temperature results in a lower viscosity, which also helps to promote the separation of the two phases.

The interfacial film can also be disrupted by adding a cosolvent to the system. For instance, certain materials like acetone or methanol are often soluble in both phases, oil and water. If added to an emulsion, such materials may tend to dilute the interfacial layer and cause some of the surfactant to migrate into the continuous phase, hence destabilizing the emulsion.

The following facilities and methods are employed in oil fields (in crude production) as well as oil refineries to assist the oil water separation process.

(a) Treating vessels are used to create a low-turbulence environment which will allow the gravitational separation of oil and water to take place. Single stage and multistage desalters are examples of these treating vessels, Figures 1 and 2. In deciding on the size of these vessels the aim is to achieve a residential time (10 minutes to 2 hours) suitable for the type and nature of the fluids (emulsions) to be processed.

(b) Electric coalescence: In the presence of an electric field, droplets can be made to coalesce very rapidly as illustrated in Figure 3. The application of an electric field can enhance the rate of liquid phase separation and can appreciably improve the performance of oil water separators. Thus the application of an electrical field within the treating vessel will promote coalescence and the formation of larger droplets[9]. Almost all emulsion separators are equipped with electric coalescers. However an essential precondition that must be satisfied before electric fields can be applied effectively is that the continuous liquid phase (oil) must be electrically non conductive (insulating) in nature. This will ensure that sufficient electric field can be established to have the desired effect on the dispersed phase which must be relatively electrically conductive (water). The research work is still in progress on this subject. The effect of water and oil phase properties on the kinetics of electrostatic demulsification has been investigated recently [15,16]. In these studies water-in-oil emulsions were prepared under various conditions. It was concluded that the viscosity of the oil phase was the most important oil related parameter which controlled the demulsification rates in the presence of an electrostatic field. The ionic strength of water phase was also found to be important. The effect of the electric field pulsation frequency on breaking water-in-oil emulsions was studied by other investigators[17]. It was shown that at pulsation frequencies between 8 Hz and 11 Hz, the separation efficiency of emulsions was highest. This range may change from one emulsion to another. However in spite of all of these advances, there is a growing demand for a new electrical technology to cope with high water content emulsions and high water cut production which can be used in crude oil dehydration and desalting units.

(c) As discussed above viscosity of oil plays an important rule on oil water phase separation, therefore viscosity of oil is decreased by the addition of diluents into the emulsion upstream of the treater and/or heating the emulsions in the treater especially in the production and processing of heavy oil or in the refinery operations [18].

(d) Emulsion breaking chemicals (Demulsifiers): Most of the petroleum emulsions are usually too stable to be broken quickly by the application of mechanical processes alone (such as settling, heat treatment, application of electrical fields, etc.). However the use of chemical demulsifiers with these processes has been established to be the most effective, convenient and cheapest method for resolving petroleum emulsions. This will increase the speed of oil-water phase separation and rate of the emulsion breaking process.[5,9] These emulsion breaking chemicals are added to the emulsions before they enter the treater[19]. This was first discovered and pioneered by W. S. Barnickel of petrolite corporation over 70 years ago. Generally these chemicals alter the emulsifying films at the oil-water interface and exert a direct influence on these interfaces. This causes a breaking or phase separation of these emulsions at lower temperatures and shorter times than would be the case if these chemicals were not used.

Oil soluble demulsifiers are the most commonly used materials which are effectively used to destabilize the water-in-oil emulsions. These demulsifiers are polydisperse, interfacial active polymers of moderate (2000-50,000) molecular weight and are mostly non-ionic block polymers with hydrophilic and hydrophobic segments. The demulsification method involves the addition of the demulsifiers in-situ in concentrations ranging from 50-300 ppm, depending on the conditions and the total effective area of the dispersed phase.

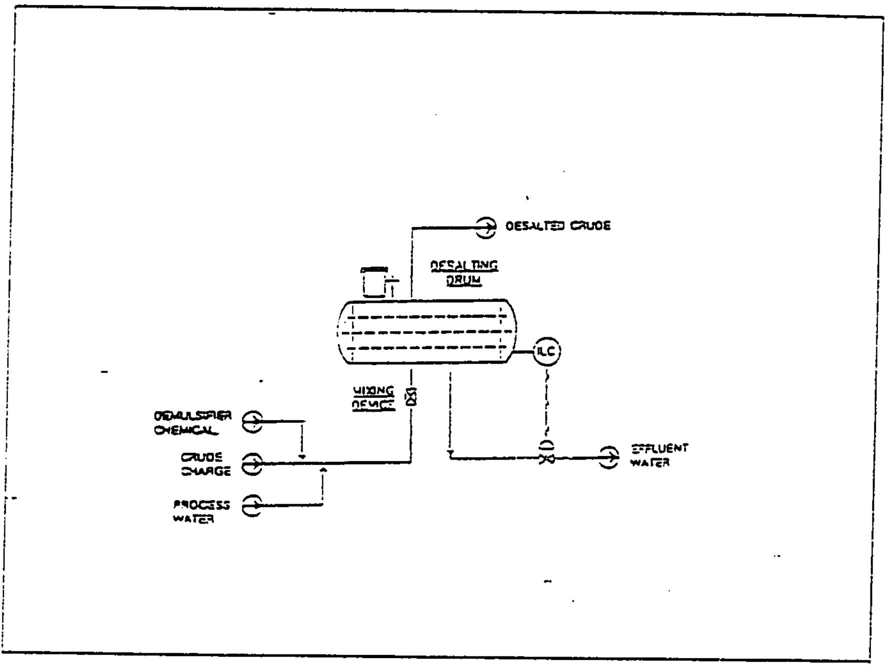


Figure 1:Single-stage Electrostatic Desalter

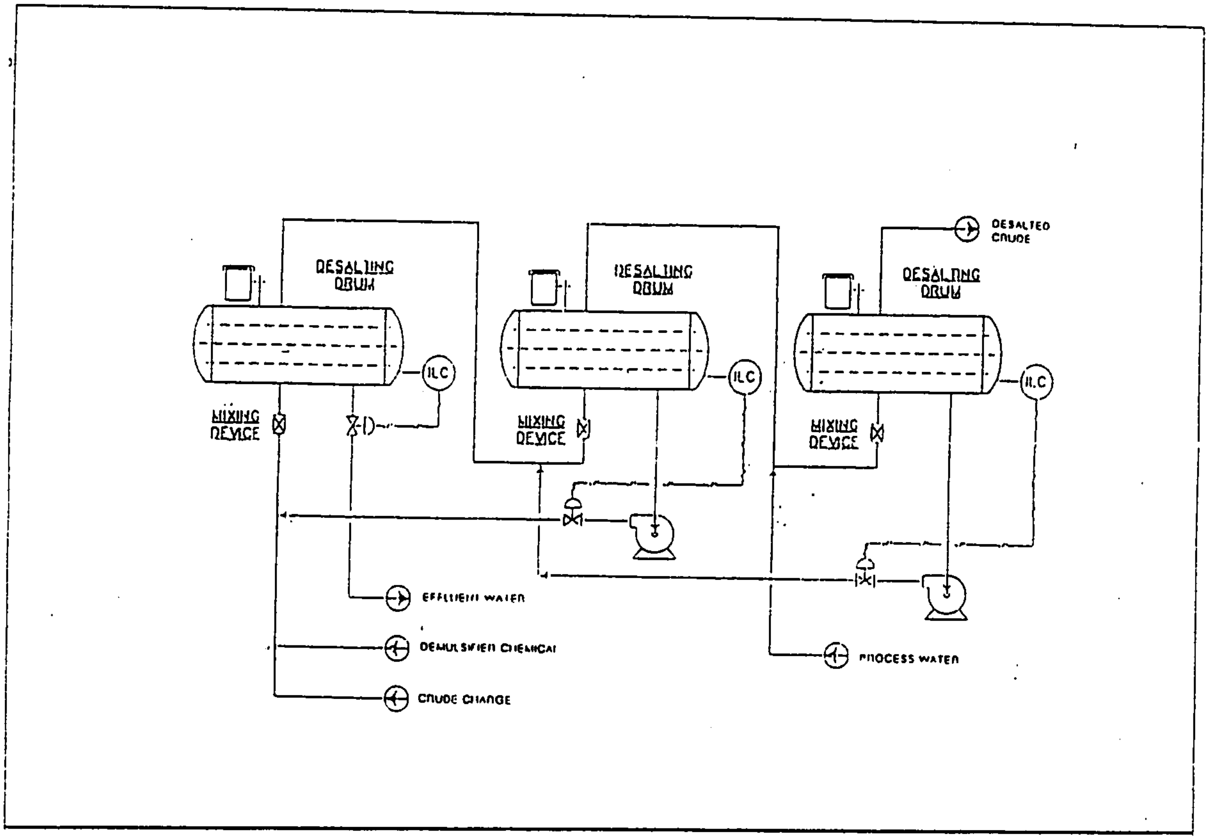


Figure 2: Multi-stage Electrostatic Desalter

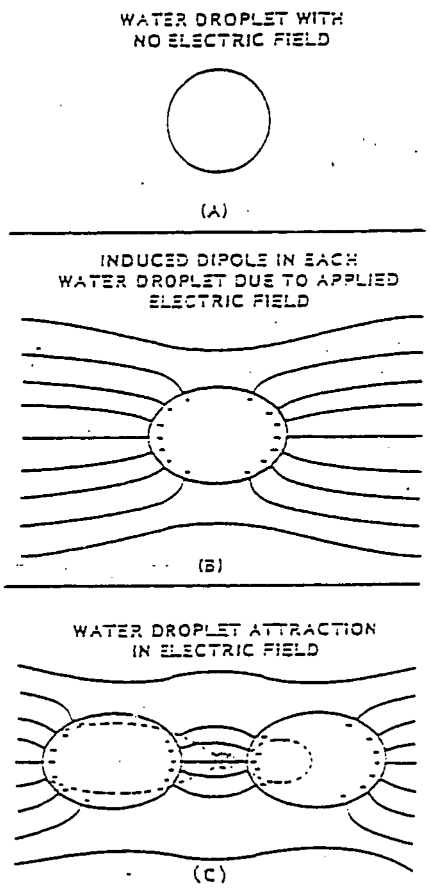


Figure 3: Electrostatically Enhanced Water Droplets Coalescence

A large number of products are developed and their preparation processes are patented. Most of these commercially available demulsifiers are blends of several chemicals. This makes them to be more effective than a single chemical. Efforts are still continuing to create and manufacture products which can be effective at lower concentrations and are more cost effective. Some of the recent patents describe some of these products [20-23]. In addition novel products are developed which are more effective in resolving tight emulsion such as those produced during fire flooding operations[24]. Moreover, some work has been carried out to develop more desirable water soluble demulsifiers which can be as effective as their oil soluble counterparts[25].

(e) Wash water is also added to emulsions before entering into the treaters to desalt the oil, remove harmful contaminants from it, smooth out process variations and minimize system upsets[7].

In general heavy oil emulsions are more difficult to treat than light crude oil emulsions as they contain a higher content of emulsifying agents than light crudes. Emulsions related to oil refinery resides (vacuum tower bottoms) are among the hardest emulsions to be treated as these emulsions are high density and high viscosity hydrocarbon materials containing a very high concentration of water molecules[26].

1.4 Objective and Scope of this Study

Produced fluids from some wells in Saudi Aramco remain in the form of stable emulsion in the surface facilities for a long period of time especially in the winter time when the produced fluids cool down quickly. This causes a significant problem for smooth operation of the Gas Oil Separation Plant (GOSP) and sometimes it results in costly equipment tripping and shut down of the GOSP.

Understanding the factors affecting oil water separation will produce effective methods which can be applied to enhance the oil production operations. This will prevent down time and will have a significant positive economic impact by avoiding production losses and costly equipment tripping.

The objective of this study is to conduct lab tests to investigate various factors affecting the stability of emulsions in some Saudi crudes which are creating problems in the field and to identify methods that will speed up the demulsification process of produced water-in-oil emulsions. In this study, a state of the art emulsion flow apparatus capable of simulating some aspects of emulsion flow in the field has been used. This system has the capability of conducting tests at various pressures and temperatures which are encountered in the field. This system has been fabricated in Saudi Aramco's Dhahran Labs R & D Center.

Tests have been carried out using the above system to examine the effect of temperature on the stability of emulsions produced in the field. Five temperatures of 150, 130, 110, 90, and 70 ^{o}F are examined. This is a very important aspect of the work, since the variations of this factor causes significant operational problems observed in the field.

In addition, tests have been conducted on four commercially available chemicals to examine their effectiveness on demulsifying field emulsions at simulated dynamic field conditions. The aim of this work is to use these chemicals under the field conditions to prevent the flow of tight emulsions into oil separators.

CHAPTER 2

LITERATURE REVIEW

2.1 Diffinition and Classification of Emulsions

Emulsions are colloidal dispersion systems where an immiscible liquid is dispersed in a continuous liquid phase of different composition. Depending on the continuous phase, petroleum emulsions can be classified into two major types[3-7]:

1. Water-in-oil (W/O) emulsions: in which water is the internal phase dispersed in oil which is the continuous or the external phase.

2. Oil-in-water (O/W) emulsions: in which oil is the internal phase dispersed in water which is the continuous or the external phase.

Figures 4 and 5 illustrate w/o and o/w emulsions.

In general water-in-oil emulsions contain 50% or less water, whereas oil-in-water emulsions contain a higher water content 80% or more. These percentages are arbitrary, however under certain conditions, o/w emulsions may exist with more than 20% water. Determining factors include [28]:

1. Relative specific gravities of oil and water: The difference in specific gravity would play important role on the stability of emulsions.

2. Dielectric constants of the internal phase: Similar charges on the dispersed bulk phase aid in emulsion stability because of repulsion of the bulk.

3. The pH of water: Many emulsifiers are designed for various pH ranges. If pH falls outside theses ranges, changes in surface tension and viscosity of the emulsifier may occur.

4. Type of emulsifying agents: Many emulsifiers which affect the stability of emulsions are sensitive to various factors such as temperature and salinity.

