Demulsification of Water in Crude Oil

by

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Abstract

The aim of this thesis was to optimize the concentration of demulsifier required to remove water from water-in-oil emulsions in the crude oil from Mabruk oil field, Libya. This was achieved by conducting a series of industrial standard Bottle-Test's on the crude oil emulsions from Mabruk oil field. Mabruk oil field is located in Libya's Sirte basin. Mabruk's crude oil has a moderate emulsion tendency easily treated by injecting an emulsion breaker (EB) into the inlet crude oil of the separation plant, to enhance oil-water separation by weakening the rigid film existing between the water and the oil that prevents the drops from coalescing. Optimizing the EB dosage in the field was a field trial based method, with dosages ranging from 5 – 100 ppm depending on emulsion stability and hardness.

The processing plant at Mabruk was the focus of the thesis. The Mabruk processing plant treats wet crude by removing gas and water out of the oil. By knowing the system characteristics, starting from the separation technology used, the fluid flow rates, the vessels retention times, the physical and chemical properties, will lead to much better screening results when selecting the demulsifier.

Experimental work is based on an industrial standard "Bottle-Test", where two blends of demulsifiers were tested against each other. The bottle test was performed on site where fresh crude oil samples were collected. The test resulted in validating the candidate demulsifier (2137-T), while the new blend was eliminated. Visual inspections methods were used to determine the performance of the different demulsifier agents in terms of water volume separated, the quality of the oil-water interface, water drop rate and oily water quality.

In conclusion, crude oil emulsions were treated using the EB chemicals, to enhance oil-water separation performance. Optimization of chemical treatment is generally accomplished in the field, by bottle testing the existing demulsifier against other demulsifier(s). The goal of this thesis was to use the bottle test technique to select the most appropriate demulsifier to reduce water-in-oil emulsions. This was achieved by using different blend(s) formulation(s) and concentrations of demulsifier.

List of Abbreviations Used

BS&W	Basic sediment and water
O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsion
O/W/O	Oil-in-water-in-oil emulsion
W/O/W	Water-in-oil-in-water emulsion
MSDS	Material Safety Data Sheet
EB	Emulsion Breaker
TDS	Total Dissolved Solids
ppm	Part per million
mg/l	Milligram per liter
µg/l	Microgram per liter
Bbl/d	Barrels per day
OWT	Oily Water Treatment
RVP	Reid Vapor Pressure
H2S	Hydrogen Sulfide
CO2	Carbon dioxide
pH	Hydrogen Number
WAT	Wax Appearance Temperature
pCFI	Pressurized Cross Flow Interceptor
RPM	Revolution per minute
GOSP	Gas, Oil, and Water Separation Plant
T/h	Ton per hour
Bar.g	Bar gauge

Acknowledgements

I would love to submit my thesis to my parents, my father in particular. He was my professor of my entire life. Also, I would present it to my beloved wife who supported me at all times. Without the God's support, I would not be here today. So, I am heartily thankful to my supervisor, Dr. Michael Pegg.

Chapter 1

Introduction

1.1 Introduction

Crude oil is a mixture of liquid and gaseous hydrocarbons mixed with water. This mixture is in the form of water-in-oil emulsion, where natural surfactants stabilize these emulsions (Al-Sabagh et al., 2011). The crude oil passes from the reservoir via the wellhead then to the processing facilities along flow lines. As the crude oil flows, significant pressure drop can be encountered, the temperature changes, and accompanied with considerable agitation. This can cause emulsions within the crude oil flow that impact the efficiency of the overall water-oil separation process.

Emulsions are stabilized by a wide range of natural materials that are found in crude oil, such as sediments, asphaltenes, natural surfactants, asphaltenes, resins, carboxylic acids, and solids such as clay and waxes (Al-Sabagh et al., 2011). To remove water from oil and oil traces from the waste water, destabilization of the emulsion is essential. Demulsification is the chemical process that leads to the partial or total removal of the dispersed phase from the continuous phase. Moreover, it can be achieved mechanically, electrically or chemically. Chemical treatments based on the addition of chemical demulsifiers are the most widely used method (Bin Mat et al., 2008).

Over the past years, lots of demulsifiers have been developed. Since the 1930s, non-ionic surfactants have been introduced and have found wide application as demulsifiers. These non-ionic surfactants contain two different groups of active materials, hydrophilic and hydrophobic. Currently, in the oil industry, the selection of a demulsifier is still based mainly on trial and error, after some screening such as bottle testing. This is known in crude oil processing as chemical field trials, which are usually carried out on site whether onshore or offshore. Successful demulsifier formulations are able to drop water amounts rapidly, provide relatively clean interfaces, and produce dry, saleable oil (Ben Mahmud, 2012).

1.2 Crude oil emulsions

There are four types of emulsions that are readily distinguished in principle, these are Oil-in-Water (O/W) and Water-in-Oil (W/O), Oil-in-Water-in-Oil (O/W/O) and Water-in-Oil-in-Water (W/O/W) emulsions. The majority of crude oil emulsion is of the Water-in-Oil (W/O) emulsion type and this will be the focus of this thesis (Bin Mat et al., 2008).

In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase, termed water-in-oil emulsion (W/O), conversely, if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion (Bin Mat et al., 2008). Figure 1.1 shows these two kinds of emulsions. Figure 1.2 shows resolved-unresolved W/O emulsion, while Figure 1.3 shows O/W emulsions treated with different EB chemicals (De-oilers).

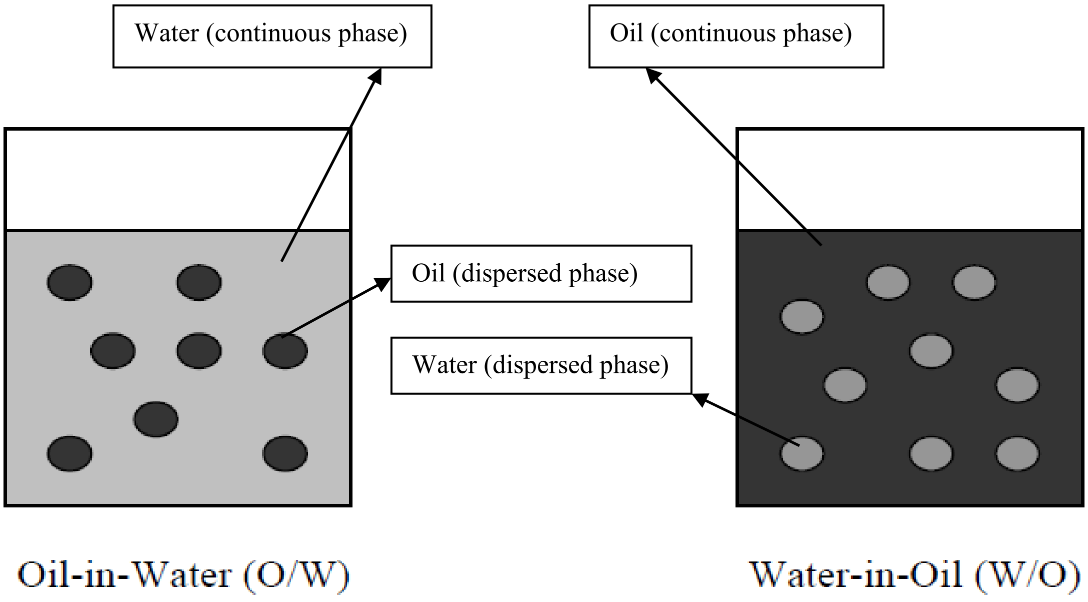


Figure 1.1 The two simplest kinds of emulsion (Bin Mat et al., 2008).

In addition to the usual emulsion types, multiple emulsions, where oil droplets are dispersed in water droplets that are in turn dispersed in a continuous oil phase (O/W/O) can occur. Table 1.1 shows where multiple emulsions might be encountered in the upstream oil industry. Bin Mat et al. (2008) postulated that, the emulsion types encountered in the petroleum industry aren't totally undesirable, where in some cases the emulsion occurrences are desirable. This based on the extra operational costs associated with the emulsion formation. For instance, if the emulsion formed at the well head, it needs extra operational costs related to the pumping capacity from the well head to the plant. In contrast, if the emulsion formed at heavy oil pipeline, it will reduce the operational costs, where the emulsion will probably reduce the overall bulk density and the drag force as well.

Table 1.1 Multiple emulsions existing in the oil field and their occurrences (Bin Mat et al., 2008).

Occurrence	Usual Type
Undesirable Emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil sand flotation process, froth	W/O or O/W
Oil sand flotation process, diluted froth	O/W/O
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable Emulsions	
Heavy oil pipeline emulsion	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhance oil recovery in situ emulsions	O/W

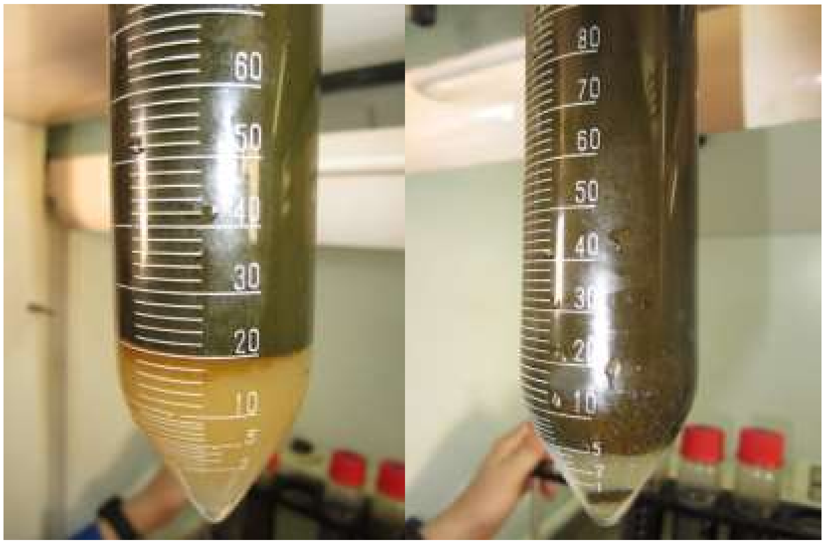


Figure 1.2 Water-in-Oil emulsions (almost resolved emulsion- Left, and unresolved emulsion- Right).

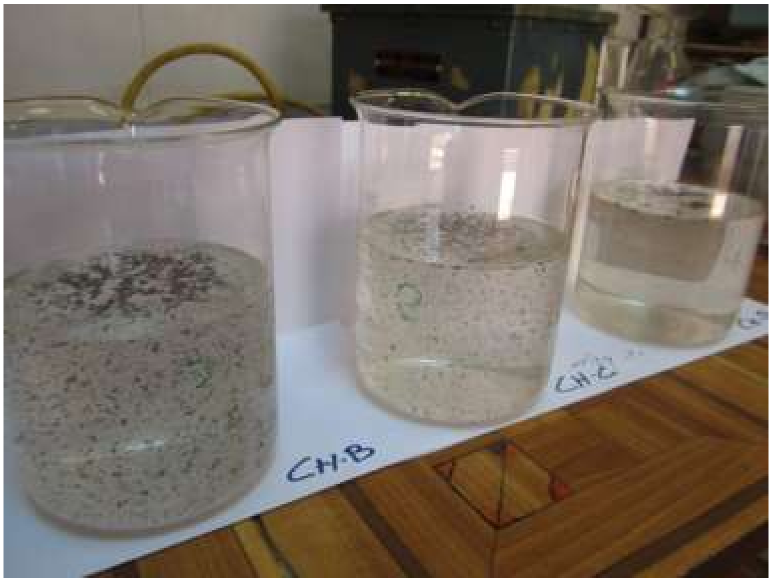


Figure 1.3 Oil-in-Water emulsions (three different de-oiler chemicals added CH-B, C&D).

1.3 Objectives and Scope

In this approach, two sides, the theoretical and the experimental have been covered. The theoretical part covers the chemistry basis of what kind of demulsifier would match Mabruk field crude oil, while the experimental is covering the experiments performed in Mabruk chemistry laboratory. Starting from preparing the demulsifier formulation(s), bottle-test procedure, to experiment's results were covered in this approach. The aim of this thesis is to optimize the concentration of demulsifier needed to resolve the regular emulsions in the crude oil from Mabruk oil field using bottle-test technique. Prior to perform the bottle test, Mabruk plant system was studied, where all the plant operational data, information and readings related to water-oil separation processes were gathered. Moreover, the oil-water separation stages were discussed as well as the treatment of the waste water. The oily-water treatment unit was evaluated, in terms of its performance and its impacts on the environment. The objective of the bottle-test is to select the most appropriate demulsifier that would match Mabruk's crude. The bottle-test includes various screening steps at the laboratory, where visual inspection methods used to evaluate the performance of different demulsifiers tested. Ideally, the effective demulsifier is able to yield a dry and saleable crude oil as well as clean oily water. At the end of bottle-test, the concentrations of the selected demulsifier were optimized excluding the cost factor. The cost factor was not considered in this thesis because; the existing demulsifier used in the field was validated.

1.4 Thesis Outline

Each chapter of this thesis is linked to one objective of the research, which is described in section 1.3. There are six chapters; each chapter contains its own introduction and description of the relative topics in order to achieve the objectives of the research.