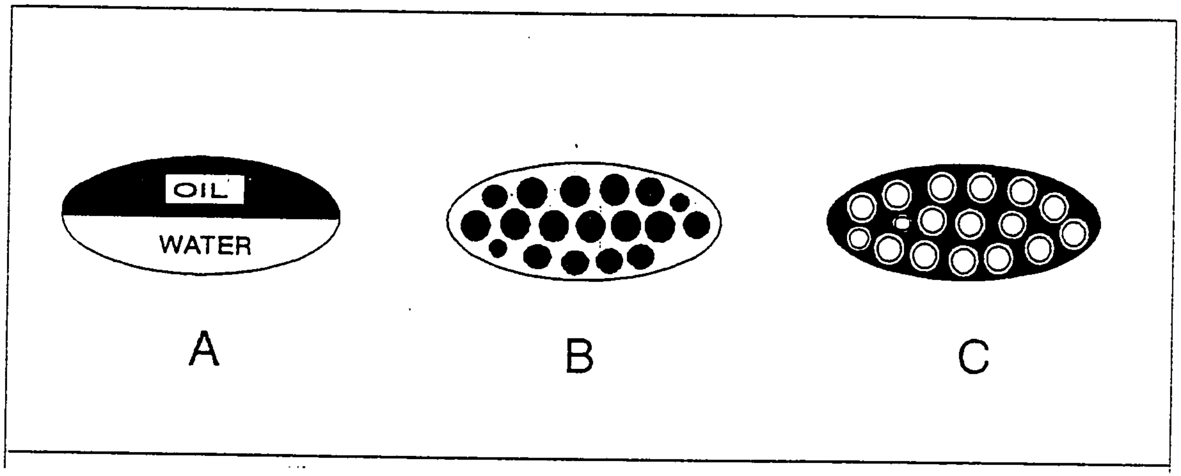
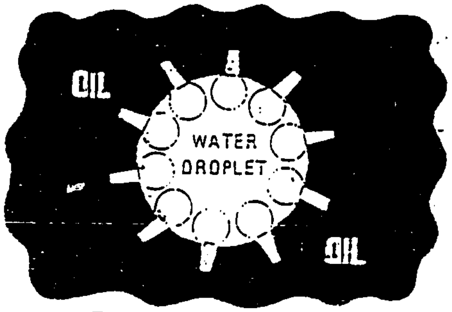


Figure 4: Schematic Representation of (A) Non-dispersed System, (B) An O/W Emulsion, (C) W/O Emulsion



This situation reversed for oil-in-water emulsions

Figure 5: Enlarged Section of W/O Emulsion

2.2 Emulsifiers

Emulsifiers are surface active materials found in the crude oil or added to it as in the case of surfactant flooding. The type as well as the amount of an emulsifier have an immediate effect on the type and stability of the resulting emulsion . An emulsifier tends to be soluble in one of the liquid phases. It thus concentrates at the interface. Four types of emulsifiers which have a stabilizing effect on the interfacial film between oil and water phases may be encountered. These are: anionic emulsifiers in which the water soluble group is negative, cationic emulsifiers in which the water soluble group is positive, nonionic emulsifiers in which the water soluble remains uncharged, and finally the amphoteric emulsifiers in which the water soluble groups are both positively and negatively charged, Fig.6. When stable oil-in-water emulsions are formed by using a cationic emulsifier the droplets will develop a positive charge on their surfaces. Therefore the type of charge imparted to the droplet can be easily deduced from the type of emulsifier used.[29]

There are four distinguishing factors which can be helpful in determining the type of emulsions formed. The dispersed phase may be either (1) moleculary soluble or (2) colloidally dispersible in water. If colloidally dispersible it is either (3) hydrophopic or (4) hydrophilic. If an oil soluble hydrophilic colloid is dissolved in oil, it is impossible to attain a stable emulsion in a water-in-oil dispersion. The same would hold true if a water-soluble hydrophobic colloid is dissolved in an oil-in-water dispersion. A hydrophilic emulsifier will favor the formation of an oil-in-water emulsion, whereas a hydrophobic emulsifier will favor the formation of a water-in-oil emulsion. In

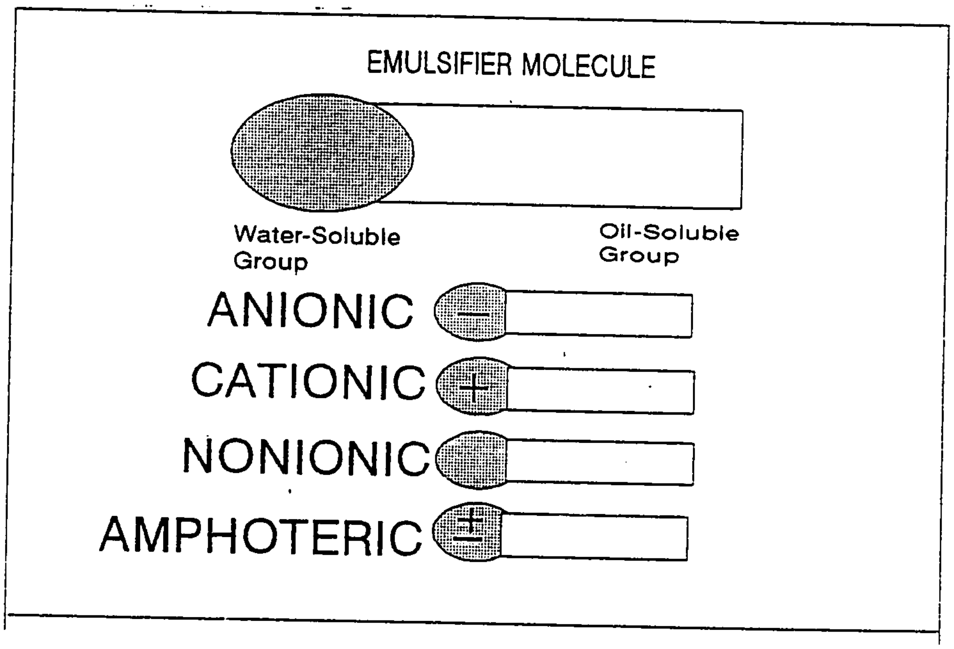


Figure 6: Types of Emulsifiers

other words, the phase in which the emulsifier is more soluble will become the external; however, any emulsifier used must have the ability to come in contact (inteface) with the oil.

The action of the emulsifier can be visualized as one or more of the following[5,7,11]:

1. It decreases the interfacial tension of the water droplet , thus causing smaller droplets to form and hence more stable emulsions result.

2. It forms a skin layer around the droplets that keeps them from coalescing into larger droplets when they collide thus promotes the formation of a stable emulsion.

3. The emulsifier molecules may be polar and align themselves in such a way as to produce similar electrical charges on the surfaces of the droplets which results in strong repulsions between them, thereby reducing oil water separation.

Naturally occurring surface active materials normally found in crude oils and act as emulsifiers are paraffin's, resins, organic acids, metallic salts, colloidal silts and clay, and asphaltenes (a general term for material with chemical compositions containing sulfur, nitrogen, and oxygen). Workover fluids and drilling mud are also sources of emulsifying agents.[3-13]

2.3 Demulsifiers

Demulsifiers are surface active agents comprising relatively high molecular weight polymers. When added to an emulsion , they migrate to the oil-water interface and rupture the stabilizing film as illustrated in Figure 7, or at least weaken it sufficiently for the emulsifying agent to be dispersed back into the oil and for droplets of the dispersed phase to attract, collide, and coalesce. There are three important actions required of a demulsifier as it gets to the oil-water intreface. [5,7,11] These are: flocculation, coalescence, and solid wetting. The faster the demulsifier gets to oil-water interface, the better the job it can do, Figures 8 and 9

1. Flocculation: The first action of the demulsifier on the emulsion involves joining together of small droplets. If the emulsifier film surrounding the water drop is very weak, it will break under this flocculation force and coalescence will take place without further chemical action.

2. Coalescence: The rupturing of the emulsifier film and uniting of water droplets is defined as coalescence. Once this process of coalescence begins, the water droplets grow large enough to settle out.

3. Solid wetting: Demulsifiers have the ability of water wetting solids concentrated at the interface causing them to disperse in the oil or oil wetting them causing them to diffuse into the water droplets.

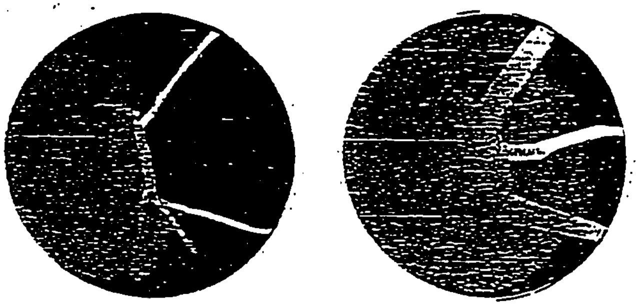


Figure 7: Rupture of Interfacial Film by Demulsifier

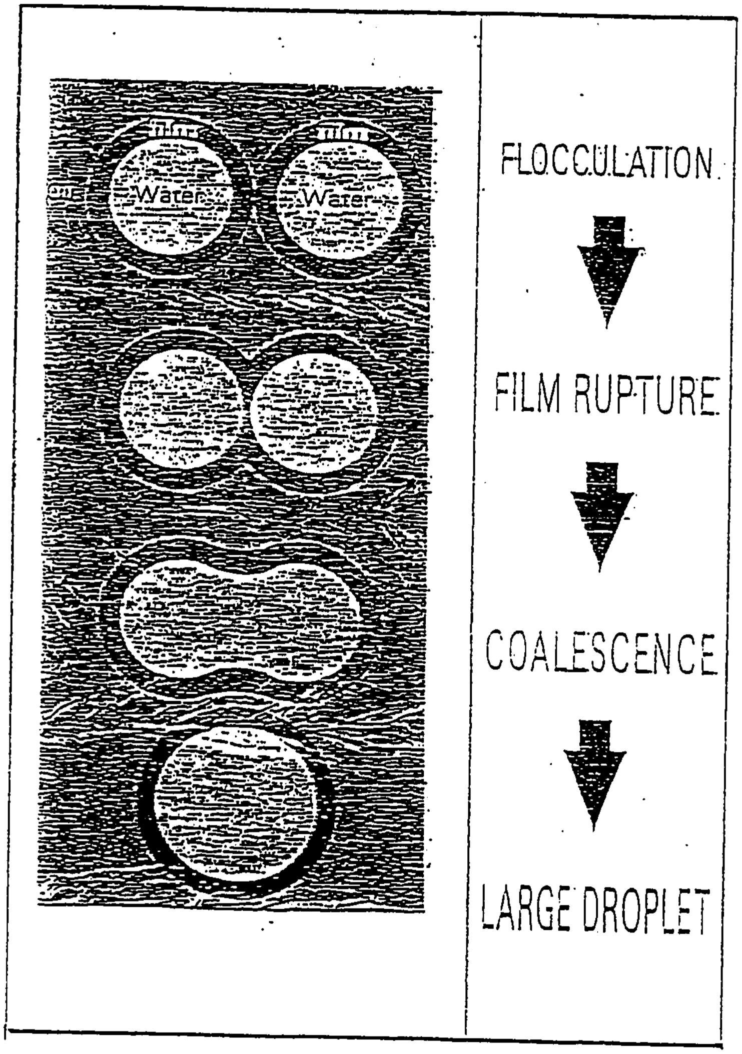


Figure 8: Process of Forming Larger Droplet in W/O Emulsion

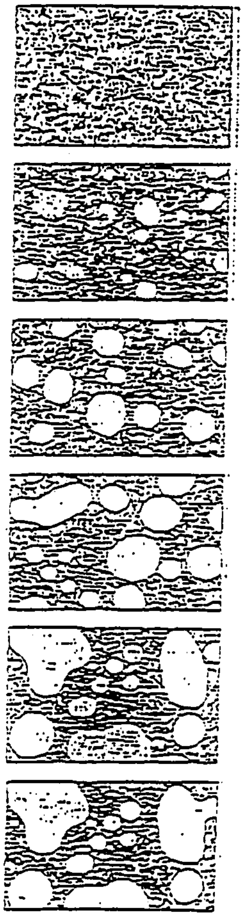


Figure 9: Coalescence of Water Droplets in W/O Emulsion

The manner in which the demulsifier neutralizes the emulsifier depends upon the type of emulsifier. Iron sulfides and clays can be water wet causing them to leave the interface and be diffused into the water droplet. Paraffins and asphaltenes could be made oil wet so they will be dispersed in the oil. It would be unusual if one chemical structure could perform all three desirable actions. A blend of compounds is therefore used to achieve the right action.

2.4 Emulsion Stability

Determining emulsion stability is one of the most important tests that can be conducted on an emulsion. The stability of crude oil emulsions depends upon the naturally occurring emulsifiers which are dispersed in the oil as well as the amount of dispersion caused by the shearing action of screens, pumps, chokes and flowlines.

Research work based on the nature of the interfacial film[3-13] has shown that the characteristics of the interfacial film with respect to strength and compatibility are of prime importance in the development of a stable emulsion. Therefore the amount of emulsifiers present in a system would strongly affect the stability of a water-in-oil emulsion having a high oil concentration. For example, an insufficient amount of emulsifier would allow the electrolytes to weaken the system's stability because of failure of coherent film formation around the bulk oil phase. Therefore the stability of the emulsions was not dependent on the interfacial film, but on the ability of such film to absorb the emulsifiers present in the media.

Also stable emulsions are formed due to the ionic charge of the internal phase. These charges can be obtained by ionization, droplet contact, and absorption. When anionic emulsifiers are present, the droplets will develop a negative charge. The positive ions present in the water phase will then surround the negative charges attached to the droplets and hence prevent coalescence through electrical repulsion. Therefore this will contribute to the stability of emulsions.[7,9,11]

Emulsion stability is considered in the light of three different processes or actions: creaming, aggregation or flocculation, and coalescence. Creaming is the opposite of sedimentation and results from a density difference between the two liquid phases. Creaming does promote coalescence by increasing droplet crowding and hence the probability of droplet-droplet collision. In aggregation two or more droplets touch only at certain points without any change in total surface area. In coalescence two or more droplets join together to form single larger drop with considerable change (reduction) in total surface area as shown in Figure10. Figure 11 shows how the distribution of droplets will appear in an emulsion with different degrees of stability.