Chapter I provides a general background, objectives and scope of this study and thesis outline. The background of crude oil emulsions and emulsion types encountered in the petroleum industry are covered.

In chapter II, the topics of emulsion stability, demulsifier characteristics, classification and formulations as well as theories and mechanism of demulsification process are discussed. Further, the factors affecting emulsion stability are illustrated. In chapter III, the Mabruk field system was studied including two main oil-water separation techniques used. In particular, wet crude oil and oily water treatment processes occurring at the gas, oil and water separation plant (GOSP) were examined. Crude oil treatment starts by receiving fresh crude oil from oil wells at GOSP inlet, and then the crude passes through various separations before transfer into storage tanks. Then, the produced dry and saleable crude oil is pumped into the export line for shipping. Further, the performance of 3-phase separator and dehydrator units was examined as well as oily water package. The oily water treatment starts at the oil-water separator, where all produced water enters, then it passes through various separation stages before disposal. The performance of the oily water treatment package was evaluated based on field reports. The treated oily-water is injected into the water disposal well, where every possible impact of the disposal process on the environment was considered.

In chapter IV, experimental and analytical procedures used in this study are presented and discussed with more details. The bottle-test is discussed in detail, where the test preparation, procedure, steps and results were explained. In the light of this, previous bottle-tests performed in Mabruk field are also discussed and analyzed. Visual techniques were used to examine the performance of two demulsifiers. The bottle-test is performed on site under the supervision of chemical specialist to accredit and validate the test results. The discussion of experimental results, which are based on the combination of the theories from the literature review and the results obtained from this research, are mentioned in Chapter V. The conclusions of this thesis are based on the demulsifier performance analysis on treating Mabruk's W/O emulsion and remarks were discussed in Chapter VI. Besides that, the recommendations for future study are also included.

Chapter 2

Literature Review

2.1 Introduction

The basic target in any oilfield is to separate water and all other undesired materials such as sand, salts, resins and others from the oil. Water is present as dispersed droplets and this is generally termed “water in oil emulsion”. The breaking of this emulsion is the main target in today’s oil producing industry. Two conditions are needed to formation of stable emulsions. These conditions are: the presence of natural emulsifier species in the crude oil and the presence of emulsifying process such as the turbulence due to transfer pump, electric submersible pump, or gas lift system.

2.2 Emulsion Stability

The stability of water-oil emulsions relies on interfacial layers, which mainly consist of colloids present in the crude oil-asphaltenes, waxes and resins. Waxes and water particles, such as clays can contribute to the stability of water-in-oil emulsions, but cannot by themselves produce stable emulsions. Besides asphaltenes, resins and waxes, emulsion stability is strongly influenced by solvents, temperature, the pH of the water phase, and the presence of solid particles such as clays and sand. Bin Mat et al. (2008) reported that the drivers of the formation of stable water-in-oil emulsion are the presence of polar compounds, e.g. nickel porphyrins, found in the asphaltenes and resins of crude. If these polar compounds are not present in the oil, then the presence of waxes and other particles will not lead to formation of stable emulsions. The most common method of determining relative emulsion stability for laboratory scale is the simple test termed bottle test (Bin Mat et al., 2008).

Ben Mahmud (2009) reported that water-soluble demulsifiers work differently from water-soluble demulsifiers, where the first displace stabilizers and the second displace colloids present at the interface. Further, water-soluble demulsifiers displace the original emulsion stabilizers exist at the interface, and make a change in wetting by creating inactive complexes. He added, “oil-soluble demulsifiers displace the colloids originally present, and neutralize the stabilization effect of additional emulsion breakers and the breakup resulting from interface film eruptions”. Table 2.1 summarizes the emulsion stabilizers that can typically occur in oilfield environment.

Table 2.1 Emulsion stabilizing agents (Ben Mahmud, 2009).

Emulsion Stabilizer	
Naturally Occurring	• asphaltenes • solid paraffins • resins • organic acid, bases as naphthenic acids and naphthenates
External Agents	• drilling fluids • stimulating chemicals • corrosion inhibitors or scale inhibitor chemicals
Fine Solids	• clay particles • sand • rust • small aggregates of asphaltenes and waxes • corrosion products • mineral scales • drilling mud

Ben Mahmud (2009) reports that emulsion stabilizers operate in two ways:

- Organic molecules, such as asphaltenes or resins that consist of a polar “head” and non-polar “tail” are able to interact both with water and paraffin in the oil matrix. Based on the electronic charge theory which will be discussed later, these molecules orient the head toward the water creating a surrounding layer (film) and use a non-polar tail to fluctuate in the paraffinic matrix. This mechanism creates the water dispersion as described in Figure 2.1.
- Fine solids such as paraffinic compounds are able to promote a more rigid film that prevents water droplets coalescing. This is the basis of the water separation mechanism. Ben Mahmud (2009) highlighted, in fact, water can separate only when the drops are big enough, such that the gravity force overcomes the strong bonds of the W/O emulsion.

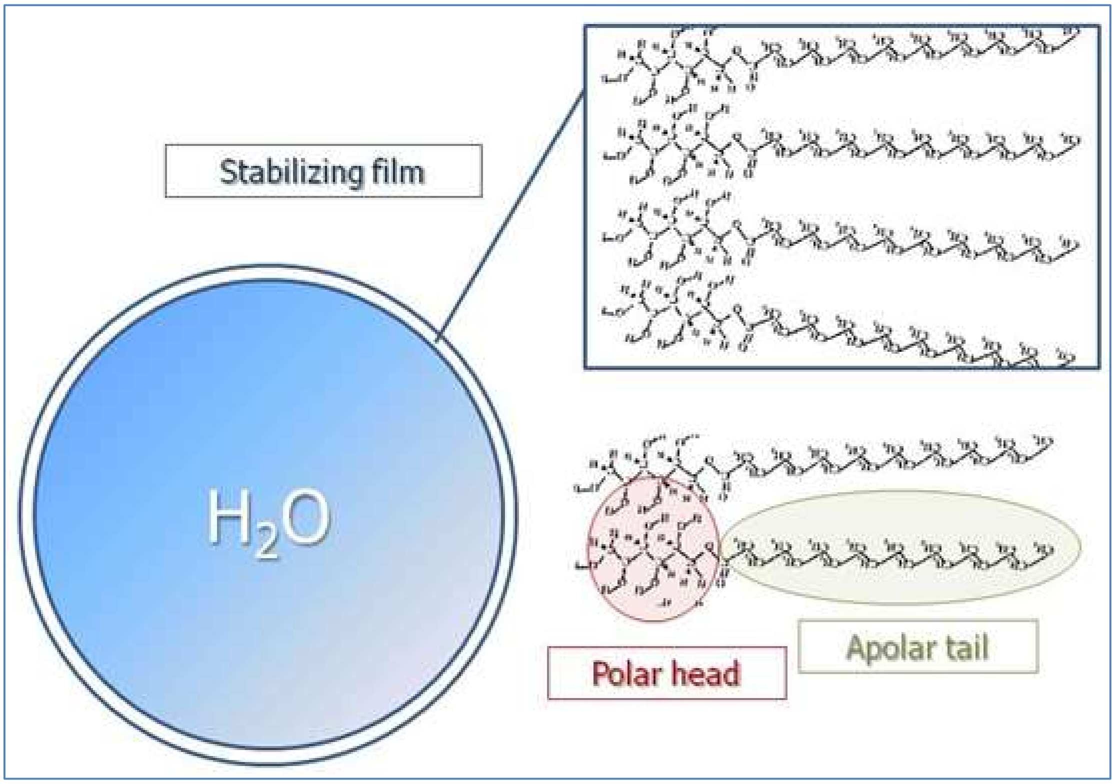


Figure 2.1 Composition of the stabilizing film (Electronic Charge Theory) (Ben Mahmud, 2009).

2.2.1 Other Factors Affecting the Stability of Emulsions

Other factors that can affect the stability of emulsions are: viscosity, specific gravity, water percentage, total dissolved solids, and age of emulsion. Ben Mahmud (2012) has described each of these factors in the following subsections.

2.2.1.1 Viscosity

An emulsion of oil of low viscosity tends to be easier to resolve than highly viscous oil. The mobility of the water droplets of high viscosity oil is much less than that for oil of high viscosity. Further, the water droplets require more time to coalesce and settle down than does an oil of low viscosity. The water droplets with higher mobility can move rapidly through low viscosity oil.

2.2.1.2 Specific Gravity

The difference between the specific gravity values of water brine and oil has a bearing on the emulsion Stability. The specific gravity of a liquid substance is defined as the weight of a given amount of that liquid at a given temperature compared to the weight of an equal volume of water at the same temperature. Faster water dropping could be possibly achieved when greater difference in specific gravities presents. Heating the emulsion increases the specific gravity difference between the oil and water, where the specific gravity of the oil decreases as well as its viscosity.

2.2.1.3 Water Percentage

The emulsifying tendency of water and oil is affected by the relative quantities of produced oil and water. This is possibly applicable till a certain degree. An emulsion of large amount of water exist is usually much easier that with too little amount of water present. The small percentage of water present, the much harder to resolve that emulsion. Ben Mahmud (2012) said, “The severity of an emulsion problem usually will diminish when the quantity of water produced by a well approaches or exceeds the quantity of oil produced”.

2.2.1.4 Total Dissolved Solids

The settling rates of brines are affected by total dissolved solids amount (TDS). It has been reported that, brackish water is faster to settle down than fresh water. More, fresh water emulsion tends to be more difficult to treat.

2.2.1.5 Age of Emulsion

Crude oil emulsions are systems attempt to attain equilibrium by time. Emulsions are usually become more stabilized with age. As a result, different chemical or extra dosing might be required to resolve such an aged emulsion. In general, fresh emulsion is easier to dehydrate than aged stabilized emulsion.

2.3 Theories of Demulsification

Many theories have been introduced concerning the problem of resolving crude oil emulsions. However, so far, there is no theory that is applicable to all kinds of emulsion. The following are the most applicable theories: reverse phase, rigid film, pH, electronic charge, temperature and surface tension (Ben Mahmud, A., 2012)

2.3.1 Reverse Phase

This theory is based on the hypothesis, that by adding a demulsifier to the water in oil emulsion, it is possible to achieve a complete reversing and produce an oil-in-water emulsion. This could be applicable to some emulsions but it is not always the case, where some emulsions are not easy to break completely and reversed to the desirable reverse emulsion.

2.3.2 Rigid Film

The principle of this theory is that, the emulsion breaking reagent is weakening or lowering the relative expansion coefficient of the rigid film. So, when the envelope surrounding the encapsulated water droplets expands due to the effect of heat, it is shattered allowing the water droplets to coalesce and settle down. In some cases, where the heating factor is absent, this mechanism might not be possibly applied.

2.3.3 pH

Another school believes that, it is not possible to resolve an emulsion without a change in the emulsifier characteristics, such as pH, neutralization, or loss of solubility. This could be possibly applied to oil-in-water emulsions, where most of the demulsifiers are cationic. However, most of water-in-oil emulsions are treated with noninonics. Ben Mahmud (2012) said, "Reverse emulsions especially may be treated by charge neutralization or pH change. Most regular emulsions are treated with non-ionics".

2.3.4 Electronic Charge

This theory is based on the assumption that says, the emulsifying agents are polar bodies and they function because of their electronic charges. So, making any disturbance of these charges will result in breaking the emulsion. Ben Mahmud (2012) highlighted, this is especially applicable to O/W emulsions. On the top of that, it is believed, the polar components are commonly found in asphaltenes and resin materials. Therefore, this theory might not be applicable to non-asphaltenic oils, where no polar bodies are exist.

2.3.5 Temperature

Some researchers thought, a small temperature increase causes a great change of state in the film of the interface. This could convert the film from a solid to a liquid and thereby affect its stability greatly. This might be true to a certain degree, but many demulsifiers work in the absence of added heat. Increasing the emulsion temperature would probably affect the demulsification process but it is not enough, where many other factors should be taken into consideration.

2.3.6 Surface Tension

This is the most common theory, that resolving the emulsion is accomplished by lowering the surface tension of the inner or the continuous phase or both. In emulsions, it is recognized that the encapsulated fluid tends to have a higher surface tension. More, the reagent reduces the surface tension of either the water or the oil or both. In general, the reagent adsorbed at the interface between the dispersed and the continuous component modifies the interfacial surface in some manner. Hence, a change in the interface rheology properties could result in resolution. Yet, the action of lowering the surface tension should stop at some point shortly allowing the emulsion to reverse.

The most applicable theories were discussed in details however some of them are not applicable to water- in-oil emulsions, such as pH theory. Nowadays, the most common demulsification theory is “surface tension theory “, which is applicable to both kinds of crude oil emulsions, the regular and the reverse emulsion (Ben Mahmud, 2012).