2.5 Surface and Interfacial Tensions

Surface tension or interfacial tension is the contracting work per unit area of a surface. This surface energy is usually referred to as a surface tension, if the surface separates a liquid from a gas as shown in Figure 12, and interfacial tension if the force acts at the boundary separating the two liquid phases as shown in Figure 13. Also surface tension can be defined as the free energy required to create a new surface area. The units of surface tension and interfacial tension are millinewtons per meter or dynes per centimeter. [3]

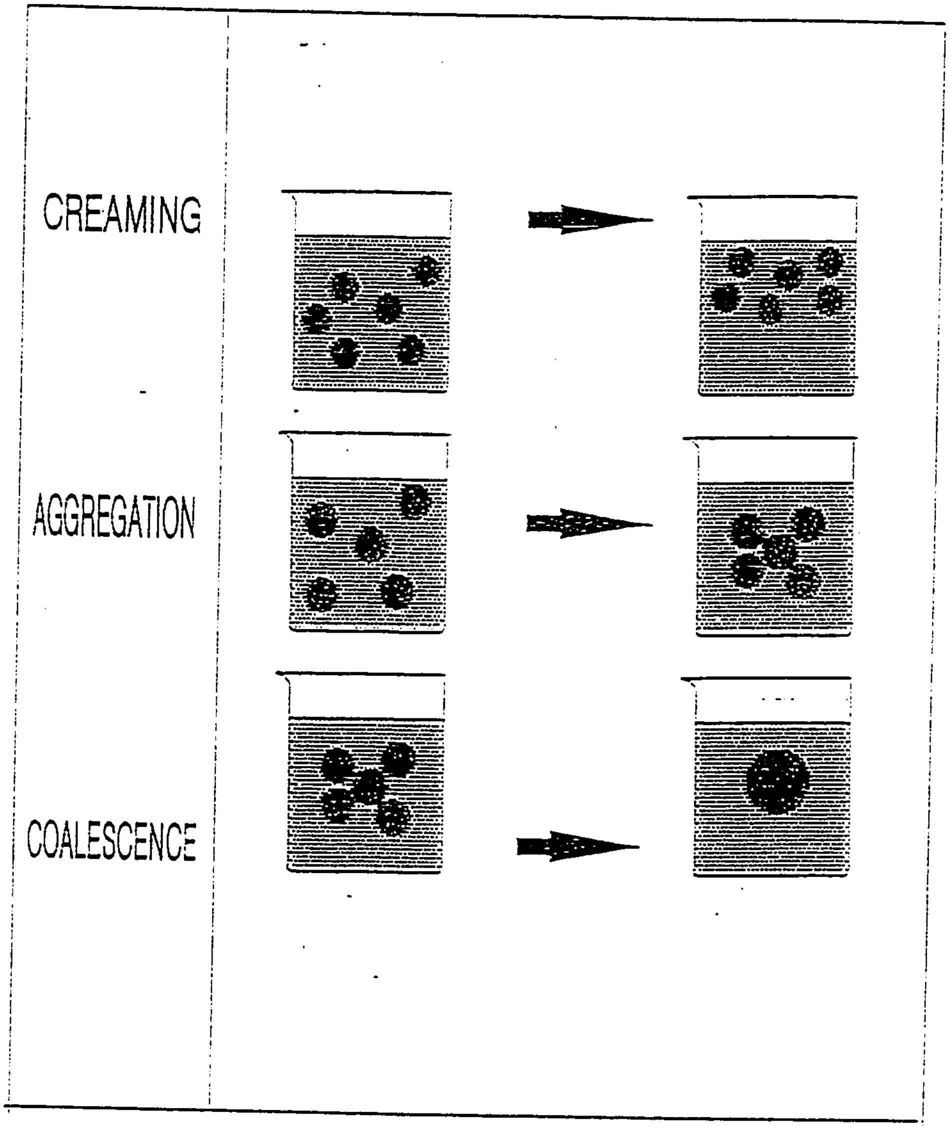


Figure 10: Creaming, Aggregation, and Coalescence in an O/W Emulsion

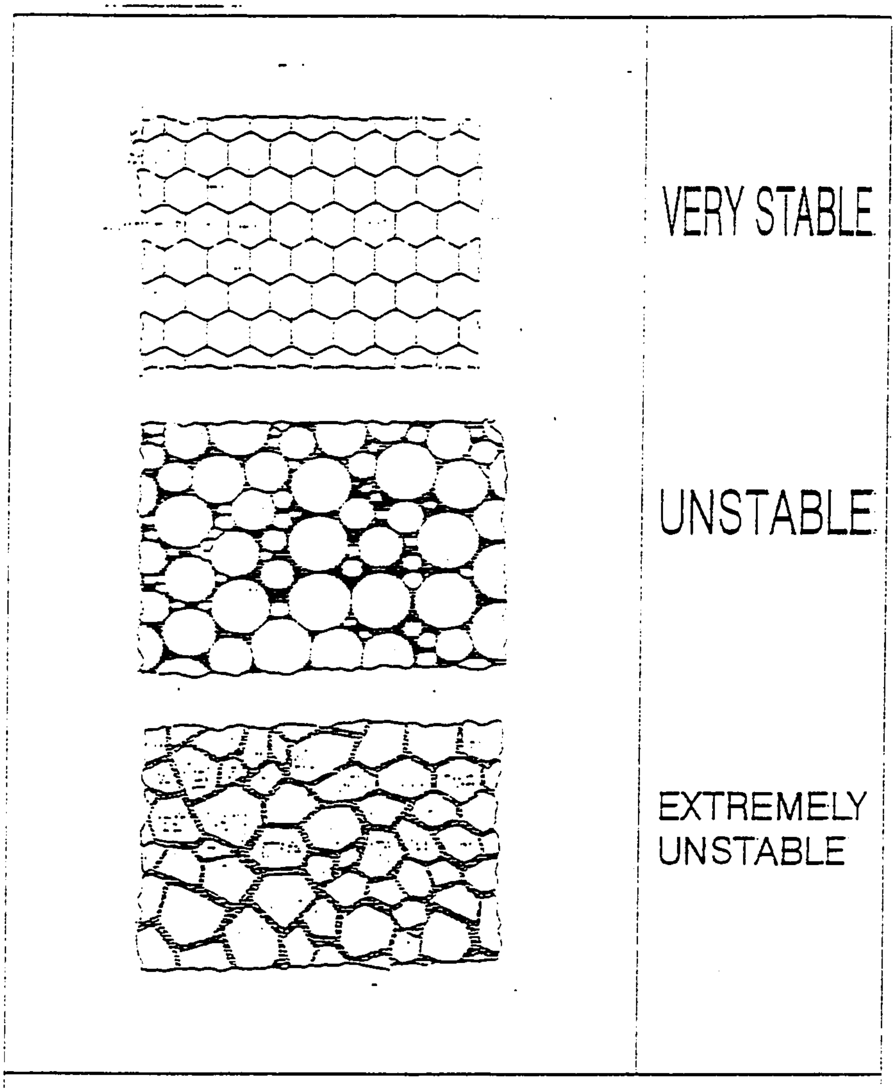


Figure 11: Representation of Various Stable and Unstable Emulsion

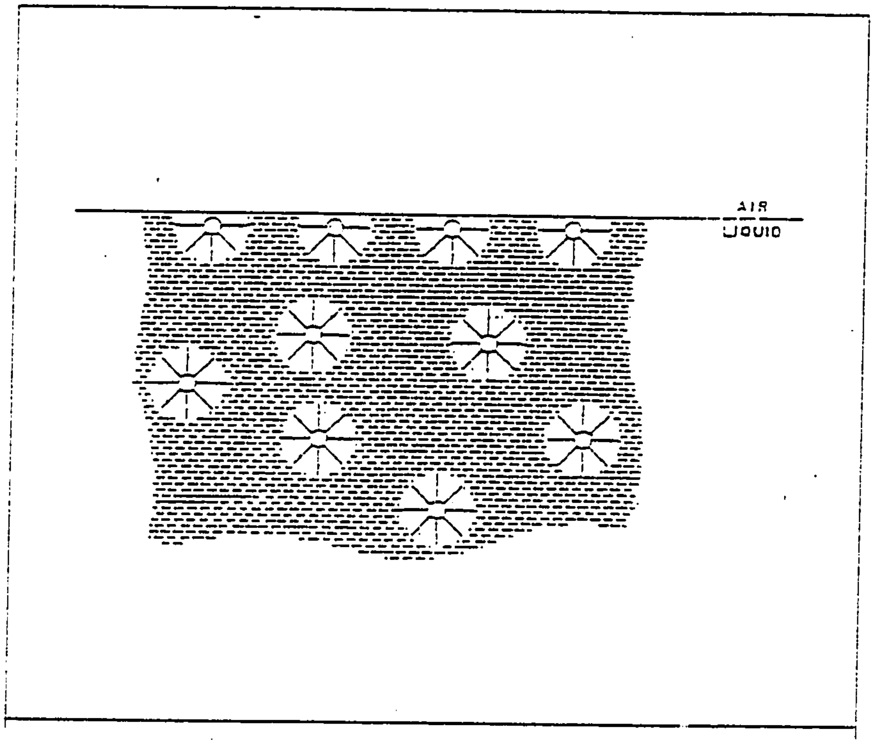


Figure 12: Forces Acting on Molecules on the Surface and in the Interior of a Liquid Layer

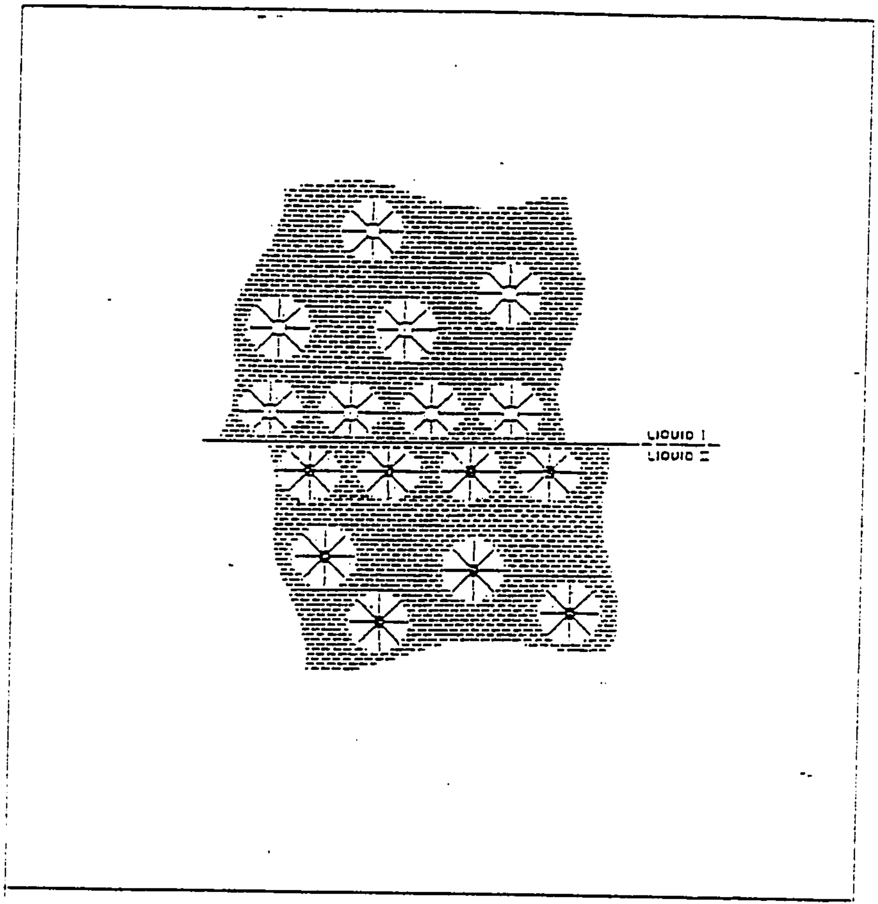


Figure 13: Forces Acting on Molecules at the Interface and in the Interior of a pair of Liquids

2.6 Derivation of Equation 1.1

For a solid spherical particle suspended in a fluid as shown in Figure 14, the following relation works:

$$B + D = W \qquad (2.1)$$

In as much as the buoyant force, B , and drag force, D, are acting in upward direction, whereas the weight, W, in lb is acting down.