2.4 Mechanism of Demulsification Process

Generally, demulsification can be defined as a phenomenon that occurs under non-equilibrium conditions, resulting in breaking up emulsions. Emulsions tend to seek stability by time until equilibrium state is reached. Chemical demulsification is mainly based on the addition of a chemical that able to accelerate the coalescence process and rapturing the thin film between the dispersed droplets. Bin Mat et al. (2008) said, “More important characteristics of a good demulsifier are sufficient surface pressure and good partition between the two phases”. He added “The role of the demulsifier, therefore, is the suppression of the interfacial tension gradient in addition to the lowering of interfacial shear viscosity, thus causing accelerated film drainage and coalescence”. In the light of this, injecting an improper demulsifier into W/O emulsion will result in bad water-oil interface and poor oily water quality. Figure 2.4 shows the effect of not injecting any demulsifier at all, injecting the wrong demulsifier, and the effect of injecting the right demulsifier.

The mechanism of demulsification and the principal role of the active material to destabilize the emulsion have been studied by many researchers. The separation mechanism of the regular emulsion is simplified in Figure 2.3. Further, it is found that the demulsification process can be divided into two or three main steps depending on the demulsification efficacy of the used demulsifier. The two main processes, flocculation and coalescence, occurred during demulsification process are described below in Figure 2.2:

(A) Adsorption and flocculation, in which the demulsifiers adsorb and displace the natural surfactant existing on the W/O interface.

(B) Coalescence, in which each two neighbor water droplets being in contact to form micro-clusters with low interfacial tension on their W/O interface.

(C) Channel formation followed by separation, in which the formed micro-clusters are collected to form macro-clusters, and then channels are formed followed by complete water separation by gravity force (Ben Mahmud, 2009).

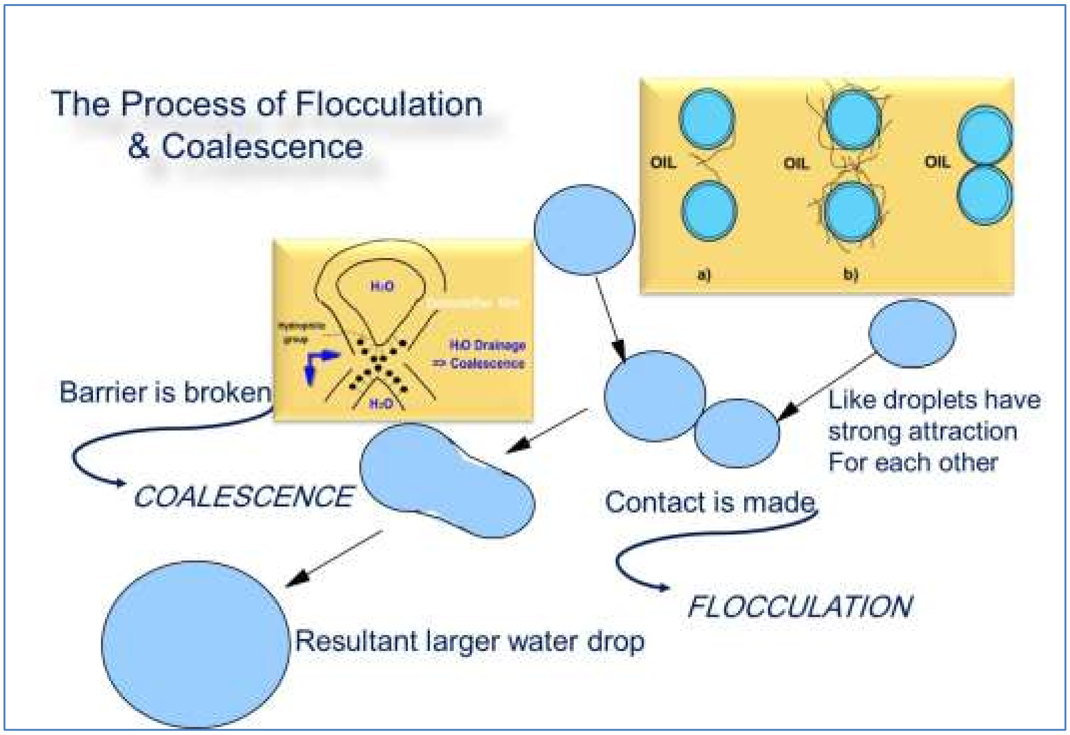


Figure 2.2 The process of flocculation and coalescence (Ben Mahmud, 2009).

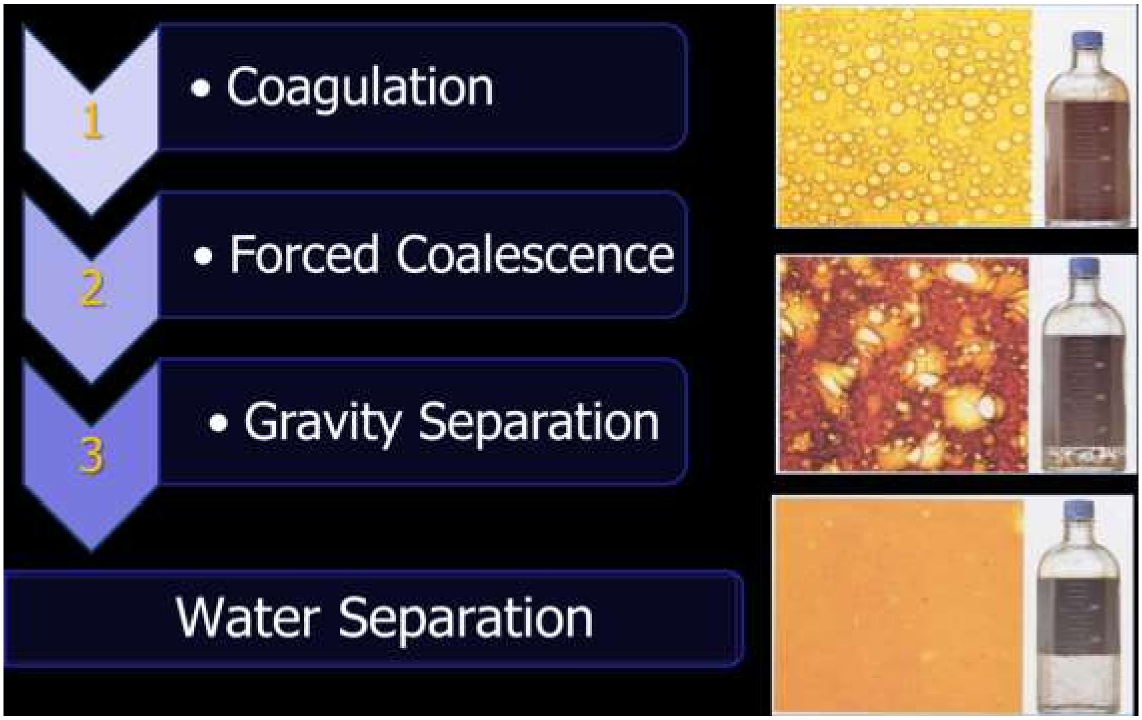


Figure 2.3 The separation mechanism of regular emulsion (Ben Mahmud, 2009)

Figure 2.4 The effects of injecting not injecting any demulsifier (left), wrong demulsifier (middle), and injecting the right demulsifier (right) (Institut français du pétrole, IFP Training, 2009).

In demulsification process of W/O emulsion, the reagent accelerates the coalescence of water droplets as well as the film rupture process. Bin Mat et al. (2008) claimed "The tendency for the drops to coalesce will be the van der Waals forces when the lamellae are thin enough, and the restoring forces will be the Gibbs-Marangoni effect". He added, the effect Gibbs-Marangoni operates because of the distortion and increase in surface area of the water drops when they get close to each other. Therefore, it can be argued that the stability of emulsions is mainly affected by the nature of the interfacial film and the reagent efficacy.

Although the mechanisms of the demulsification process are not totally understood, the selected demulsifier must be able to weaken the rigid film, and accelerate the coalescence process. The three main parameters that affect the volume and speed of water separation are:

1. Settling time: In a steady state condition as it is at Mabruk's plant at normal operation condition, the water separates along the time. This time is related to the stability of the emulsion.
2. Temperature: if the temperature of the emulsion rises, its viscosity decreases and the mobility of the water increase. In this condition, the water drops can coalesce and separate easily.

3. Usage of demulsifier: it is a chemical able to weaken the rigid film existing between the water and the oil that prevents the drops coalescence. It acts displacing the film stabilizer and the fine particles to create a less rigid film easy to break.

The best results are achievable by selecting a demulsifier able to work at the operational system parameters such as residence time, temperature and turbulence. The demulsifier dosage is usually in the range of 5 – 100 ppm, depending on the hardness of the emulsion (Ben Mahmud, 2009).

2.5 Classification of Demulsifiers

The chemicals used as demulsifiers can be classified according to their chemical structure, their application, or according to the oil type used. Two major groups of chemicals are used, non-ionic demulsifiers and ionic demulsifiers. The formulation of the demulsifier is based on a blend of different active materials in organic solvent, where a typical composition contains surfactants, flocculants and wetting agents (Ben Mahmud, A., 2009). Al-Sabagh et al. (2011) mentioned, there are also anionic, cationic, nonionic and amphoteric surfactants that have been used as demulsifiers. Emulsion breakers are typically tailored for site or crude oil type. The most effective demulsifier formulations were achieved by the combining of all four types of demulsifiers. The history of development and evolution of chemical demulsifiers is shown in Table 2.2.

Table 2.2 The development of chemical demulsifiers. (Al-Sabagh et al., 2011)

Year	Demulsiflers
1920–1930	Soap, naphtenic acid salts and alkylaryl sulphonate, sulphated caster oil
1930–1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized caster oil and sulphosucinic acid ester
1940–1950	Fatty acids, fatty alcohols, alkylphenols
1950–1960	Ethylene oxide, propylene oxide copolymer, Alkoxylated cyclic p-alkylphenol formaldehyde resins
1960–1970	Amine alkoxylate
1970–1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980–1990	Polyesteramine and blends

2.6 Demulsifier Preparation

The preparation of a new potential demulsifier is based on either the chemistry laboratory or some analysis software. However, the common way to prepare a new formulation is the laboratory based method, where different blends are formulated. Al-Sabagh et al. (2011) reported that the combination of oil-soluble demulsifiers and water-soluble demulsifiers produced great result in water separation.

The prepared blends aimed to be tested in the laboratory during the bottle testing or later in the field during field trials. The candidate product 2137-T used in Mabruk field is a blend of polymeric compounds in heavy aromatic solvent based on the product's material safety data sheet (Appendix-A). More, the formulation of the other product Blend-X isn't known (Allegrucci, A., personal communication, June, 2012). Demulsifiers can be used singularly or in combinations of two or more. According to the material safety data sheet of the product 2137-T, the following is the composition of the candidate demulsifier 2137-T:

1- 1,2,4-Trimethylbenzene: < 5 % (vol.)
2- Aromatic solvent (high boiling point): 10 - 20 % (vol.)
3- Heavy aromatic solvent: 725 mg

Bin Mat et al. (2008) reported, "The best polymeric surfactants used nowadays throughout the world are alkoxylated material derivatives. Because they are alkoxylated, they are considered as nonionic polymers". The oil characteristics including physical and chemical properties are very important factor that should be taken into consideration when preparing a blend of demulsifier. Sometimes, singular formulation is not effective enough to resolve a certain petroleum emulsion. Further, mixtures of nonionic, cationic or anionic materials are used together.

Bin Mat et al. (2008) stated that the commercial demulsifiers used to break up W/O emulsion are blends of oil soluble and water soluble demulsifiers. However, the most effective demulsifiers to resolve W/O emulsions are oil-soluble (hydrophobic). It is common to formulate the oil soluble demulsifiers in organic solvent alone. Such as, xylene, tetrahydrofuran, dioxane, lower alcohols and light gasoline fractions are also used as a solvent.

The most used polymer in the demulsification industry is reagent that contains both groups, hydrophilic and hydrophobic. Upon adding the polymeric surfactant to the crude oil emulsion, it mobilizes itself and moves towards the interface between water and oil phase molecules. The hydrophilic groups orient themselves towards water while the hydrophobic groups orient themselves towards the oil phase (Ben Mahmud, 2009).

Chapter 3

Mabruk Field System

3.1 Introduction

The most important objective of any oil production facility is the separation of water and other undesired materials from the produced crude oil. The breaking of crude oil emulsions is/still considered one of the more challenging problems in today's petroleum industry. Produced water became the problem number one in Mabruk field, where the produced water quantities were rising with time. Mabruk is a mature oil field located in the Libya's Sirte basin as shown in Figure 3.1. The reason behind the water encroachment is that, during the productive life of any oil well producer, water will be produced in unacceptable quantities. This water comes originally from the reservoir associated with the hydrocarbons. More, water gradually breaks through the hydrocarbon-bearing region of the formation. Then, at the end, water becomes part of the production from the wells regardless of the method of recovery (Swedan, 2012).