$$B = \left[\frac{\pi d^3}{6}\right] \delta_f \qquad (2.2)$$

$$W = \left[\frac{\pi d^3}{6}\right] \delta_s \qquad (2.3)$$

For $N_R < 0.4$ the drag coefficient, C_D , for a sphere is equal to $24/N_R$. Thus for a laminar or viscous flow the drag force in lb is equal to:

$$D = C_D \, \rho \left[\frac{v^2}{2}\right] A$$

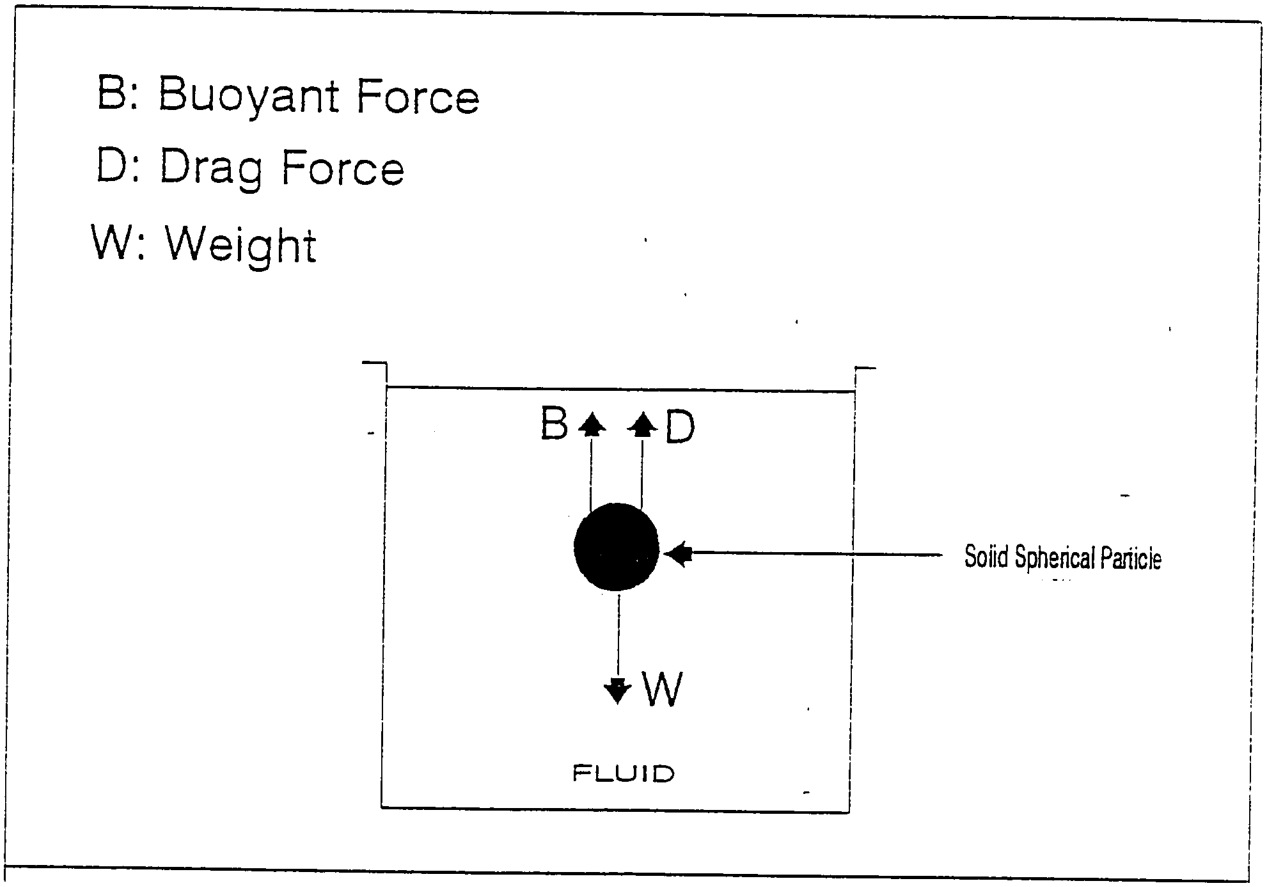


Figure 14: Forces Acting on a Solid Spherical Particle Suspended in a Fluid

$$N_R = \frac{\rho v d}{\mu f}$$

$$A = \pi r^2 = \pi d^2/4$$

$$D = \frac{24}{\rho v d/\mu f} \rho \frac{v^2}{2} \frac{\pi d^2}{4} = 3 \mu f v \pi d \qquad (2.4)$$

Substitute 2.2, 2.3, 2.4 in 2.1 to get

$$\left[\frac{\pi d^3}{6} \right] \delta_f + 3 \mu f v \pi d = \left[\frac{\pi d^3}{6} \right] \delta_s$$

$$\delta = \rho g$$

$$\left[\frac{\pi d^3}{6} \right] [\delta_s - \delta_f] = 3 \mu f v \pi d$$

$$v = \frac{d^2 [\delta_s - \delta_f]}{18 \mu f}$$

$$v = \frac{2gr^2 [\rho s - \rho f]}{9 \mu f}$$

$$v = \frac{2gr^2 [\rho d - \rho c]}{9 \mu c} \qquad \text{------------------------------------} \qquad (2.5)$$

2.7 Previous Studies

The chemical demulsification process was pioneered by William S. Barnickel [33], a pharmaceutical chemist from St. Louis, Minnesota (USA), who discovered that mixing a minute proportion of a properly selected chemical composition with a petroleum emulsion under suitable operating conditions cause the water to separate.

Cairns, et al. [6] studied the effect of crude oil-water interfacial properties on water-in-oil emulsion stability. They found that the conditions favorable for the formation of a stable water-in-oil emulsion are a high oil-water viscosity ratio and a rapid initial adsorption of natural surfactants (rapid fall in interfacial tension). This should be followed by a rapid rise in interfacial viscosity. The high interfacial viscosity exhibited under some conditions is due in part to the presence of basic surface-active species in the interface. The asphaltene content of a crude oil does indicate the existence of a high interfacial viscosity.

Kimbler, et al. [31] were the first to make an extensive study of the physical characteristics of the film adsorbed at the crude oil-water interface. They used the horizontal type film balance to determine pressure build up behavior of films at liquid-liquid interfaces, and found that interfacial films formed by different crude oils varied markedly in their physical characteristics and that these somehow contributed to the formation of organic deposits such as paraffin.

Dunning et al. [30]made extensive studies on the physical characteristics of the film adsorbed at the crude oil-water interface. They reported the existence of metals in the materials adsorbed at the petroleum-water interface. Porphyrin complexes contributed to a major extent to film formation at the interface. In addition, they reported that about 12.5% of the separated materials consisted of high molecular weight aliphatic hydrocarbons.

Singh and Pandey[12] studied the physical characteristics of natural crude oil-water interfacial films as a function of crude oil pH and the ionic composition of water. They also studied the effect of demulsifiers on film properties and correlated emulsion stability to film pressure. They conclude the following:

- As the concentration of salt in water is increased the separation of emulsified water decreased.

- As the pH value increases, emulsions become more stable and difficult to separate.

- As NaOH concentration increases, the ionization of natural acids increases in crude oil , thus increasing the effective surfactant concentration and hence the interfacial tension and particle size decrease and the interfacial viscosity increases.

Cottrell [32] invented the electrical technique for resolution of emulsions. The effect of water and oil phase properties on the kinetics of electrostatic demulsification has been investigated by Hano, et al.[15] and Bernie, et al. [16]. Water-in-oil emulsions prepared under various conditions were studied. It was concluded that the viscosity of the oil phase and the ionic strength of the water phase were among the most important oil related parameters which control demulsification rates under an electrostatic field.

Chillingarian, et. al. [9] studied the electrical resolution of oil field emulsions. They found that the application of electrical field is a powerful tool for causing dispersed droplets to rapidly collide with each other and for overcoming the resistance of stabilizing films. An induced dipole attraction between droplets provides a strong aid in accomplishing the collision and coalescence of droplets and hence promotes good water separation.

The effect of electric field pulsation frequency on breaking water-in-aromatic solvent emulsion in a continuous flow electrostatic coalescer cell was investigated by Drelich et. al. [17]. Their findings were as follows:

- The electric field strength was confirmed to be the controlling parameter for demulsification.

- The separation efficiency of a water-in-oil emulsion (containing from 0.08% to 0.2% water) was found to exceed 80% for a 25 second nominal residence time.

- The electric field strength should not exceed 140 KV/m

- A maximum in separation efficiency was observed for pulsation frequencies between 8 Hz and 11 Hz.

CHAPTER 3

THE EXPERIMENTAL APPARATUS AND PROCEDURES

3.1 The Experimental Setup

The setup is designed to simulate the behavior of the emulsion under dynamic conditions at the pressures and temperatures that exist at the Gas Oil Separation Plant in the oil field. A schematic diagram of the experimental setup used is shown in Figure 15. It consists of the following parts:

1. Test Cell: This cell or separator is a large high pressure high temperature vertical vessel with 1100 cc capacity. It is placed inside the oven. This cell is equipped with a double window system. These windows are used to transmit the light through the cell to examine the behavior of the fluid inside the cell. The test cell will be initially charged with oil and brine or field emulsions, and then the other parts of the system are used to prepare and examine emulsions at various dynamic conditions. The stability of the emulsion within the test cell is monitored with time to assess the effects of temperature, chemical addition, and

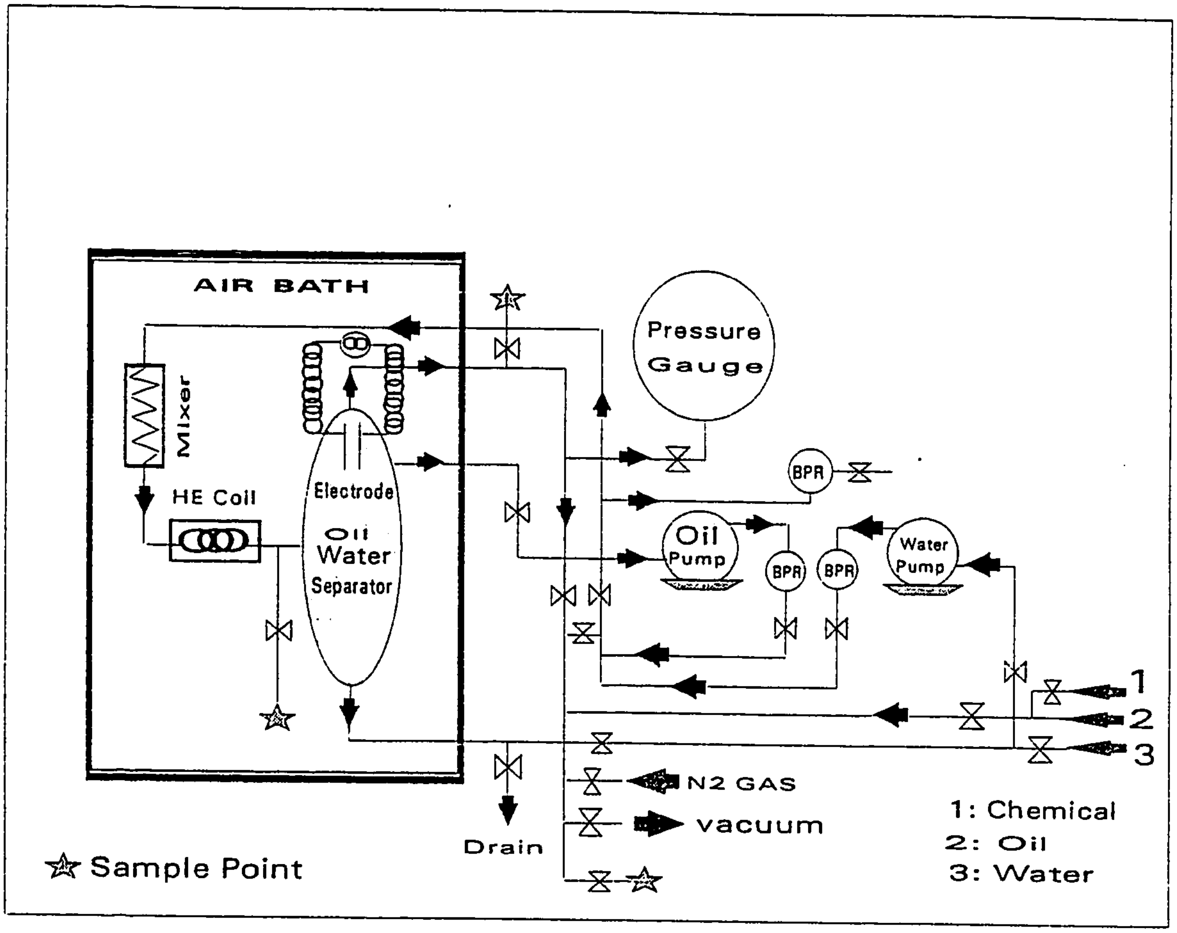


Figure 15: Simplified Diagram of Emulsion Flow Apparatus

water-oil ratio.

2. Mixer: Mixes oil and brine to create an emulsion. Various static mixing elements are used in this system. Depending on the conditions, various length and numbers of these mixers will be used to create emulsions which are similar to those experienced in the field. These mixers are placed inside the oven.

3. Coil Tube: This is about 100 ft long and is placed inside the oven. It allows the emulsion created by the mixer to be reconditioned before entering into the separator(test cell).

4. Pumps: Two identical pumps are used to remove oil and brine from the cell and feed into the mixing system to create an emulsion. By changing the rates of pumping, one can simulate the flow of oil with various water cuts.

5. Back Pressure Regulators (BPR): Two back pressure regulators are used in the system which operate at 50 and 110 psig pressures. The 50 psig BPR is used initially when the system is charged with oil. This allows degassing the oil to 50 psig, as is done in the Gas Oil Separation Plant (GOSP) at the Saudi Aramco fields. The 110 psig BPR is used to main a system pressure like that used in dehydrators and desalters at Sauid Aramco GOSP.

6. Brine Pump: This positive displacement pump(PDP) is used to charge the system with brine as well as to displace oil from the oil sample cylinder into the test cell during the charging.

7. Chemical Pump: This is an HPLC metering pump used to inject chemicals into the system.

8. Vacuum Pump: The vacuum pump is used to create vacuum, remove oxygen from the system during the charging, and to degas all brine solutions used in charging the system to remove any oxygen gas.

9. Oven: This oven is used to house the test cell, mixer, and coil tube. It is equipped with refrigerated circulator bath, radiator, and fan system. It is capable of creating various stable and constant testing temperatures ranging from 60 to 220°F.

10. Valves: Various valves are used in charging, discharging, and cleaning the system.

11. Thermocouples and Gauges: To monitor the temperature and pressure of the system.

12. Electrodes: The test cell is equipped with electrodes and various other parts such as transformers, a circuit breaker, and electrical switches to apply the electrical potential to accelerate the coalescence of emulsion droplets during the emulsion breaking phase of the test to simulate the conditions that exist at dehydrators and desalters at the GOSP.