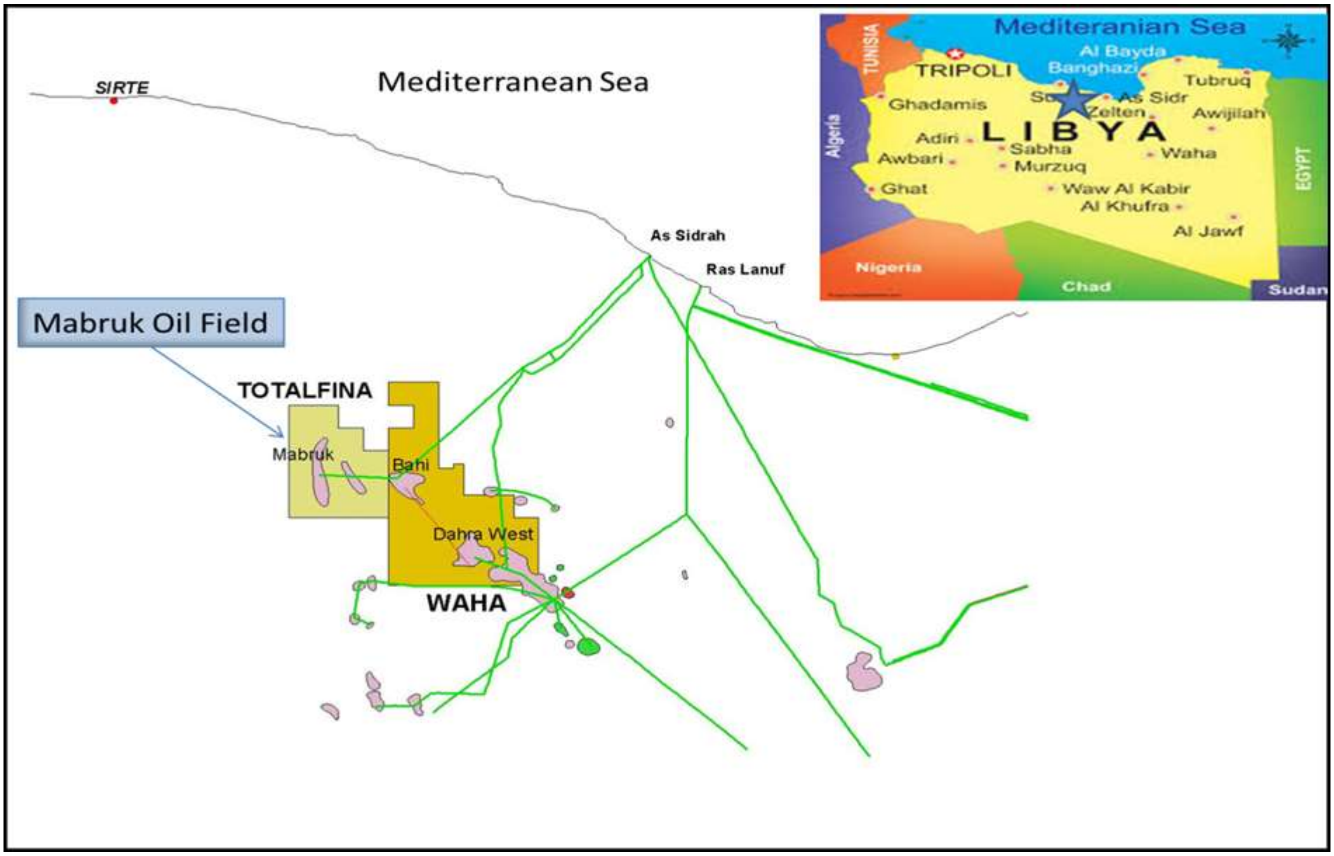


Figure 3.1 Mabruk oil field location (Swedan, 2012).

3.2 System Overview

All production fluids are routed through Mabruk trunk line, where flow lines of producer oil wells are collected in nine satellites. Every bunch of oil well producers is gathered in one satellite, where each satellite has one oil manifold and one trunk line. Then, these trunk lines gather in one main trunk line, which enters the Gas, Oil and Water Separation Plant (GOSP). A schematic process and flow diagram of the GOSP is provided in Figure 3.2. At the plant, various separation processes occur, where the majority of the associated water is removed as well as substantive quantities of dissolved gases are extracted (Swedan, 2012).

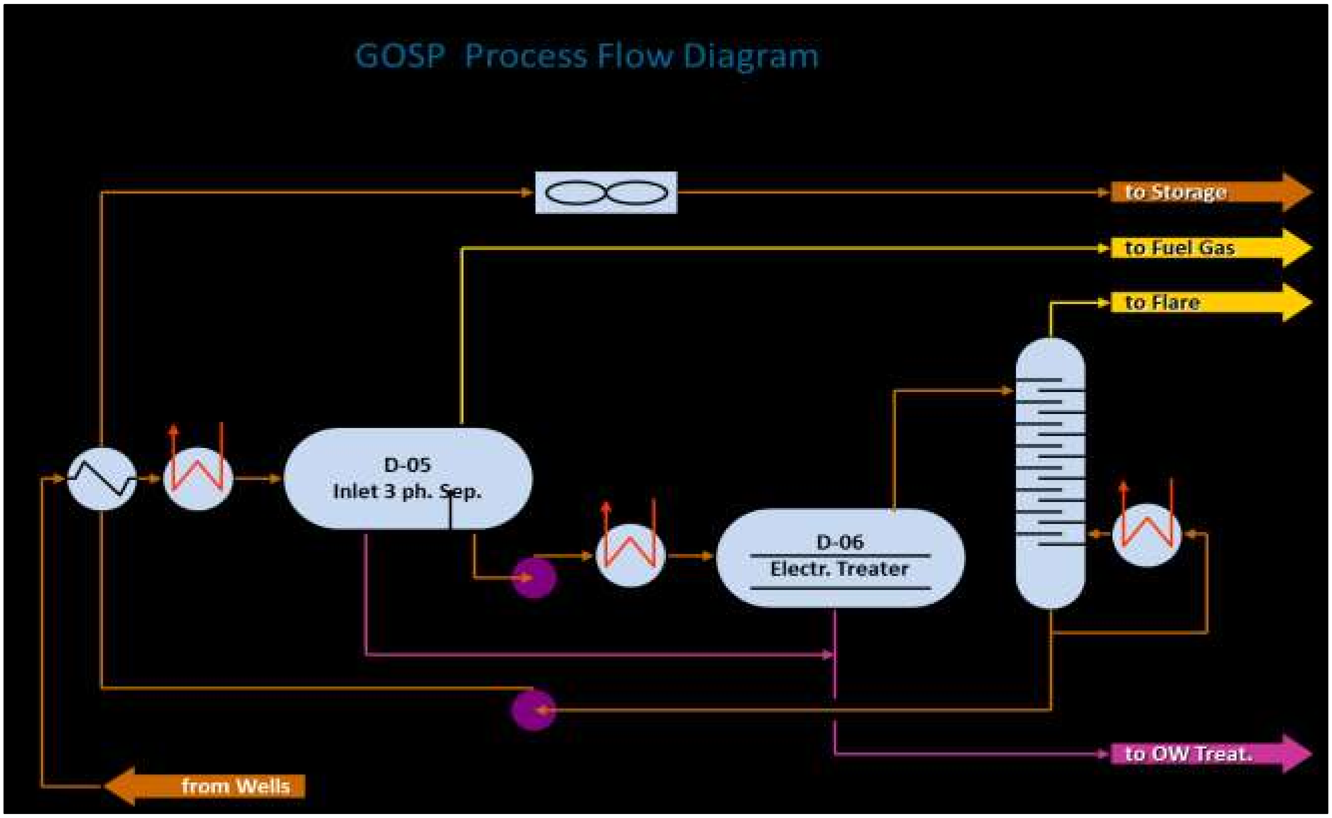


Figure 3.2 Flow diagram of Gas, Oil & Water Separation Plant (Swedan, 2012).

Different chemicals are being injected around the field to treat various operation related trouble-shootings. Several troubles are found in oil fields, such as corrosion, scaling, waxing, bacteria, foaming and emulsion. These chemicals are injected at different injection points, scattered around the field, located at satellites, flow lines, and at the plant. Figure 3.3 shows the locations of different chemicals used in in Mabruk field including W/O demulsifier. When locating the demulsifier injection point, the demulsifier should be introduced where the flow through the system will provide optimum shearing. This will ensure a uniform distribution of the demulsifier, maximizing its action and minimizing its consumption at the same time (Ben Mahmoud, personal communication, June, 2012). Therefore, the injection point of W/O demulsifier was designed and located upstream the heat exchanger (E-05). The following Figure 3.3 is simplified chemical injection diagram of the system:

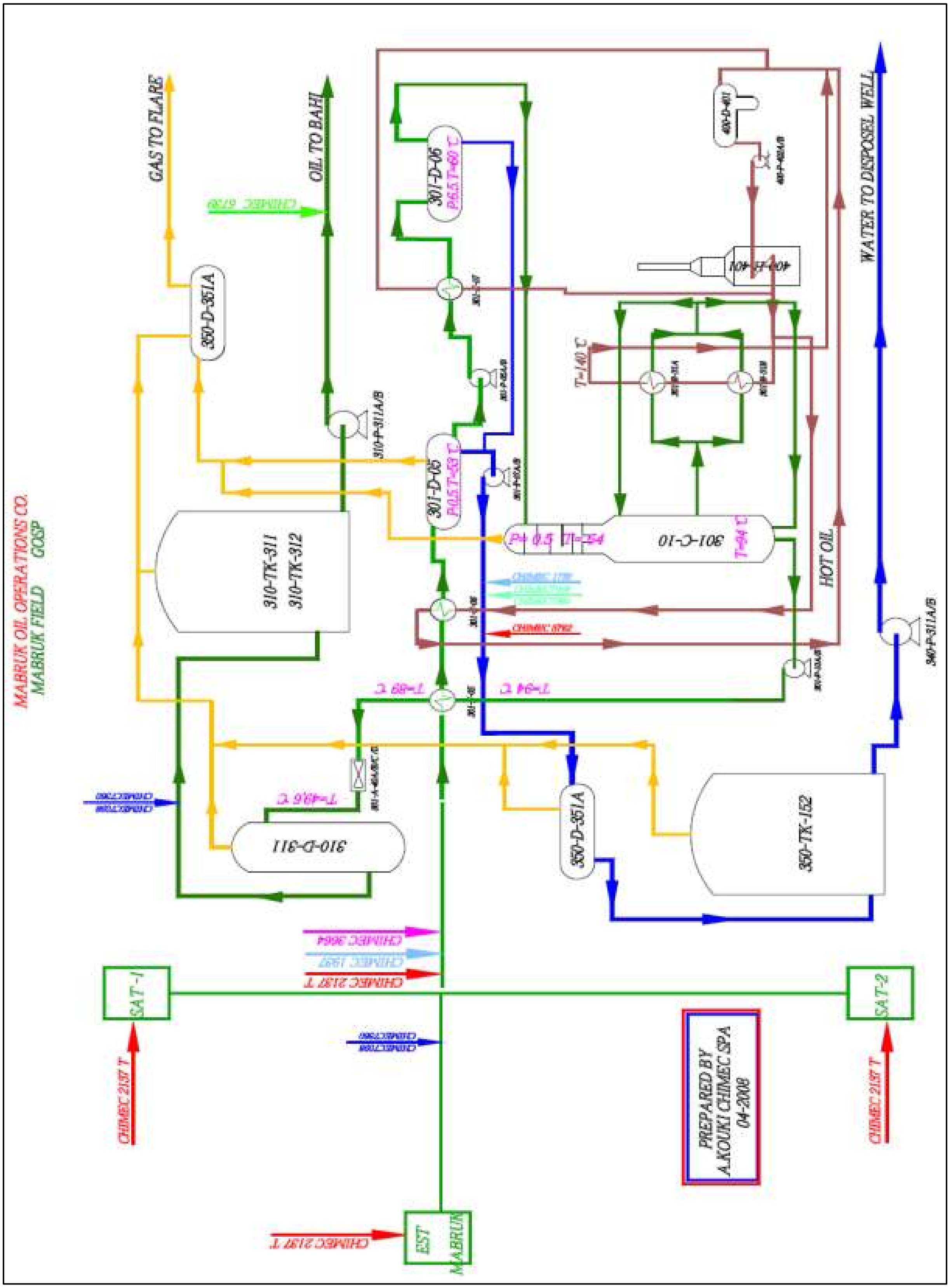


Figure 3.3 Chemical injection & Flow Diagram of Gas-Oil & Water Separation Plant (GOSP) (Aubourg, 2005)

3.3 Establishing Mabruk Field Conditions

Mabruk's crude oil has a moderate emulsion tendency that is easily treated. The main influencing factors for a proper water-oil separation at the plant (GOSP) are the increasing levels of water from oil wells, and the low retention time due to the size of the separation units (Aubourg, 2005).

Aubourg (2005) reported, the treatment is aimed at obtaining good separation at GOSP resulting in:

Base sediments and water (BS&W) < 0.20 % at oil export line (shipping), oil-in-water quality on separated water < 40 ppm. The injection points for the treatment as currently performed in Mabruk field are at the Gas, Oil, and Separation Plant (GOSP) inlet on continuous treatment basis. Moreover, the proposed demulsifier dosage is ranging from 6-8 ppm (based on seasonal variances –winter/summer).

Table 3.1 shows the BS&W% data for the period of June 1st – June 23rd, 2012 with an ideal average BS&W of 0.3% (< 0.5%) out of the dehydrator (de-salter) going to the stripper. The remaining water content can be extracted easily in the storage tanks down to < 0.2% as required (the shaded row is for the bottle-testing date June 22, 2012) (Swedan, 2012).

Table 3.1 BS&W% and process parameters for 3-phase separator and dehydrator.

Date (2012)	Total Yield Bbl/d	Chem. Dosage (ppm)	Sep. Pressure (bar)	Sep. Temp. (^{O}C)	Dehyd .Press. (bar)	BS&W % Pro.Sep inlet	BS&W % Sep. outlet	BS&W % Hyd. outlet
01/06	35155	8	1	59	6	20.08	3.00	0.22
02/06	34700	8	1	59	6	16.00	1.80	0.50
03/06	34060	8	1	60	6	19.59	5.67	0.45
04/06	34655	8	1	60	6	18.90	1.90	0.32
05/06	34561	8	1	60	6	19.33	2.20	0.43
06/06	33548	8	1	60	6	17.93	2.03	0.38
07/06	34423	8	1	60	6	17.36	2.20	0.18
08/06	34861	8	1	60	6	19.74	2.33	0.30
09/06	34403	8	1	60	6	19.36	2.33	0.22
10/06	33415	8	1	60	6	15.43	2.40	0.40
11/06	32568	8	1	60	6	16.33	1.60	0.15
12/06	31564	8	1	61	6	13.33	1.40	0.15
13/06	33036	8	1	61	6	19.92	1.70	0.18
14/06	34258	8	1	60	6	20.79	1.80	0.15

Continued Table 3.1,

Date (2012)	Total Yield Bbl/d	Chem. Dosage (ppm)	Sep. Pressure (bar)	Sep. Temp. (^{o}C)	Dehyd. Press. (bar)	BS&W% Pro.Sep inlet	BS&W % Sep. outlet	BS& W% Hyd. outlet
15/06	34992	8	1	60	6	21.48	1.60	0.17
16/06	35087	8	1	60	6	22.41	2.40	0.13
17/06	34649	8	1	60	6	23.47	2.53	0.20
18/06	34708	8	1	60	6	23.25	1.73	0.27
19/06	34536	8	1	60	6	21.99	1.70	0.20
20/06	34489	8	1	60	6	21.16	1.53	0.35
21/06	35738	8	1	60	6	21.74	1.87	0.13
22/06	**34128**	**8**	**1**	**60**	**6**	**23.38**	**2.80**	**0.25**
23/06	34166	8	1	60	6	24.65	2.67	0.20

Legend: The shaded row stands for the bottle-test day.

3.4 System and Current Treatment

The treatment of fresh crude oil and produced oily water were described in the following subsections in detail. Further, the performance of 3-phase separator, dehydrator and oily-water package were examined.

3.4.1 Wet Crude Oil Treatment

All production fluids flowing from the oil-wells are routed through the plant trunk line to the plant. At the Gas, Oil and Water Separation plant (GOSP), most of the gas and water are removed from the wet crude oil. The fluids are passed through a heat exchanger (E-05) where they are heated by hot crude oil from an upstream stripper (C-10). It is then passed through a second heat exchanger (E-06) which uses a hot oil supply as the heating medium as shown in Figure 3.4 (Aubourg, 2005).

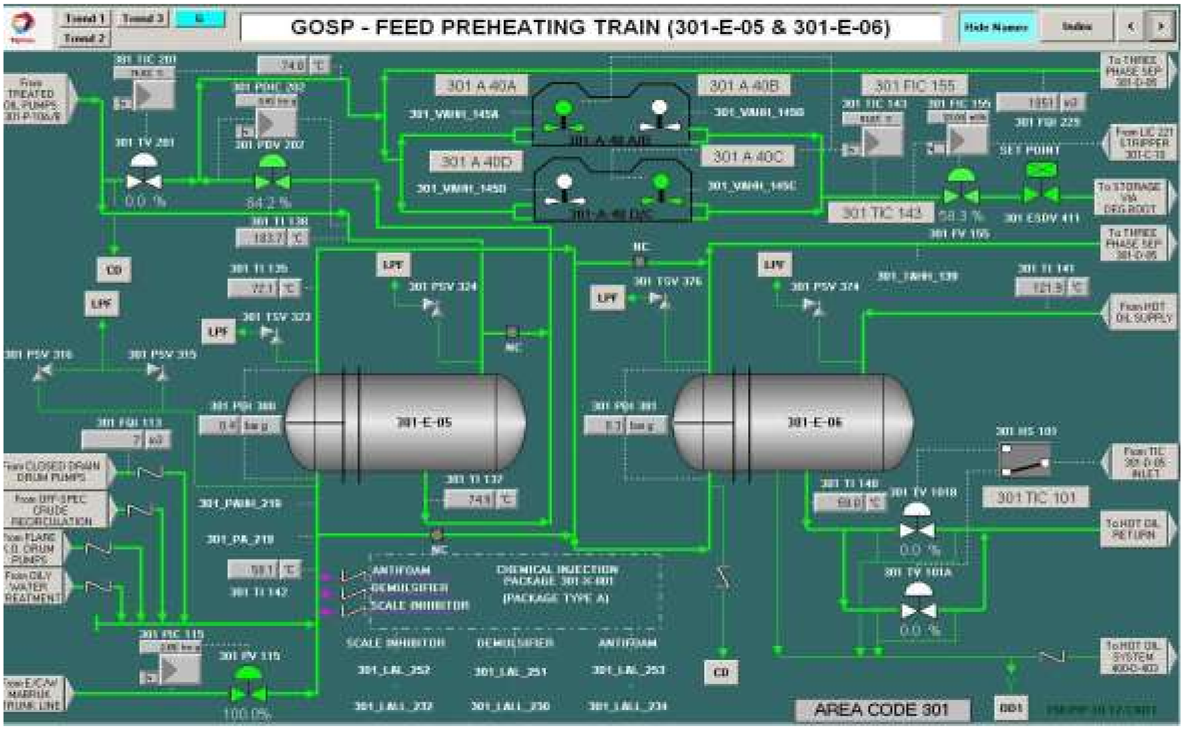


Figure 3.4 GOSP feed preheating train (E-05 and E-06) (Swedan, 2012).

Once the fluid has been heated, it is passed through to a three-phase separator (D-05). The function of the separator is to separate the incoming stream into a gas, oil and water streams. The 3-phase separator is described in Figure 3.5, where the gas is discharged from the 3- phase separator under pressure control to the fuel gas system. The produced water is pumped from the 3- phase separator to the oily water treatment package (Aubourg, 2005).

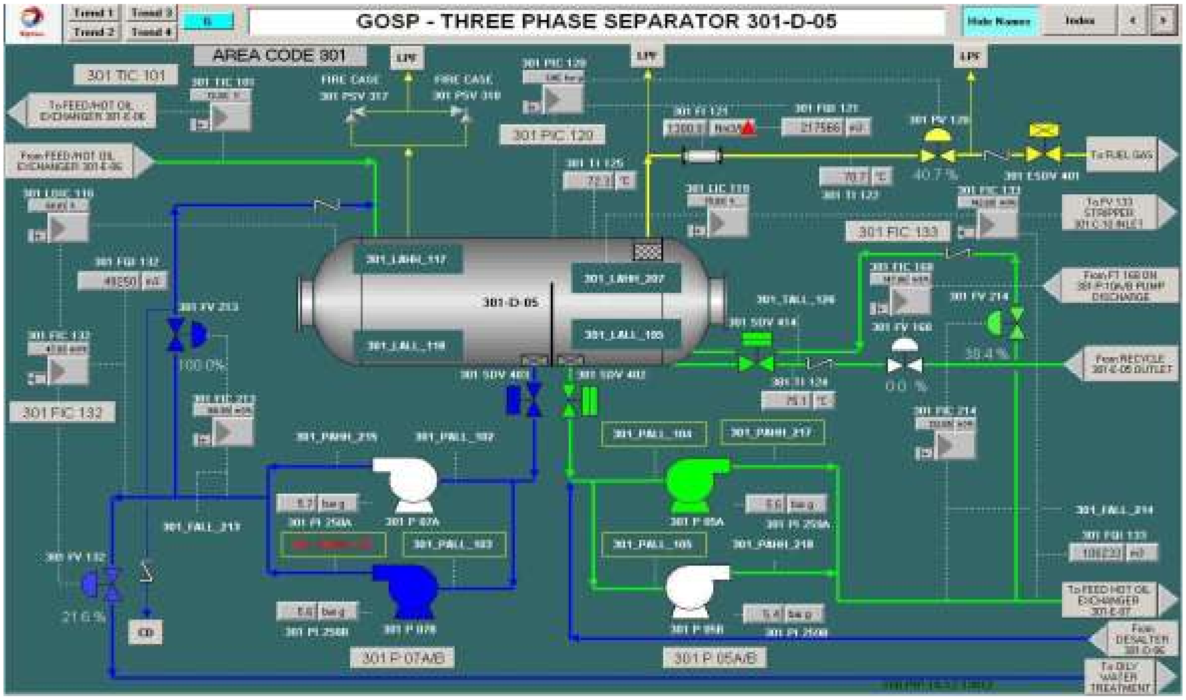


Figure 3.5 GOSP three phase separator (D-05). Legend: Green for crude oil, blue for water and yellow for gas (Swedan, 2012).

The dewatered crude oil is pumped (P-05) to another heat exchanger (E-07) where it is heated by the hot oil supply. The crude oil then flows to a de-salter (dehydrator) (D-06) as shown in Figure 3.6, where any additional salts present are removed by electrostatic means with no wash water is added (Aubourg, 2005).

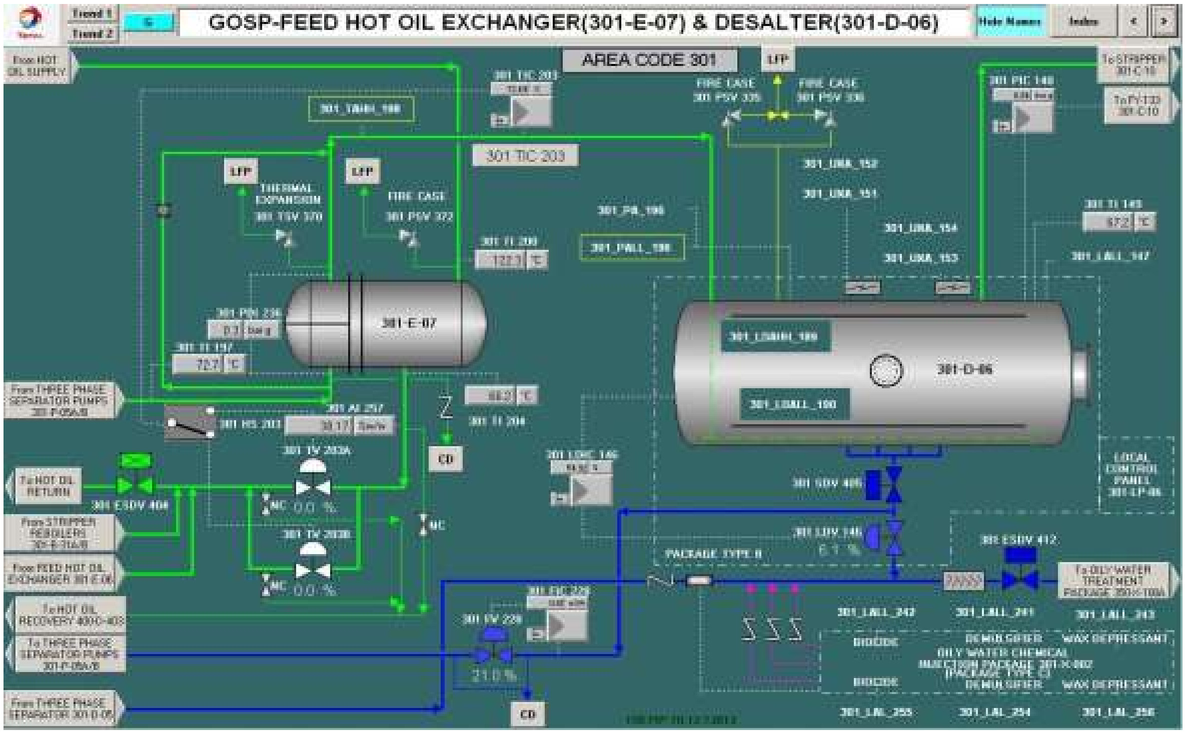


Figure 3.5 GOSP-feed heat exchanger (E-07) and de-salter (D-06) (Swedan, 2012).