3.2 Functions of the Experimental Apparatus

Static bottle tests in atmospheric conditions could not be used to fully examine the field produced emulsions as it does not represent the field conditions where emulsions are treated under dynamic conditions at different temperatures and pressures under an electrostatic field as well as under different shear rates. Therefore a laboratory system which is able to simulate various aspects of emulsion flow under the field condition(designed and built in Saudi Aramco Labs R & D Center in Dhahran) was used in running the laboratory tests. The capabilities and functions of this apparatus are:

a) To examine phase separation of emulsions :
  - At dynamic conditions
  - At pressures and temperatures similar to those encountered in GOSP
  - Under the influence of an electrostatic field
  - At different shear rates

b) To test field emulsions:
  - With different water cuts
  - At various temperatures and pressures

c) To creat emulsions from various crude oil samples:
  - With different water cuts
  - At various temperatures and pressures
  - At different shear rates

d) To test and investigate:
  - The effect of demulsifying chemicals to break field emulsions
  - The combined effects of temperature and demulsifier on demulsification of emulsions
  - The emulsification tendency of various produced crudes

e) To use effectively in:

- Assisting field operations by optimizing the use of demulsifying chemicals in breaking field emulsions.
- Selecting the most effective product by conducting comparitve tests among various demulsifiers

This laboratory system was used to examine the effect of temperatures of 70,110, 150, 190 and 220 °F on the stability of emulsions produced in the field. It was also used to test the effectiveness of various demulsifying chemicals on breaking oil field produced emulsions at these temperatures.

3.3 Preparation of Oil or Emulsion: Oil or emulsion samples are collected from the well-head by the brine displacement method in 5-gallon cylinders. Then they are depressurized to 50 psig to remove the evolved gas associated with the produced fluids. This is done to simulate the field conditions. After this the pressure in the cylinder is raised to 110 psig to make it ready to be charged to the system.

3.4 Preparation of Brine: Associated brine with the produced oil will be brought to the laboratory, filtered, degassed, and then used in charging the system. Synthetic brine will be prepared with the same chemical composition as the field brine if enough field brine could not be obtained.

3.5 Experimental Procedures

The system is first flushed with Nitrogen(N_2) gas to remove most of the oxygen (O_2) gas. Then N_2 gas is removed using the vacuum pump. After evacuation the system, the system is charged and flushed with brine solution. Then using the PDP pump, oil or emulsion is introduced into the system from the top of the test cell to a given level. The system temperature is then raised to the test condition. The oil and water pumps are started simultaneously to circulate the fluid through the mixer and the coil tube at the required rates (110 cc/min) to create emulsions. If the test condition calls for the addition of any demulsifier, then the demulsifying chemical is also introduced into the system during the circulation. During the circulation stage, the level of emulsion and water phases inside the cell are closely monitored over time. Once the fixed circulation time of 20 minutes is completed, then all the pumps are stopped and the produced emulsions are monitored. Again the levels of oil and water are monitored inside the test cell over time. A residence time of 10 minutes is allowed. This is used to assess the stability of the emulsions prepared. The power for the coalescing electrodes is also turned on during this stage. In order to assess field emulsions, sometimes only one pump was used to circulate the emulsion and examine its behavior at various conditions and in the presence of demulsifiers.

Discharge of the Cell: After the required emulsification or demulsification stages are completed, the cell is discharged. The oil phase is be collected into the 100 ml centrifuge tubes which are heated to 150°F then centrifuged and demulsified by the addition of demulsifying chemicals to determine its water content of the sample.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Examination of the Effect of Temperature on Field Emulsion

The effect of temperature on the stability of emulsions produced from well-B of the test area was studied. Samples of field emulsions were charged into the dynamic flow system in the lab, then these emulsions were examined under the dynamic conditions at various temperatures of 70, 110, 150, 190, and 220°F. It was observed that by increasing the temperature field emulsions gradually broke down to oil and water. At 220°F charged emulsion was completely broken down to oil and water without addition of any demulsifying chemical. As shown in Table 1 and Figure 16, at 190°F about 39% by volume of the fluid remains in the form of emulsion, at 150°F this was about 65% , at 110°F this was 75%, and at 70°F up to 85% of the fluid remains in the form of emulsions.

Table 1:The Effect of Temperature on Stability of Emulsion Produced from Well-B

TEMPERATURE (^{o}F)	CHEMICAL (PPM)	TOTAL EMULSION (%)	TOTAL EMULSION AFTER HEATING & CENTRIFUGING (%)
70	0	85	47
110	0	75	46
150	0	65	45
190	0	39	34
220	0	0	0

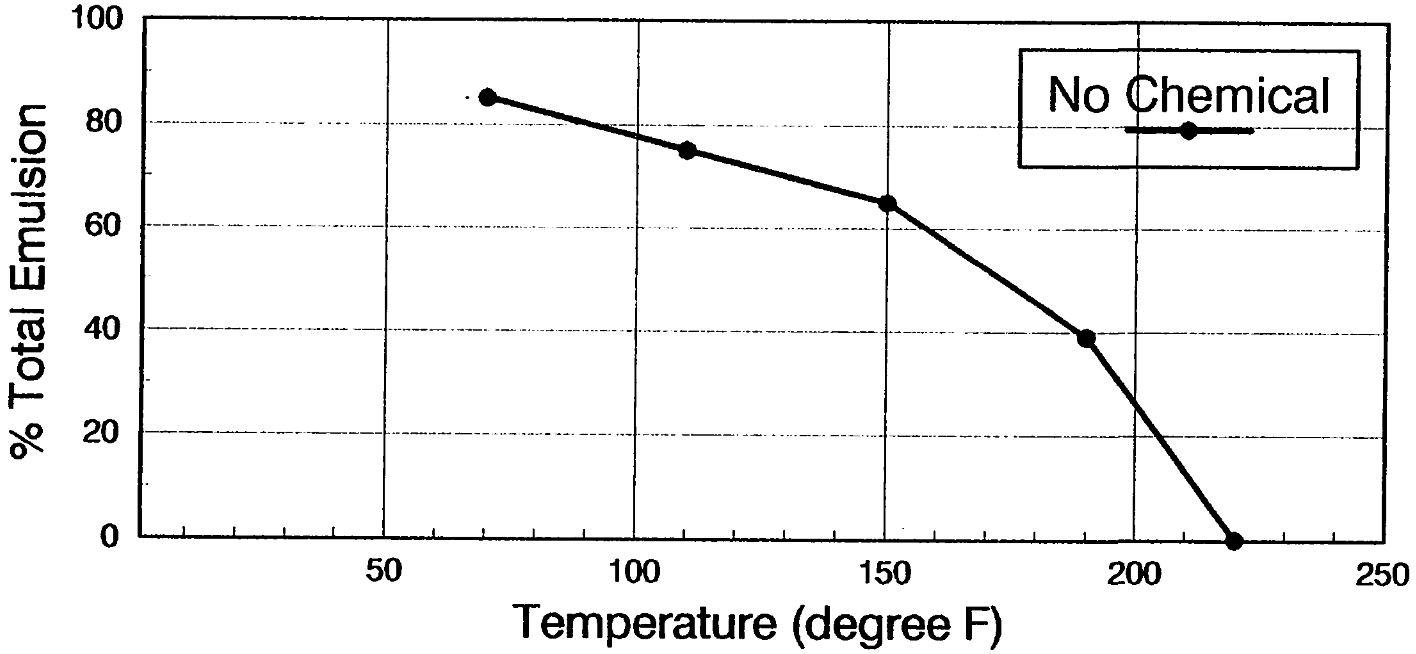


Figure 16:Effect of Temperature on Stability of the Emulsion Produced from Well-B

4.2 Effect of Aging on Emulsions

Fluids produced from well-B normally consist of two layers, top and bottom layers. The top layer (which is less than 10% of the produced fluid) is a clean oil with only a few percent of water. It is a very low viscosity material as shown in Table 2, and it remains the same with time (up to 3 months). The bottom layer (which is over 90% of the produced fluid) is a thick layer of water-in-oil emulsion with a water content of about 50 to 65%. This emulsion has very high viscosity (over 300 cp), as shown in Table 3 and high density (about .96 g/cc). This emulsion is stable and with time it even becomes thicker (gel like material) under static condition. This aged emulsion exhibits a shear thinning effect, by stirring it becomes thinner again and its viscosity decreases to that of freshly produced emulsions.

4.3 Effect of Various Demulsifying Chemicals on Tight Field Emulsions

Extensive tests were conducted to examine the effect of four commercially available (widely used by Saudi Aramco) demulsifiers (See Appendix) on resolving tight field produced emulsions from well-B under dynamic conditions similar to those exist in the field at various temperatures of 70, 110, 150, 190^{o}F. These demulsifiers are: Champion , Atros, Petrolite, and Exxon. All of these chemicals can resolve field produced emulsions completely, however their effectiveness was not the same at various temperatures as shown in Table 4 and Figure 17 and briefly discussed bellow:

Table 2: Viscosities at Various Temperatures for an Oil Separated from an Emulsion Produced from Well-B

TEMPERATURE (°F)	APPARENT VISCOSITY (CP)
76	15
90	11
100	10
110	8
120	7
130	6
140	6
150	6
160	5
170	5
180	4
190	4
200	3

Table 3: Viscosities at Various Temperatures for an Emulsion Produced from Well-B

TEMPERATURE (°F)	APPARENT VISCOSITY (CP)
70	>300
80	>300
90	>300
100	>300
110	>300
120	>300
130	>300
140	>300
150	>300
160	230
170	173
180	130
190	85
200	10

Table 4: Concentrations of Various Demulsifiers Required to Break Produced Emulsions from Well-B at Various Temperatures

TEMP.	Champion	Atros	Petrolite	Exxon	Atros + Champion (50% EACH)	Atros + Petrolite (50% EACH)
(°F)	CONC. (ppm)	CONC. (ppm)	CONC. (ppm)	CONC. (ppm)	CONC. (ppm)	CONC. (ppm)
70	80	100	106	114	111	134
110	48	57	60	70	29	65
150	20	35	27	40	23	34
190	6	14	8.5	15	4.5	20
220	0	0	0	0	0	0

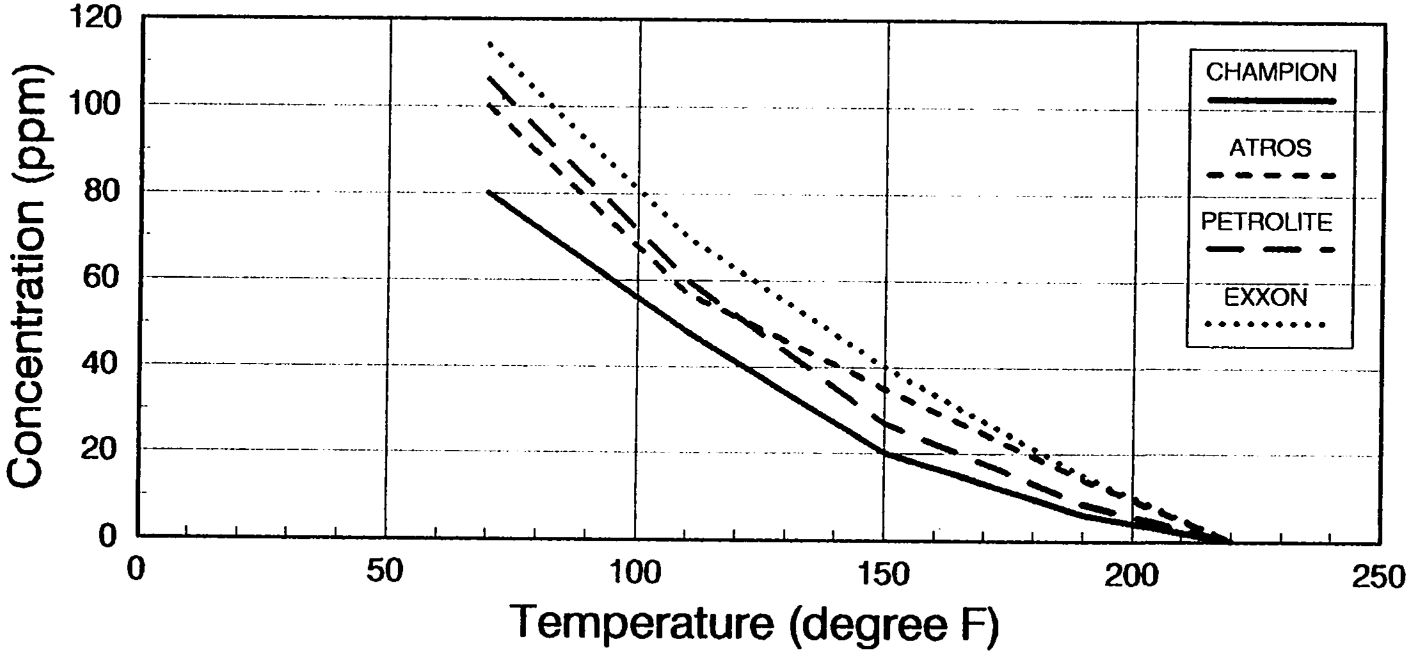


Figure 17: Concentration of Various Demulsifiers Required to Break Emulsions Produced from Well-B at Various Temperatures

1) **Champion Demulsifier** was the most effective chemical to resolve the field emulsions. It required only 80, 48, 20, and 6 ppm at 70, 110, 150, and 190 °F respectively to completely resolve these emulsions as shown in Table 4 and Figure 18.

2) **Atros Demulsifier** was the next effective product to resolve these emulsions. It required 100, 57, 35, and 14 ppm at 70, 110, 150, and 190 °F respectively to completely resolve the field emulsions as shown in Table 4 and Figure 19. However at temperatures of about 150°F and above, Petrolite out performed Atros and only 27 ppm and 8.5 ppm were needed to resolve emulsions at 150 and 190 °F respectively as shown in Table 4 and Figure 20.

3) **Petrolite Demulsifier** was in the third place in term of its effectiveness in resolving the field emulsions at low temperatures. The amounts of demulsifier needed to completely break the emulsions were 106 ppm and 60 ppm at 70 and 110 °F respectively as shown in Table 4 and Figure 21.

4) **Exxon Demulsifier** was in the fourth place to break the tight emulsions. It required 114, 70, 40, and 15 ppm at 70, 110, 150, and 190 °F respectively as shown in Table 4 and Figure 22.

Due to the fact that presently demulsifier Atros is used in the field, if any demulsifier other than Atros is to be applied at the well-head, it must be compatible with this chemical. Tests were carried out using a 50/50 combination of Atros with Champion as well as with Petrolite. It was observed that these chemicals can be used together with no adverse effect and emulsions were resolved completely as shown in Table 4 and Figures 23 and 24.

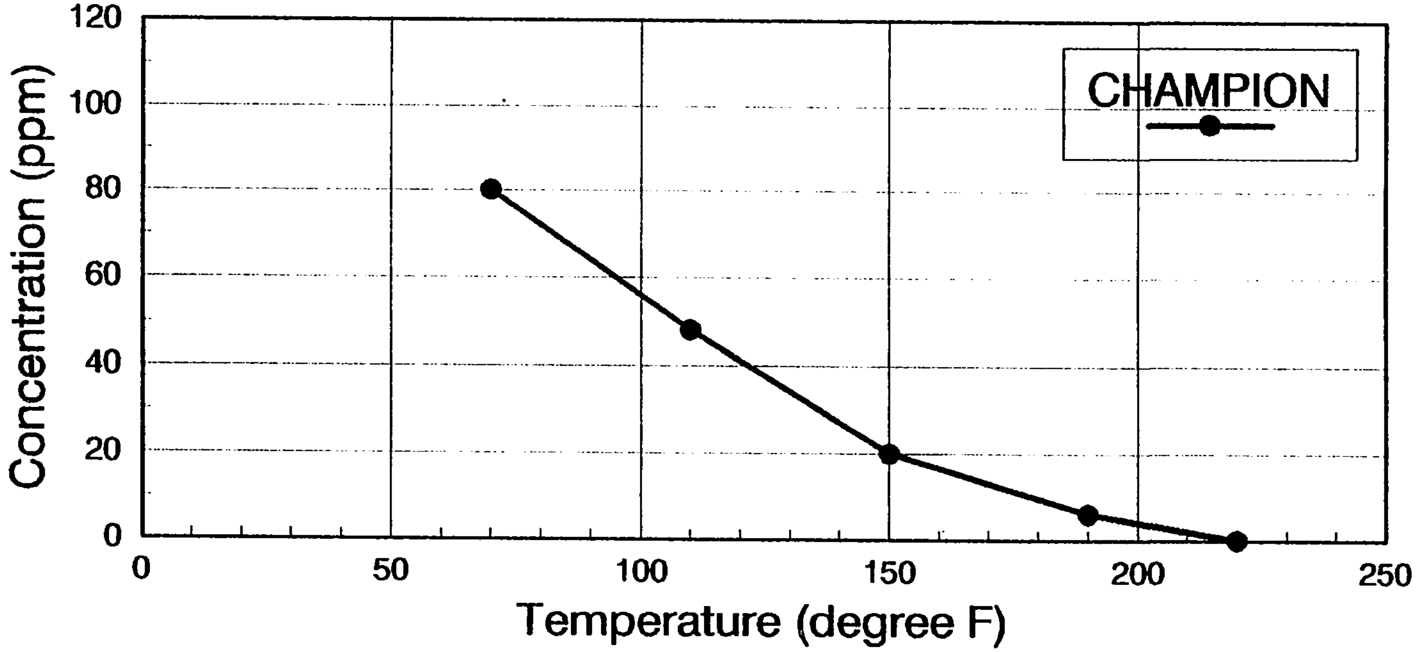


Figure 18:Concentration of Champion Demulsifier Required to Break Emulsions Produced from Well-B at Various Temperatures

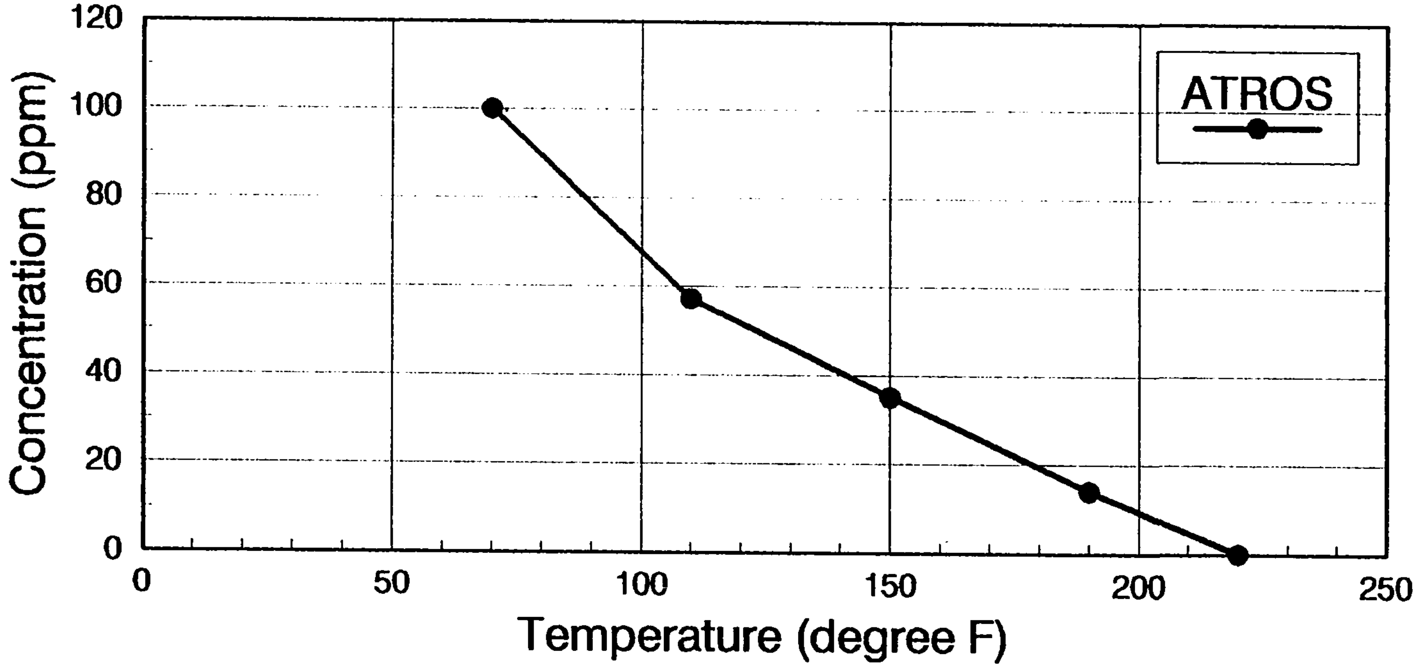
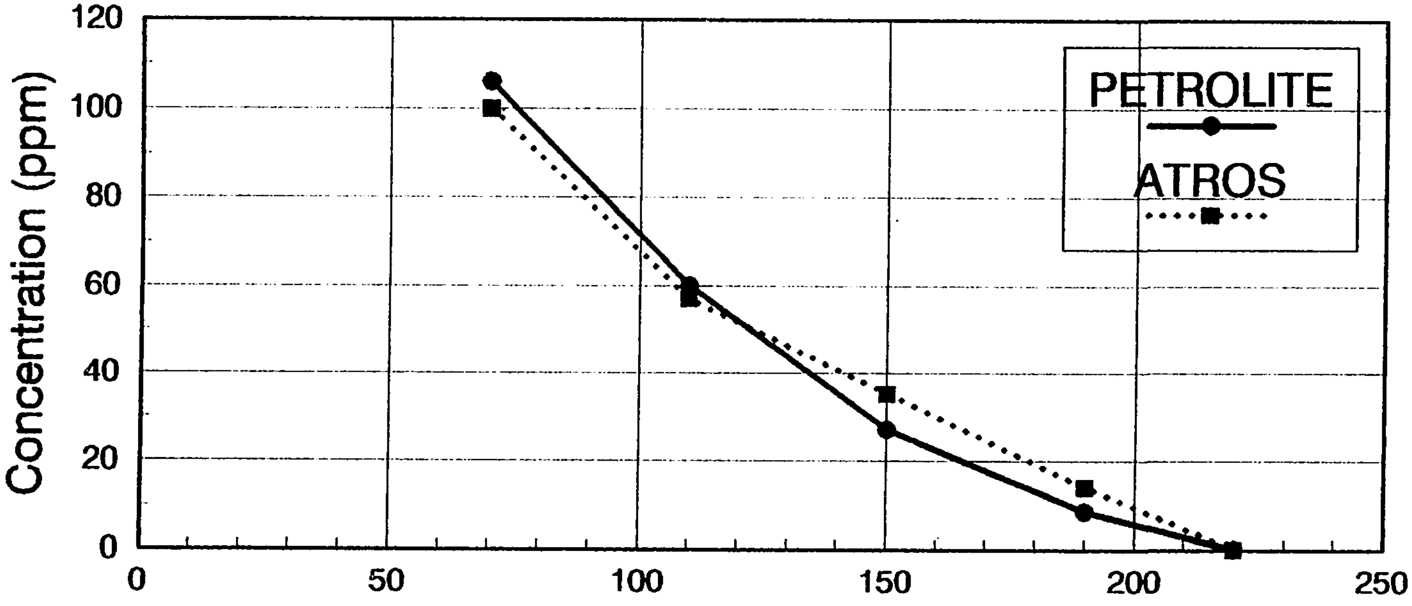


Figure 19:Concentration of Atros Demulsifier Required to Break Emulsions Produced from Well-B at Various Temperatures



Temperature (degree F)

Figure 20:Concentration of Atros and Petrolite Demulsifiers Required to Break Emulsions Produced from Well-B at Various Temperatures

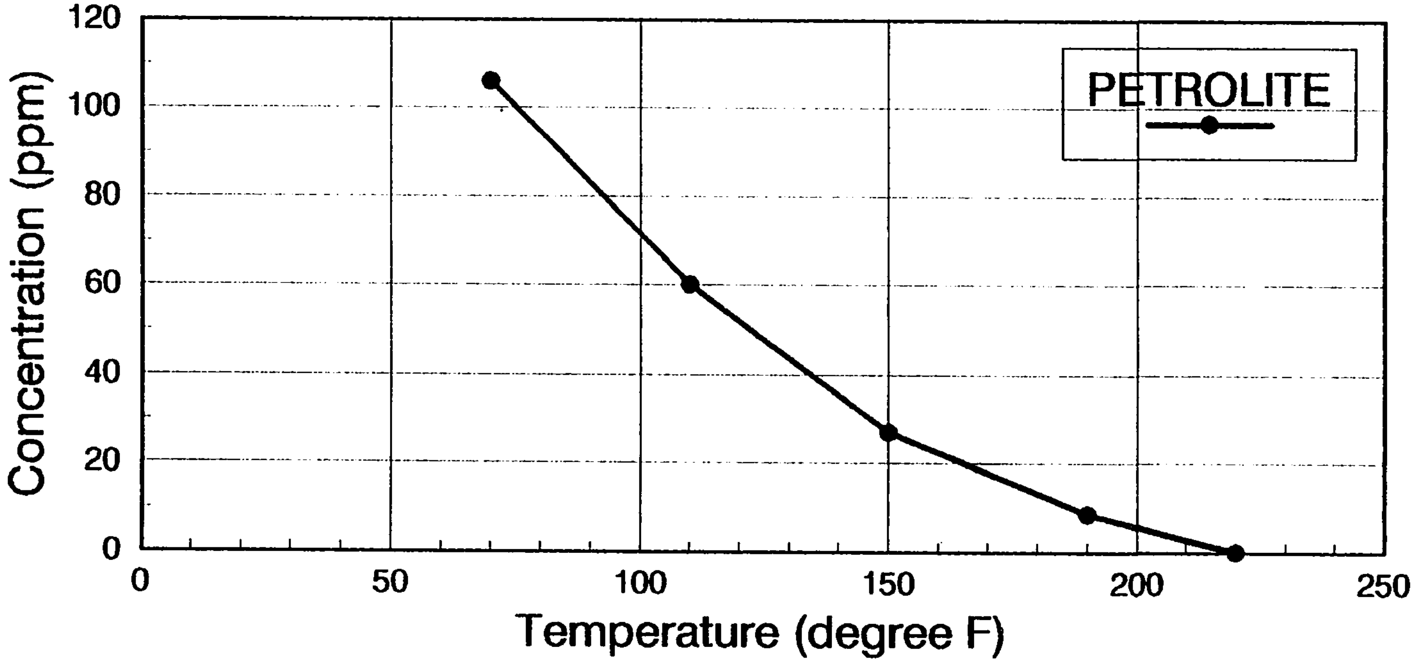


Figure 21:Concentration of Petrolite Demulsifier Required to Break Emulsions Produced from Well-B at Various Temperatures