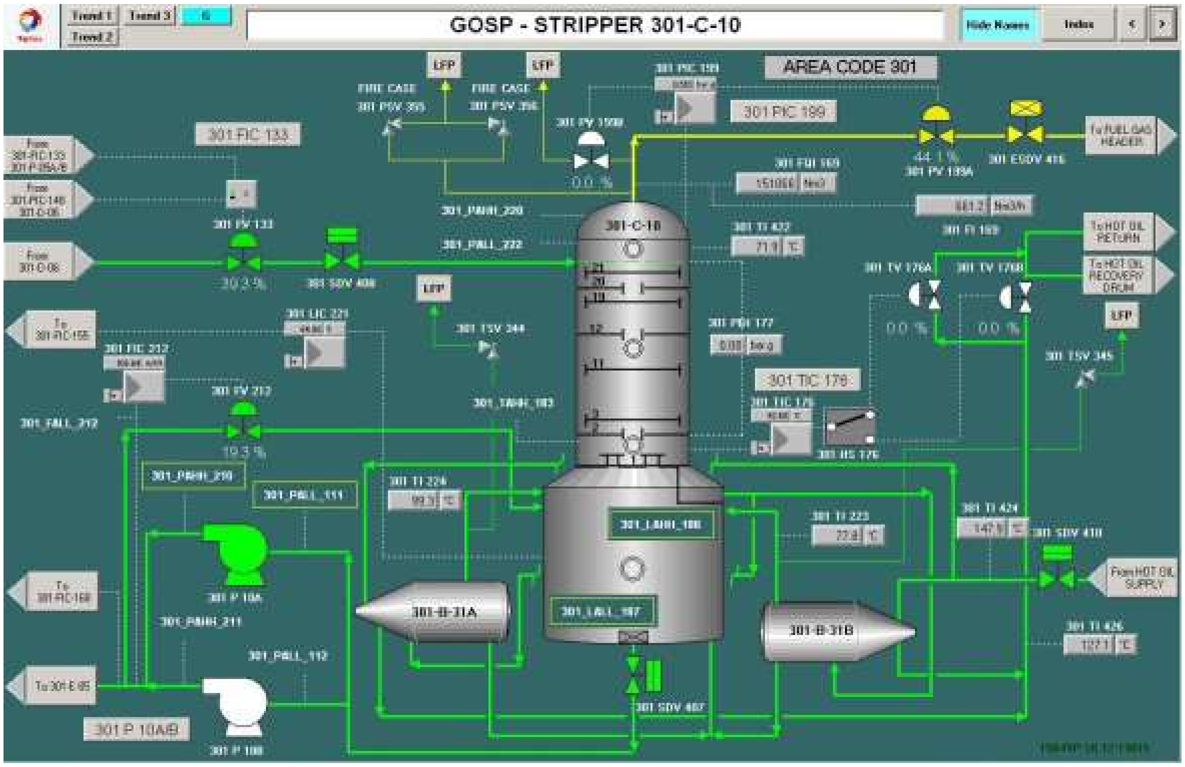


Figure 3.7 GOSP-stripper (C-10) (Swedan, 2012).

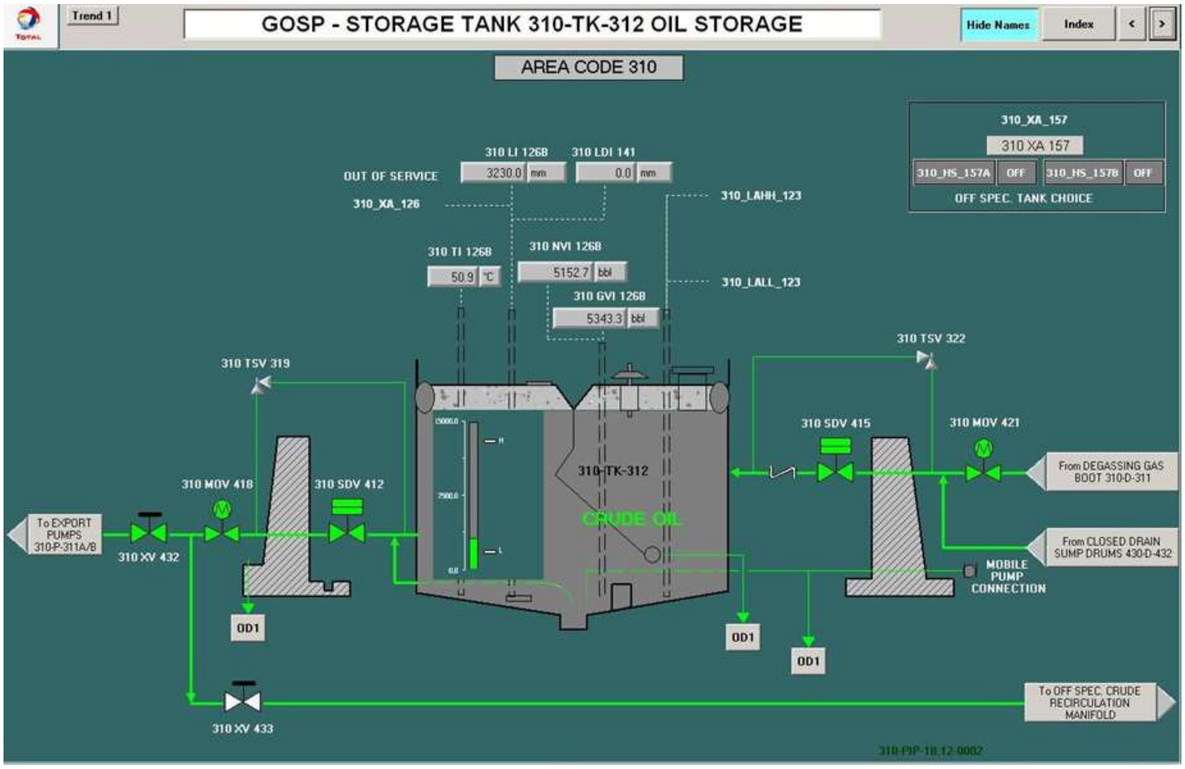


Figure 3.8 GOSP-oil storage tank (Tk-312) (Swedan, 2012).

As described in Figure 3.6, the desalted oil then flows to a stripper column (C-10), which further removes gas from the oil stream. This oil stream is then pumped through the first heat exchanger (E-05) where heat is transferred to the incoming production fluid line. It is then further cooled by an air cooler (A-40) before being sent to storage tank (Tk-312) as shown in Figure 3.8 (Aubourg, 2005). The current chemical, Demulsifier 2137-T is injected upstream of the 3-phase separator at 7 ppm on average (calculated for total fluids). Separated water is removed on by oily water package. Samples of oil are collected daily at outlets of production separator and dehydrator, where the results show very good water separation and dehydration by the current demulsifier.

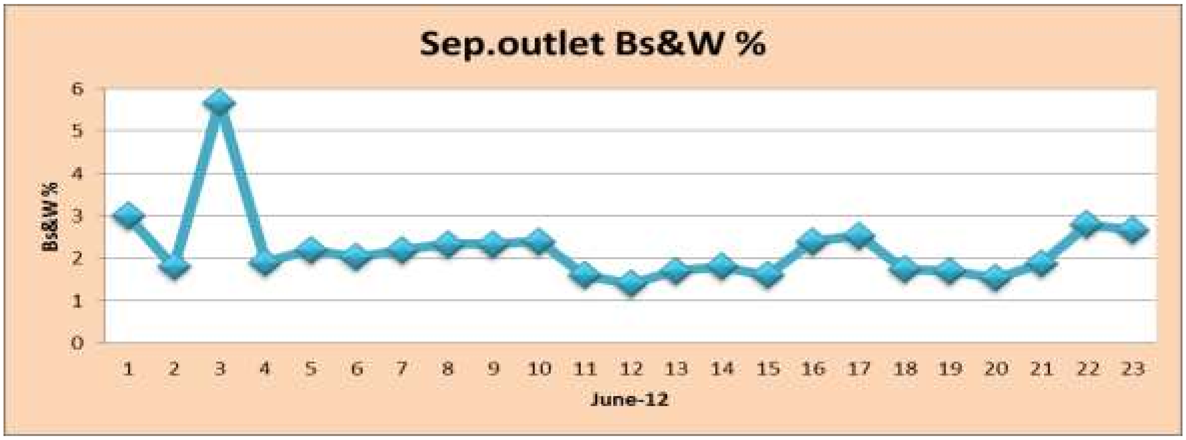


Figure 3.9 Water content at the Separator outlet.

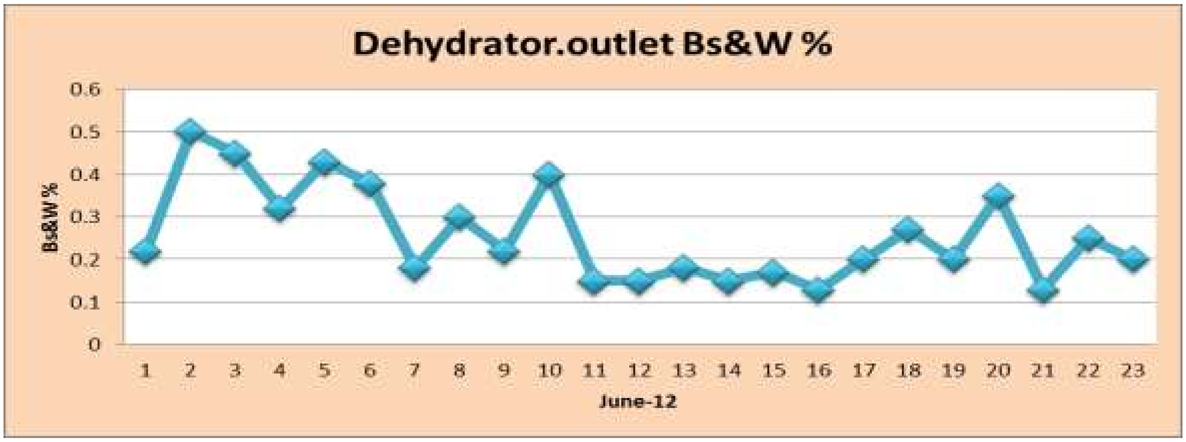


Figure 3.10 Water content at the dehydrator outlet for June 2012.

As stated above in figures 3.9 and 3.10, the separation process is working at good conditions and indicates high performance, where the target of less 0.5% water content out of the dehydrator is achieved (Aubourg, 2005).

3.4.2 Produced Water Treatment and Disposal

The water separated out at the demulsification stage at the plant-processing facilities contains residual oil and finely dispersed solids. The oil is present as dispersion in water or oil-in-water emulsion, termed reverse emulsion. The concentration of residual oil is usually too high for discharge into the environment. In addition, the residual oil also has economic value (Aubourg, 2005).

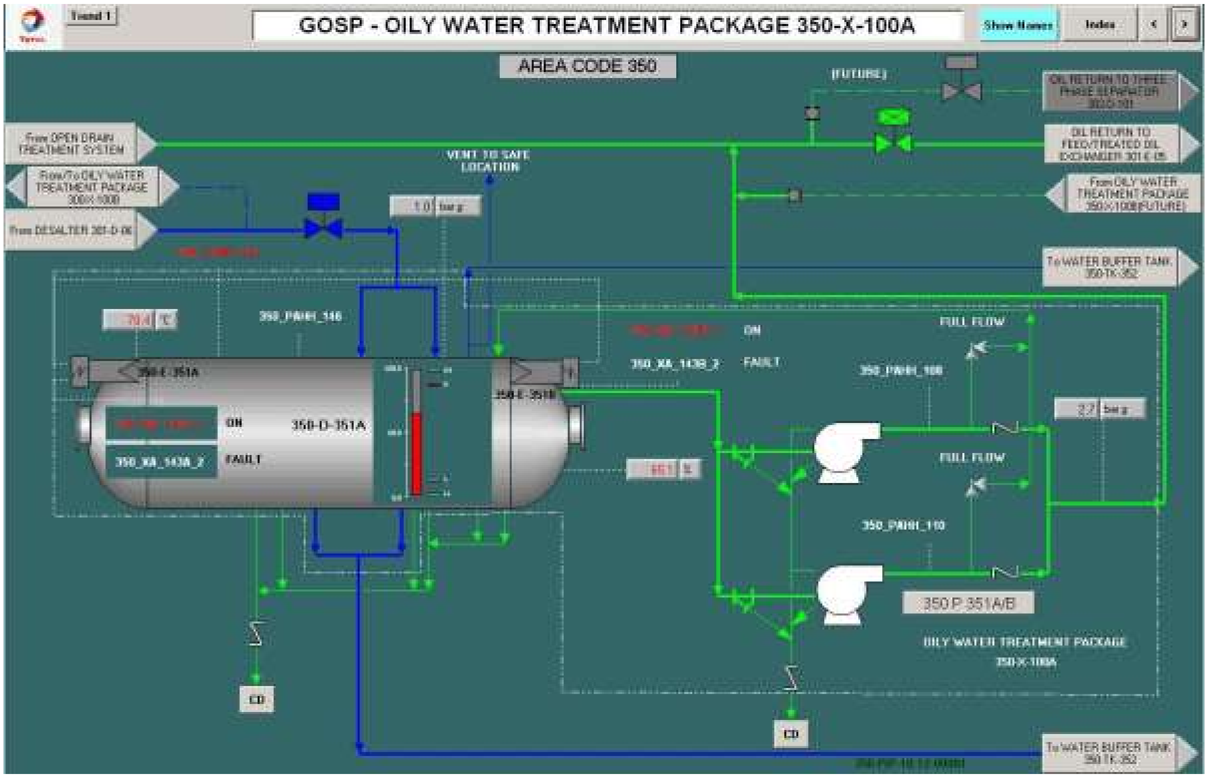


Figure 3.11 GOSP-oily water treatment package (Swedan, 2012).

Aubourg (2005) reported, the demulsifier chemical used to treat O/W emulsion is also termed coagulant or flocculent. Coagulation and flocculation treatment is a method to separate fine solids and colloids dispersed in water phase. He added, prior to disposal, the oily water is treated to remove residual oil in an Oily Water Treatment (OWT) unit (350-X-351A/B), which is described in Figure 3.11. The purpose of the oily water treatment package is to produce de-oiled waste water suitable to be discharged according to the local regulations or suitable for the use in water flooding system. Discharging oily water with high oil content could possibly lead to big environmental impact. As water includes many kinds of dissolved solids, suitable water treatment methods have been selected according to the water quality. As per Mabruk plant design, the oily water unit is a compact oil/water separator of the Pressurized Cross Flow Interceptor (PCFI) type.

3.4.2.1 Performance Evaluation of the Oily Water Treatment Package

In August, 2008, the performance of the oily water treatment separator has been evaluated at normal and steady state operations. The average residual free and separable oil content of the separator discharge has been determined, taking into consideration all recorded lab results.

Osenga et al. (2008) reported that, it has been found that, the oily water separator is performing according to the contract design value which is <40 mg/l free and separable oil in the treated discharge stream as described in Figure 3.12. The average of the total oil discharged out of the oily water treatment package into the disposal system is less than 40 mg/l that the Libyan regulations are strict to 40 mg/l maximum allowed discharge limit (onshore).

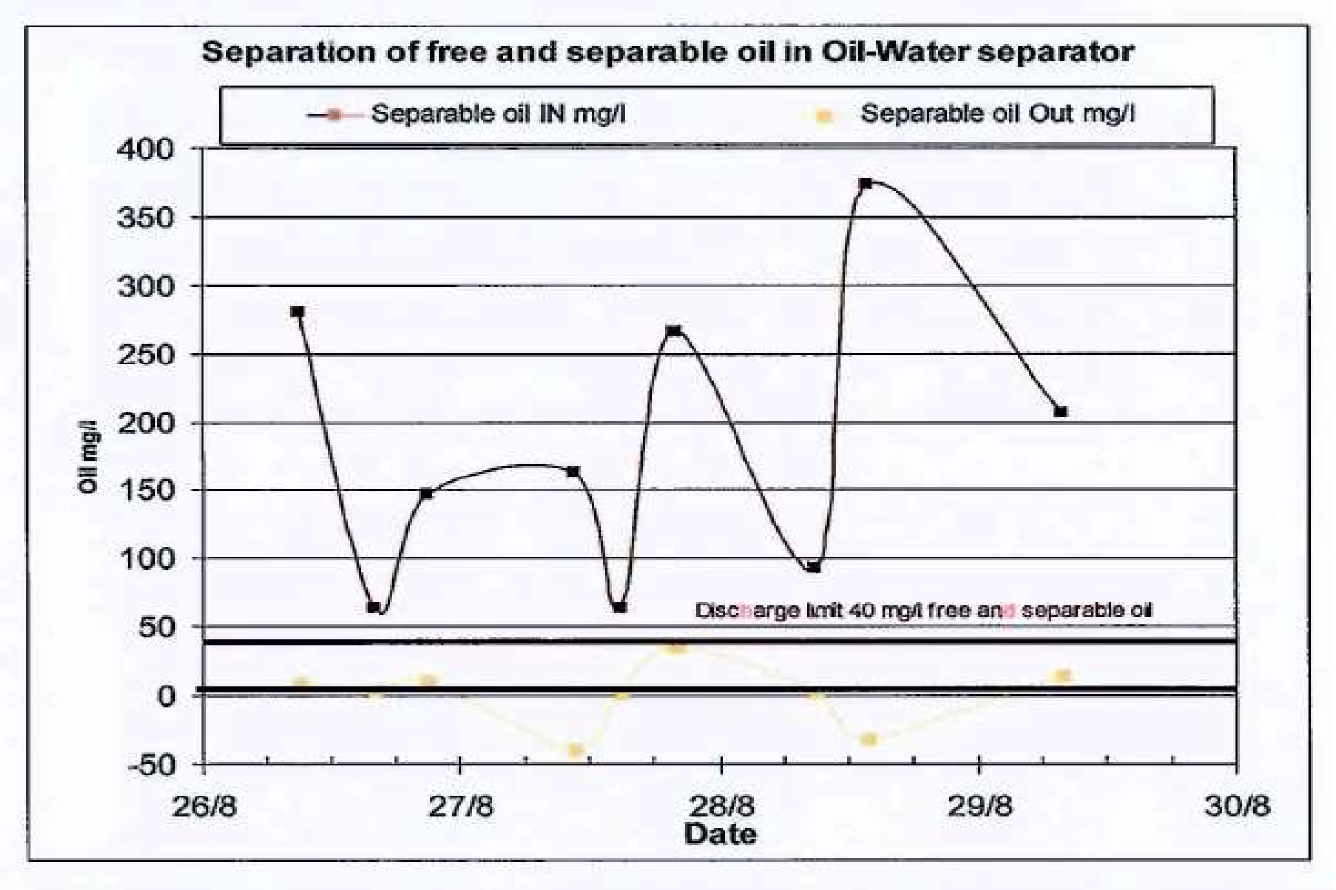
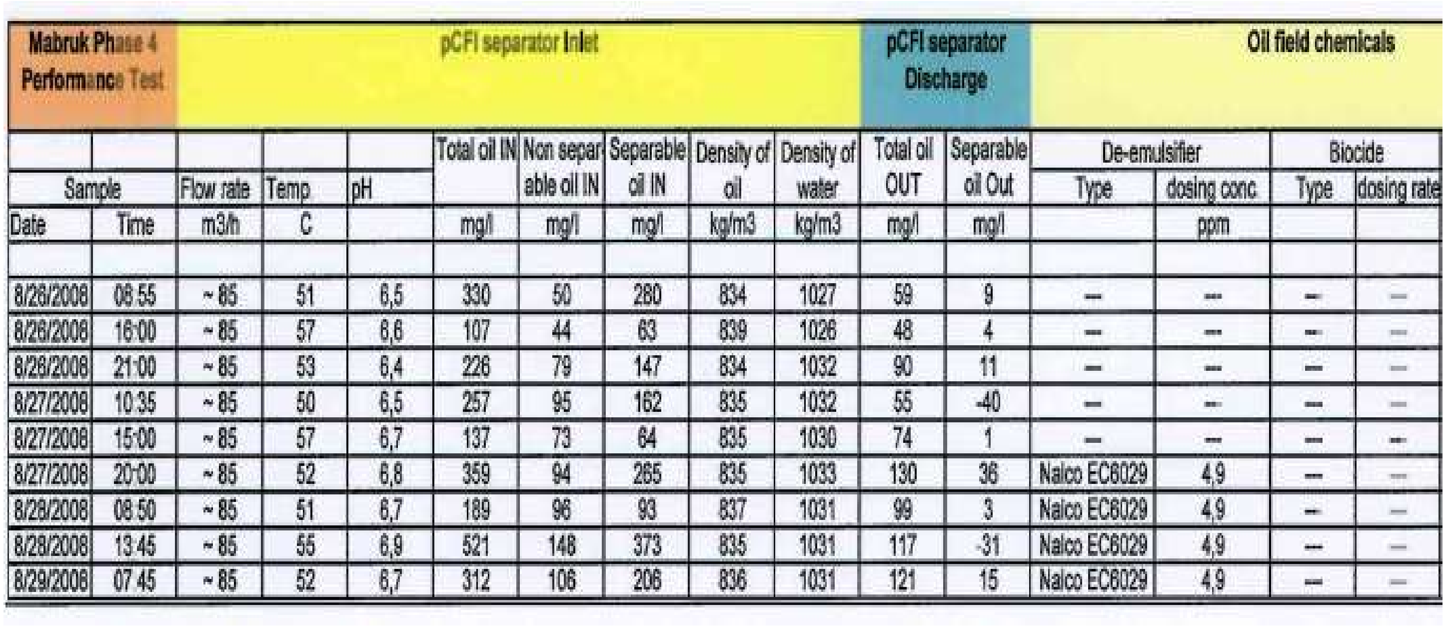


Figure 3.12 Free and separable oil content at the inlet/outlet of the oil-water separator (D 351-A) (Osenga, et al., 2008).

Table 3.2 The test results of total and free-separable oil contents for the oil-water separator in/out streams (Osenga et al., 2008).



Mabruk Phase 4 Performance Test		pCFI separator Inlet								pCFI separator Discharge		Oil field chemicals			
					Total oil IN	Non separable oil IN	Separable oil IN	Density of oil	Density of water	Total oil OUT	Separable oil Out	De-emulsifier		Biocide	
Sample		Flow rate	Temp	pH								Type	dosing conc	Type	dosing rate
Date	Time	m3/h	C		mg/l	mg/l	mg/l	kg/m3	kg/m3	mg/l	mg/l		ppm		
8/26/2008	08:55	~ 85	51	6,5	330	50	280	834	1027	59	9	—	—	—	—
8/26/2008	16:00	~ 85	57	6,6	107	44	63	839	1026	48	4	—	—	—	—
8/26/2008	21:00	~ 85	53	6,4	226	79	147	834	1032	90	11	—	—	—	—
8/27/2008	10:35	~ 85	50	6,5	257	95	162	835	1032	55	-40	—	—	—	—
8/27/2008	15:00	~ 85	57	6,7	137	73	64	835	1030	74	1	—	—	—	—
8/27/2008	20:00	~ 85	52	6,8	359	94	265	835	1033	130	36	Nalco EC6029	4,9	—	—
8/28/2008	08:50	~ 85	51	6,7	189	96	93	837	1031	99	3	Nalco EC6029	4,9	—	—
8/28/2008	13:45	~ 85	55	6,9	521	148	373	835	1031	117	-31	Nalco EC6029	4,9	—	—
8/29/2008	07:45	~ 85	52	6,7	312	106	206	836	1031	121	15	Nalco EC6029	4,9	—	—

There was another technical report issued by another contractor, concerning the water-oil package's performance as shown in Table 3.3. The two Tables (3.2) and (3.3) summarize the water quality entering and exiting the water-oil separator D-351 as well as, the water quality of the buffer tank outlet stream (TK-352). The buffer tank is the last separation stage for oily-water before it is pumped into the disposal well (Osenga et al., 2008) (Sewdan, 2012).

Table 3.3 Produced water characteristics (Sewdan, 2012).

Parameter	CFI (D-351A) Inlet, GOSP	CFI (D-351A) Outlet, GOSP	Buffer Tank (TK-352) Outlet, GOSP
Temperature, ^{0}C	50.8	50.6	51.9
Specific Gravity @ 20 ^{0}C	1.0340	1.0341	1.0341
Total Dissolved Solids, mg/l	50,465	50,731	50,771
Dissolved Carbon Dioxide, mg/l	128	163	165
Dissolved H_2S, mg/l	3.5	3.5	6
Dissolved Oxygen, µg/l	10	15	10
Total Suspended Solids, mg/l	5.1	4.3	6.3
Oil In Water, ppm	117.5	41	10

Based on the two technical reports issued by different contractor companies (summarized above), both show the oil content (free and separable) at the buffer tank outlet is below the allowed limit as planned. Specification of maximum oil content of produced water is 40 ppm. This limit was set by reservoir geophysical properties in order to maintain the disposal well injectivity index at the required level. Therefore, by abiding such a crucial environmental regulation, it is now possible to argue that oily-water treatment package is running in environmentally friendly manner.

3.4.2.2 Produced Water Disposal

The treated water from the oily water treatment separator units enters the water buffer tank 350-TK-352. The treated water from the buffer tank is normally continuously disposed through the water disposal network as described in Figure 3.13, where, the treated oily water is disposed into a disposal well (A-22i) as per Mabruk plant's design. Further, the disposal well is a part of the water flooding system, where the treated water is being injected into water injection wells to recover more oil quantities produced from the reservoir (Secondary recovery phase) (Aubourg, 2005).