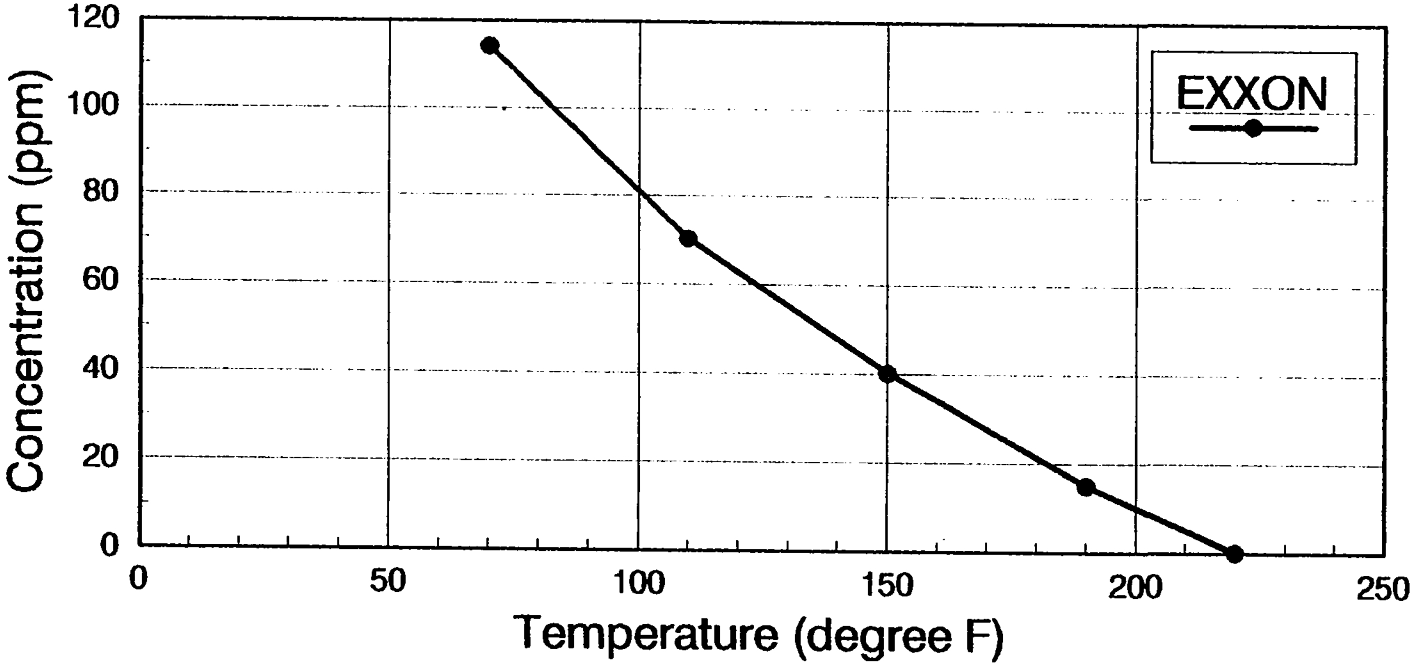


Figure 22:Concentration of Exxon Demulsifier Required to Break Emulsions Produced from Well-B at Various Temperatures

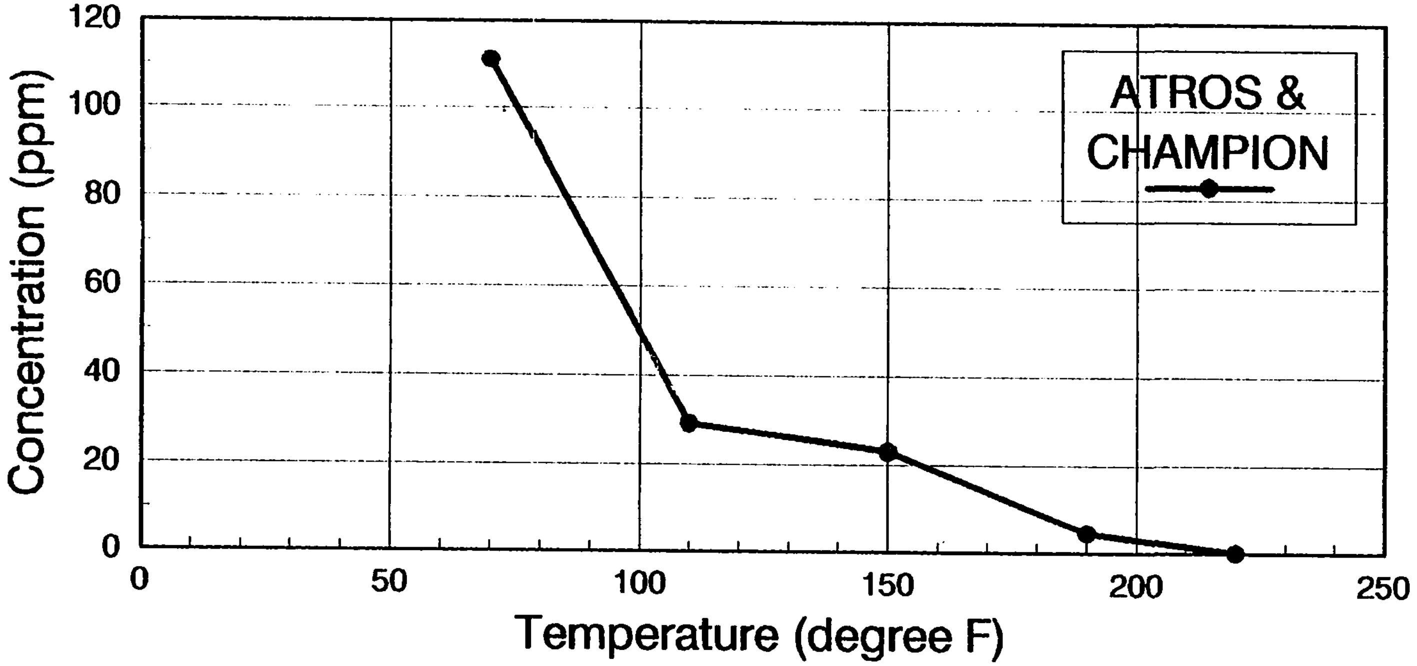


Figure 23:Concentration of Mixed Demulsifiers (Atros+Champion) Required to Break Emulsions Produced from Well-B at Various Temperatures

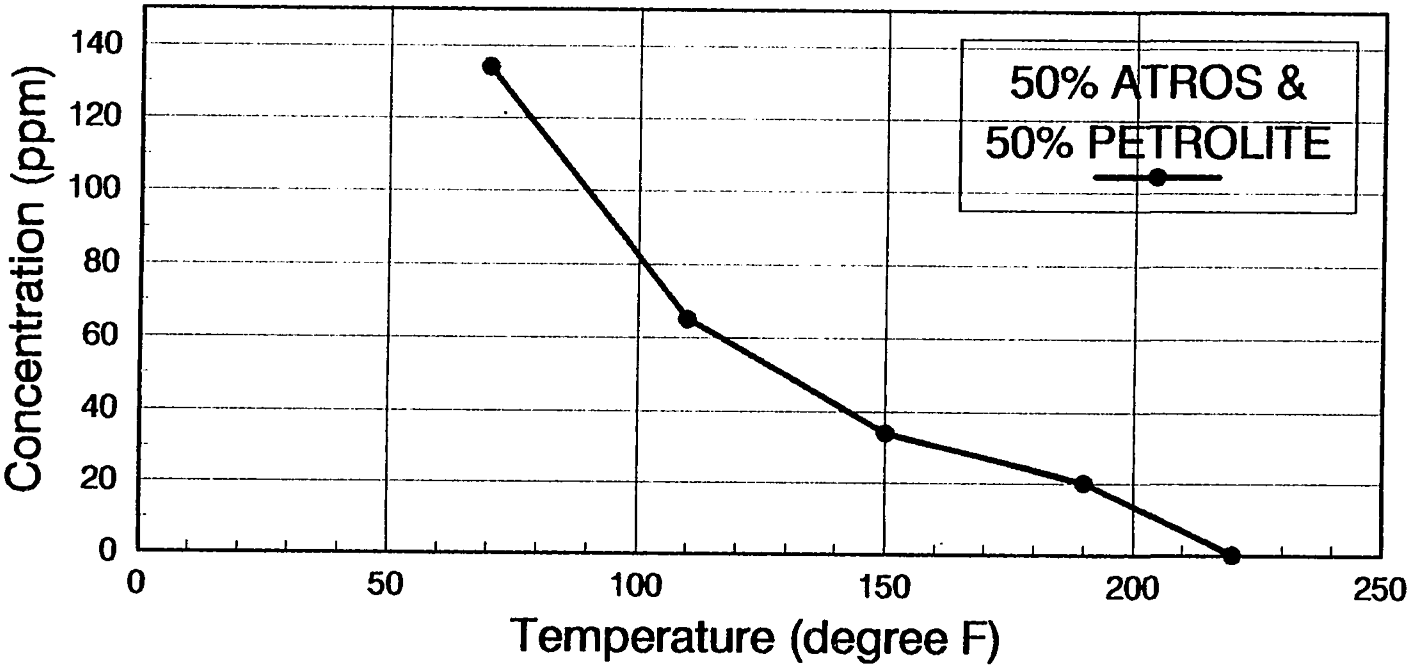


Figure 24:Concentration of Mixed Demulsifiers (Atros+Petrolite) Required to Break Emulsions Produced from Well-B at Various Temperatures

In addition it was also observed that chemicals were more effective when a reasonable mixing and flowing time were applied (10-20 minutes). No adverse effects were observed at a longer mixing time (up to 2 hours) at these concentrations tested. In addition to these dynamic tests, some static tests (test tube tests) were conducted at atmospheric conditions. It was observed that to resolve these tight emulsions, some mixing was required as well as a higher concentration of chemicals compared to the dynamic test at high pressure as discussed above.

Based on these test results, good mixing is needed to resolve these tight emulsions. In the field this can be achieved by injection of the chemicals at the well-head. This will allow a reasonable time and mixing to break tight emulsions before they enter into the GOSP. The addition of these chemicals at the well-head will also prevent further formation of tight emulsions as the temperature of the fluid decreases while flowing to the GOSP, especially in the cold season of the year.

4.4 Behavior of Fluids Produced from a Non-problem Well (Well-A)

Tests were conducted to examine the emulsification of fluids produced from a non-problem well (well-A) and compare the results to those obtained from problem well (well-B). A sample of oil produced from well-A (non-problem well) was charged into the system and its behavior was examined under the dynamic conditions at various temperatures of 70, 110, 150, 190, and 220 ^{o}F. It was observed that this oil exhibited a low emulsification tendency and only small quantity of Champion was used to resolve the formed emulsion. The rate of demulsifier needed to overcome the minor emulsion formation tendency is shown in Table 5. This is similar to that of presently applied in the field. A comparison of chemical usage for this well (well-A) with well -B is shown in Table 6 and Figure 25. It is clear that the chemical usage for well-B (problem well) is much higher than that of well-A (non-problem well). Depending on the temperature, the required levels are 10 to 15 folds greater.

4.5 SARA Analysis of Oil Samples

SARA analysis of the following samples were done by deasphaltening and HPLC method.

4.5.1 Produced fluid from well-B:

The following oil fractions were separated from produced fluids from this well:

a) Oil layer separated by gravity from produced fluid from well-B

b) Oil layer separated by centrifuging the emulsion sample remained from step (a)

c) Oil layer separated by further centrifugation at 160^{o}F of the emulsion layer remained from step (b)

d) Oil layer separated by a complete resolution of emulsion layer, by application of heat and addition of demulsifier, from the step (c)

Table 5:Concentrations and Feed Rates of Demulsifier Required to Break Weak Emulsion Resulting from Oil Produced from Well-A at Various Temeratures

TEMPERATURE	DEMULSIFIER: CHAMPION	
(^{O}F)	CONCENTRATION (ppm)	RATE (gallons/1000bbls)
70	5.0	0.21
110	1.5	0.07
150	1.4	0.06
190	0.3	0.01
220	0.0	0.00

Table 6: Comparison of Concentrations and Feed Rates of Champion Demulsifier Required to Break Emulsions Produced from Wells A and B at Various Temperatures

TEMP.	WELL - B	WELL - A	WELL - B	WELL - A
(°F)	CONC. (ppm)	CONC. (ppm)	RATE (gallons/1000bbls)	RATE (gallons/1000bbs)
70	80	5.0	3.3	0.21
110	48	1.5	2.0	0.07
150	20	1.4	0.8	0.06
190	6	0.3	0.2	0.01
220	0	0	0	0

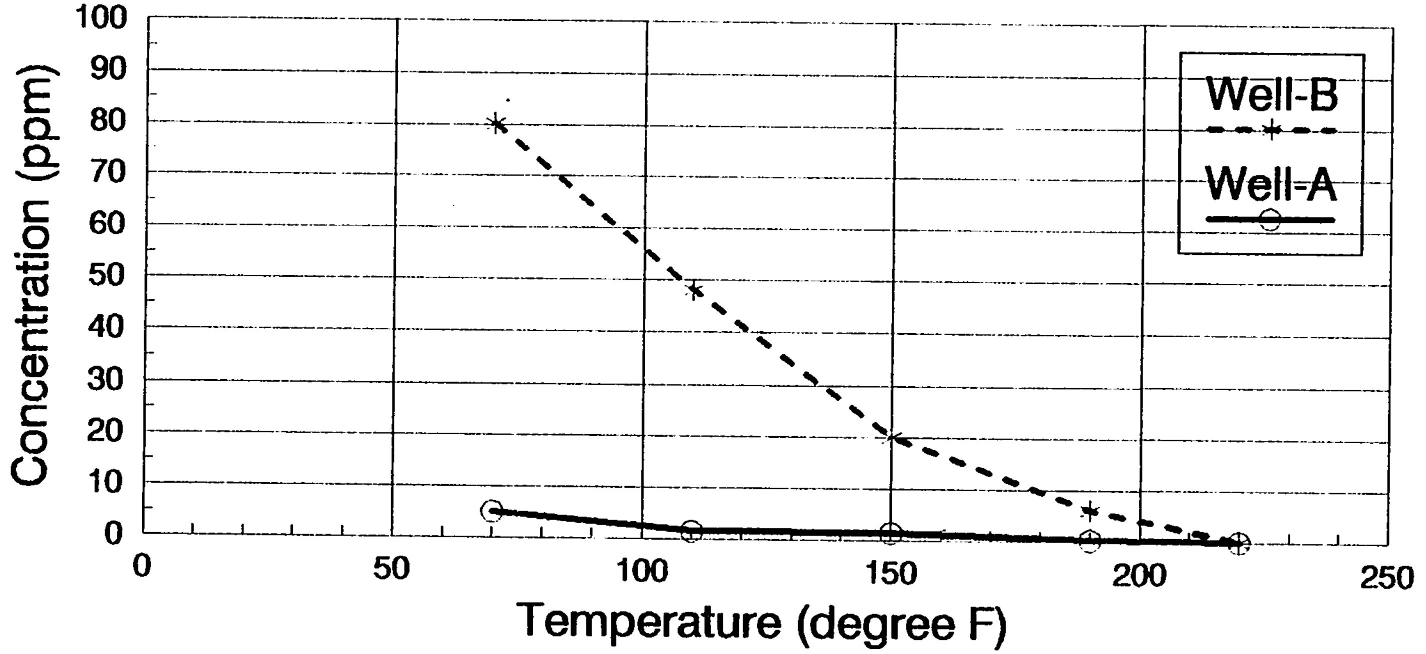


Figure 25:Comparison of Concentrations of Champion Demulsifier Required to Break Emulsions from Wells A and B at Various Temperatures

From the analyses shown in Table 7, it is clear that the asphaltene contents of oil samples collected in the above steps are in the order d>c>b>a.

4.5.2 Oil sample from well-A:

There was no emulsion produced from well-A and oil was separated easily by gravity from the produced fluids from this well. Therefore there was only one sample where SARA analysis was conducted on. The result of this test is shown in Table 8.

By examination of Tables 7 and 8, it is clear that asphaltene content of oil from well-A is very similar to the oil phase from well-B which separated by gravity. In addition from the data shown in Table 7 it is clear that generally oil samples which were separated easily contained less asphaltene than those oil samples which were separated from tight emulsions using centrifugation or addition of demulsifiers. Therefore this may be an indication that high concentration of asphaltene material in the produced fluids is one of the causes which promotes the emulsion formation in well-B.

4.6 XRD Analysis of Solids Separated from Emulsion Samples

There were no solids produced form well-A and only less than 0.1% solids were separated form some samples of emulsions from well-B using centrifuge and heat. Chemical composition determination of these solids using XRD indicates that Calcite ($CaCO_3$) and some Graphite (C) were present in these solids samples. Presence of these solids may also promote the formation

Table 7: Compositional Data of Crude Oil Obtained from Well-B

Well #	Sample Type	Saturates Wt %	Aromatics Wt %	Resins Wt %	Asphaltenes Wt %
WELL - B	Top Oil Separated From The Produced Emulsion By Gravity	45.1	44.4	8.1	2.4
WELL - B	Oil Separated From The Produced Emulsion By 1st Stage Centrifuge And Heat	45.0	44.6	7.2	3.2
WELL - B	Oil Separated From The Remaining Emulsion By 2nd Stage Centrifuge And Heat	36.5	44.0	13.4	6.1
WELL - B	Oil Separated From The Remaining Emulsion By 3rd Stage Centrifuge And Heat And Addition Of Demulsifier	40.0	43.5	9.5	7.0

Average Normalized Asphaltenes = 4.3%

Table 8: Compositional Data of Crude Oil Obtained from Well-A

Well	Sample Type	Saturates Wt %	Aromatics Wt %	Resins Wt %	Asphaltenes Wt %
WELL - A	Oil Separated From The Produced Fluids By Gravity	40.1	45.4	11.9	2.6

of tight emulsions. However as the quantities of these solids are negligible their effect on stabilizing the emulsion will be limited.

4.7 Bottle Testing vs. Dynamic Flow Testing

Tests were conducted using emulsion produced from well-B in static bottle testing where Champion demulsifier was added and mixed well and then examined the emulsion separation in static condition. These results (Table 9) were compared as shown in Tables 10 and 11 to the dynamic flow tests results. It is clear from Table 10 and Figure 26 that much higher concentrations of Champion demulsifier were used to break the emulsion at static condition especially at lower temperatures. This is due to the following :

1. Presence of electric field in the dynamic condition accelerates the coalescence process.

2. Turbulent flow in the dynamic condition accelerates the demulsification process in such a way that the faster the demulsifier it gets to the interface the better job it can do in neutralizing the action of emuslifiers present at the interface.

Tests were also conducted at dynamic condition but with the absence of electrostatic field and the result showed that the concentration of Champion demulsifier required to resolve the emulsion was increased by about 30 percet as illustrated in Tables 10 and 11 and Figure 26.

Table 9: Concentrations and Feed Rates of Champion Demulsifier Required to Break Emulsions Produced from Well-B at Various Temperatures

From Bottle Test Tube Tests

TEMPERATURE (^{O}F)	CONCENTRATION (ppm)	RATE (Gallons/1000bbls)
70	210	8.8
110	114	4.8
150	45	1.9
190	12	0.5

Table 10: Comparison of Concentrations of Champion Demulsifier Required to Break Emulsions Produced from Well-B at Static and Dynamic Conditions at Various Temperatures

TEMPERATURE	STATIC	DYNAMIC (with electric field)	DYNAMIC (without electric field)
(^{O}F)	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)
70	210	80	110
110	114	48	64
150	45	20	26
190	12	6	7

Table 11: Comparison of Feed Rates of Champion Demulsifer Required to Break Emulsion Produced from Well-B at Static and Dynamic Conditions at Various Temperatures

TEMPERATURE	STATIC	DYNAMIC (with electric field)	DYNAMIC (without electric field)
(°F)	Rate (gallons/1000 bbls)	Rate (gallons/1000 bbls)	Rate (gallons/1000 bbls)
70	8.75	3.33	4.58
110	4.75	2.00	2.67
150	1.88	0.83	1.08
190	0.50	0.25	0.29

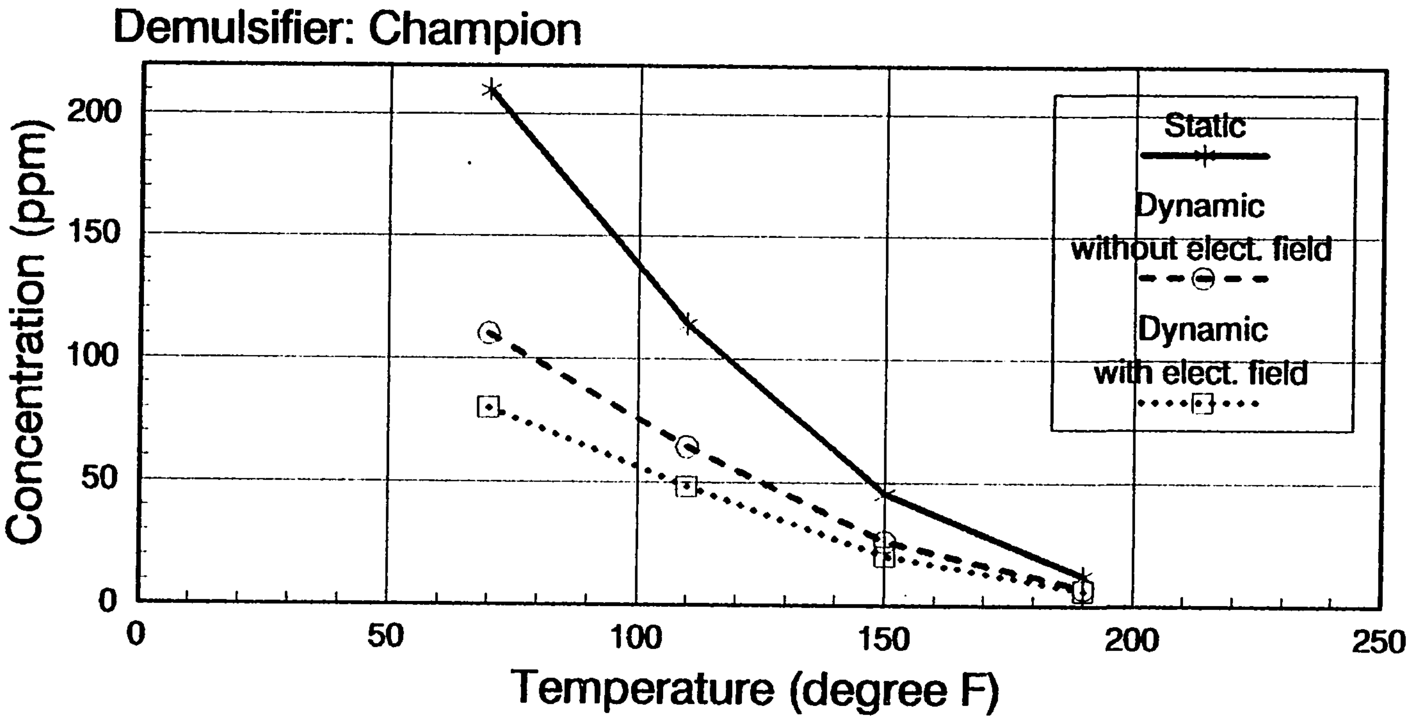


Figure 26:Concentration of Demulsifier Requird to Beak Emulsions from Well-B in Static Tests and Dynamic Flow Tests at Various Temperatures

CHAPTER 5

CONCLUSIONS

1) At 220 °F field produced emulsions become very unstable. This is a strong evidence that tight emulsions do not form in the reservoir formation, but are predominantly formed during the flow of the fluids in the well and within the flow lines as produced oil cools down while it is mixing with the produced brine.

2) It is observed that heating field produced emulsions helps the resolution of tight emulsions. The lower the temperature of the emulsion is the harder it is to break it to oil and water phases and the larger are the quantities of demulsifying chemicals needed.

3) Produced fluids from problem wells consist of two phases as follows: The top layer which is an oil rich phase (with only a few % water). This is a low viscosity (15 cp at 76 °F) low density material (0.86 g/ml) . The bottom layer is a high viscosity (>300 cp at 70 °F) high density (0.92 g/ml) water-in-oil emulsion with a high water content (50-65% by volume) which becomes thicker with time. This thickening of produced emulsions may have a negative impact on the initial

production rates of shut-in wells when they are put back into the production stream.

4) Addition of demulsifying chemicals will resolve tight emulsions produced in the field; however, it requires good mixing with the emulsion. Lab tests indicate that there was no negative impact observed by a long mixing time of demulsifiers with the produced fluids from well -B at the concentrations tested. In the field a good mixing can be achieved by addition of demulsifying chemical at the well-head.

5) Comparison of test results for fluids produced from problem wells with those from non-problem wells indicates that the concentration of demulsifiers needed to resolve tight emulsions from problem wells are over 10 folds greater than that of non-problem wells .

6) Addition of demulsifier at the well-head in problem wells will resolve field emulsions and will prevent further emulsification (emulsion formation) during the flow of fluid from the well to the GOSP.

7) For the oil investigated, appendix, the effectiveness of four commercially available demulsifiers in resolving tight emulsions produced in the field are in the following order:

At temperatures 70-150^{o}F: Champion > Atros > Petrolite > Exxon
At temperatures 150^{o}F and above: Champion > Petrolite > Atros> Exxon

8) Comparison of concentrations of Champion demulsifier required to break

emulsions at static and dynamic conditions indicates that the amount of demulsifier needed to resolve emulsions at static condition is three to four times greater than that needed at dynamic condition under electrostatic field and 30 percent greater than that needed at dynamic condition in the absence of electrostatic field. This shows the importance of studying the demulsification process under dynamic condition which represents the condition that exists in the oil fields.

9) Asphaltene content of oil produced from a problem well (well-B) is greater than that of a non-problem well (well-A). As asphaltene promotes emulsion formation it is one of the major factors contributing to the production of tight emulsions form problem wells.

10) Small amounts of solids were present in the produced fluids from the problem well (well-B), whereas no solids were present in fluids produced from a non-problem well (well-A). Since the quantities of these solids in the produced fluids are negligable their effect on stabilizing the emulsion is expected to be limited.

NOMENCLATURE

A: Largest projected area, sq. ft.

B: Buoyant force, lb

C_D: Drag coefficient, dimensionless

d: Diameter of sphere, ft

D: Drag force, lb

g: Gravitational acceleration 32.174 ft/s^2= 9.81 m/s^2

HE: Heat Exchanger

HPLC: High Performance Liquid Chromatography

HPPT: High Pressure Production Trap

IFT: Interfacial Tension, dynes per centimeter

N_R: Reynold's Number, dimensionless

PDP: Positive Displacement Pump

rd: Radios of the dispersed droplet, ft

v: Settling velocity, ft/s

δf: Specific weight of fluid phase, lb/ft^3

δs: Specific weight of solid phase, lb/ft^3

μf: Viscosity of fluid phase, cp

μc: Viscosity of continuous phase, cp

ρc: Density of continuous phase, lb/ft^3

ρd: Density of dispersed phase, lb/ft^3.

SARA: Saturates Aromatics Risins Asphaltenes Analysis

XRD: X-Ray Diffraction

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APPENDIX

ANALYSIS OF PRESSURIZED OIL FROM WELL-B

Sampling Conditions:

Location	:	HPPT at the GOSP
Pressure	:	230 psig
Temperature	:	115 °F

Hydrocarbon Analysis:

Component	Mole Percent	Density g/cc @ 60°F	°API 60/60°F	Molecular Weight
Nitrogen	0.05			
Carbon Dioxide	1.46			
Hydrogen Sulfide	0.82			
Methane	3.66			
Ethane	5.25			
Propane	7.20			
iso-Butane	1.16			
n-Butane	4.99			
iso-Pentane	2.07			
n-Pentane	3.93			
Hexanes	5.51			
Heptanes	5.64			
Octanes	5.80			
Nonanes	5.03			
Decanes plus	47.43	0.8910	27.1	283
Total	100.00			

Pressurized Oil Density:

Pressure, psig	Temp., °F	Density, lbs/cu.ft.
235	94	51.56
280	140	50.30
1500	140	50.73

DEMULSIFICATION CHEMICALS

DEMULSIFIER #	DEMULSIFIER NAME
1	CHAMPION KXZ1031
2	ATROS 2841
3	PETROLITE PSR390
4	EXXON SA133

VITA

Name : Abdul Karim Mohammad

Family Name : Al-Jaziri

Nationality : Saudi

Personal Data : Born in November 1, 1965
Married since September 1991

Education : B. S. Degree in Chemical Engineering
from King Fahd University of Petroleum & Minerals
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Professional Activities : **Membership**
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Society o f Petroleum Engineers (SPE)

Paper

"New Mercury-Free PVT System Produced Data Evaluation", Presented at ROP Conference, France, 1992, The First International Conference on Chemistry in Industry, Bahrain, 1992, Technical Exchange Meeting, Dhahran, 1992