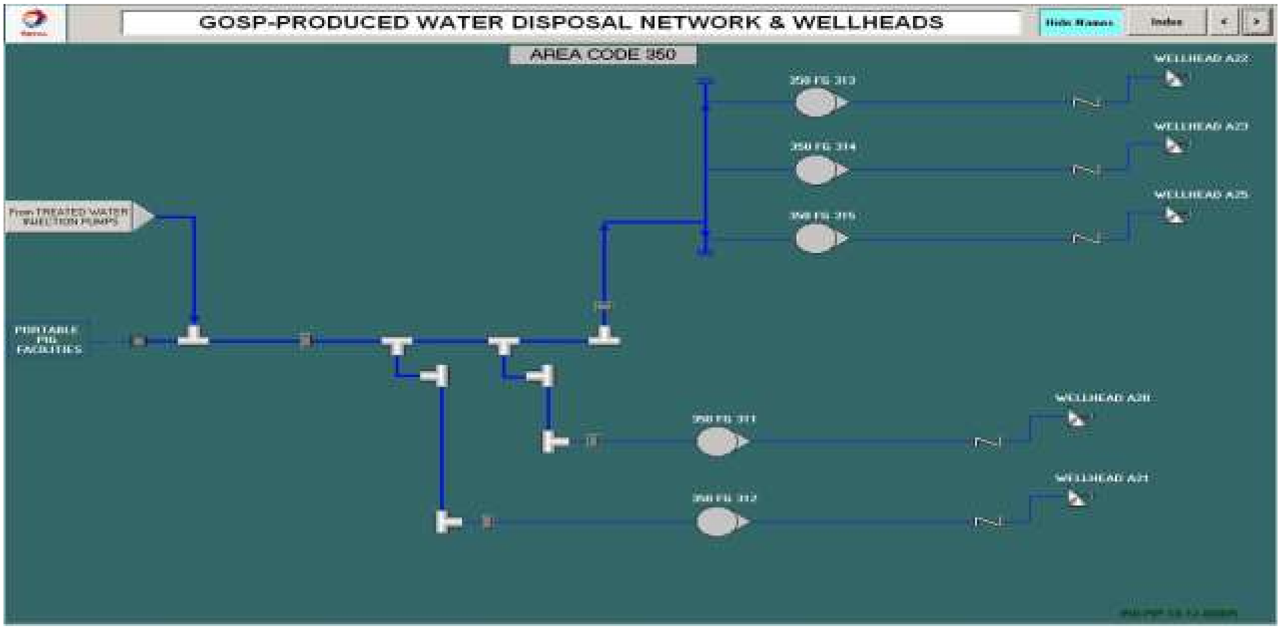


Figure 3.12 Produced water disposal network (Swedan, 2012).

3.4.3 Product Specifications

The following, Table 3.4, shows the specifications of the produced crude oil. These specifications must be achieved by the field operator to produce dry and saleable crude oil accepted in the petroleum market. The treatment of dissolved gases as well as salts was not discussed in this thesis. However, the specifications related to associated gases and salts were not difficult to achieve (A. Ben Mahmoud, personal communication, June, 2012).

Table 3.4 Treated crude oil specifications (Aubourg, 2005).

Treated Crude specifications	
RVP	<11 psia
BSW	<0.2%
Salt content	55 PTB (157 mg/l)
H_2S content	55 ppm wt

(Note: - Actual export product RVP spec is 13 psia, but Process trains to be designed for 11 psia)

Legend: RVP, Reid Vapor Pressure. PTB, Pound per Ton Barrels. ppm wt., part per million (weight basis). psia, pound per square inch (absolute)

3.5 Key Design Data

The following table shows the key design data for main equipment at the existing oil production process units:

Table 3.5 Key design data of the existing oil production process at GOSP (Aubourg, 2005).

D-05 Three Phase Separator		
Duty		1 x 100%
Operating Pressure	Barg	1
Operating Temp.	ºC	60
Inlet Flow Rate	T/h	236
D-06 De-salter		
Duty		1 x 100%
Operating Pressure	Barg	5
Operating Temp	ºC	65
Inlet Flow Rate	T/h	149
C-10 Stripper		
Duty		1 x 100%
Operating Pressure	Barg	0.5 – 0.8
Operating Temp	ºC	92

3.6 Fluid Physical and Chemical Properties

3.6.1 Oil Properties

Mabruk's crude oil is a mix of three different reservoirs, Mabruk, Dahra and Garian. At the inlet of the separation plant, all the trunk lines are gathered in one trunk line. The stability of emulsions is largely affected by the presence of fine solids or external agents. The physical properties of Mabruk crude are given in Table 3.6, where it is readily noticeable that the 3 reservoirs are paraffinic. Therefore, it is recommended to study the chemical and physical properties of these reservoirs when selecting the demulsifier.

Table 3.6 Mabruk crude oil physical properties (Aubourg, 2005).

Oil Properties			
Parameter	Mabruk	Dahra	Garian
Density @ 15°C, kg/m^3	851 (WM) 855 (ECM)	830 (DSE) 857 (DN)	824 (GN)
Viscosity @ Reservoir conditions, cP	2.6 (WM) @ 59C/1200 psi 2.1 (ECM) @ 58C/1200 psi	0.72 (DN) @ 77C/1500 psi 1.3 (DSE) @ 68C/1250 psi	0.95 (GN) @ 102C/2400 psi
Wax Appearance Temperature, °C	30	33	27
Wax Composition	n/a	n/a	n/a
Pour Point, °C	-6	-3	-12
GOR (Sm^3,Sm^3)	5.4 (WM) 12.5 (ECM)	78 (DN) 6 (DSE)	2 (GN)

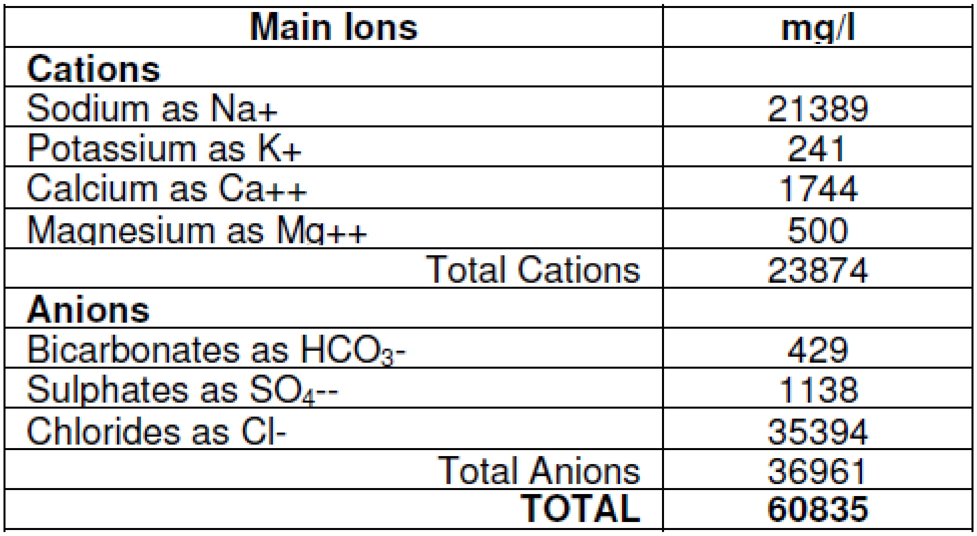
Legend: WM (West Mabruk), ECM (East Central Mabruk), DN (Dahra North), DSE (Dahra South East), GN (Garian North)
GOR (gas oil ratio), cP (centi- Poise), n/a (not available)

The Chemical properties of the feed crude oil is provided for the 3 crude oils (Mabruk, Dahra and Garian) are given in the attached appendix-B (Table-1 and Table-2). These tables contain the feed compositions for Mabruk crude oil, and (Dahra & Garian) crude oils respectively. The simulations were carried out to predict the feed flow rates for the incoming years using PRO/II software (Aubourg, 2005).

3.6.2 Water Properties

Wet crude oils are pumped from producer oil wells to separation plant (GOSP), where the majority of water and gas quantities are removed. The feeding fluid contains dissolved gas and water. Further, water content of the inlet stream exceeds the average of 20% in most cases. The inlet water cut value is ranging from 20 to 35%, depends on several operational conditions related to the feeding oil wells, where more than 60 oil wells are feeding Mabruk plant, working ideally 24/7. Water properties of the 3 reservoirs are given below in tables 3.7 and 3.8 (Aubourg, 2005).

Table 3.7 Water composition for Mabruk reservoir (Aubourg, 2005)



Main Ions	mg/l
Cations	
Sodium as Na+	21389
Potassium as K+	241
Calcium as Ca++	1744
Magnesium as Mg++	500
Total Cations	23874
Anions	
Bicarbonates as HCO_3-	429
Sulphates as SO_4--	1138
Chlorides as Cl-	35394
Total Anions	36961
TOTAL	**60835**

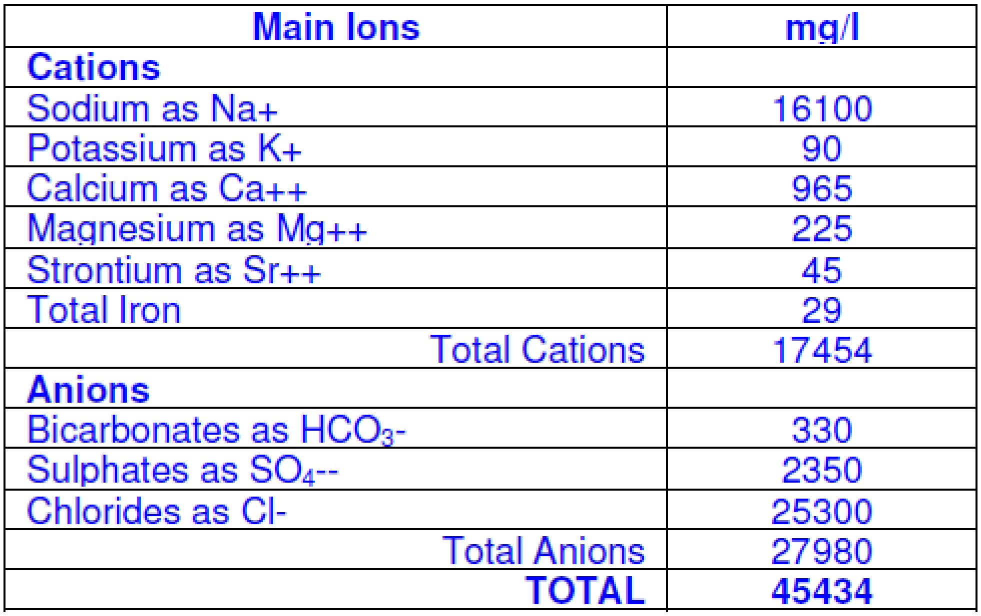
The following are dissolved gases values and the water characteristics for Mabruk reservoir (water)

Dissolved Gas: CO_2: 42 ppm mol.

H_2S: 200 mg/l

Water characteristics: pH: min: 6, max: 7.3, density @ 20°C: 1040 kg/m3 and conductivity @ 20 °C: 80.35 µS/cm.

Table 3.8 Water compositions for Dahra and Garian reservoirs (Aubourg, 2005).



Main Ions	mg/l
Cations	
Sodium as Na+	16100
Potassium as K+	90
Calcium as Ca++	965
Magnesium as Mg++	225
Strontium as Sr++	45
Total Iron	29
Total Cations	17454
Anions	
Bicarbonates as HCO_3-	330
Sulphates as SO_4--	2350
Chlorides as Cl-	25300
Total Anions	27980
TOTAL	**45434**

The following are dissolved gases values and the water characteristics for Dahra/Garian reservoir (water)

Dissolved Gas: CO_2: 32 ppm mol (max 150 mg/l), H_2S: 200 mg/l and water pH: min.: 6, max.: 7.3

3.7 Wax Appearance Temperature and Pour Point

Mabruk oil is characterized as a waxy crude oil, where its pour point ranges from -12 to -6 °C. More, Mabruk crude oil is a mix of three different crude oils. These crude oils are originally come from three reservoirs, Mabruk, Dahra and Garian. As per Table 3.9 given below, the three crude oils show waxing tendency at different temperatures. Although, the presence of waxy or paraffinic materials could possibly increase the emulsion stability, Mabruk oil has a moderate emulsion tendency, not difficult to treat. Table 3.9 given below shows the pour point and the wax appearance temperature (WAT) for each reservoir.

Table 3.9 Pour point and (WAT) for each reservoir (Aubourg, 2005).

Reservoir	WAT, °C	Pour Point, °C
MABRUK crude	30	-6°C
DAHRA crude	33.5	-3°C (Well A4)
GARIAN crude	27.3	-12°C (Well A1)

The melting and crystallization points of the waxes are important for stabilizing the properties of waxes. If the melting point is exceeded at the oil-water separation facilities, the waxes will mainly act as a component in the crude oil bulk. Hence, their activities at the oil-water interface are normally substantially decreased. Aubourg (2005) stated, according to the field's operation database of Mabruk field, there is no report available to check the possibilities of asphaltenes or naphthanes crystallization occurrence. Also, referring to the current operational parameters applied at the oil-water separation facilities, there is no concern in relation to the above (Ben Mahmoud, personal communication, June, 2012)

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Chapter 4

Experimental Materials and Methods

4.1 Introduction

To achieve the outlines of the objectives and the scope of the research, several materials, experimental and analytical procedures used in this study are presented and discussed with more details in the following sections. The chemicals and methods used in this study depend exactly on the research needed by considering all factors except cost saving. This is because the existing chemical used to treat the water-in-oil emulsion in Mabruk field was validated (Ben Mahmoud, personal communication, June, 2012).

4.2 Experimental Methods

Ben Mahmud (2012) reports that the Bottle Test procedure allows the identification of the best combination of active demulsifying agents depending on the crude characteristics and system parameters. The best active materials combination is the one that breaks the emulsion and balances the following parameters: higher water drop, lower residual salt content, best interface quality, low interface volume with tin shape, best quality of separated water and lowest residual emulsion content. Once the oil achieves the specification required (salt content, residual BS&W, T.V.R.) it is ready to be shipped to the terminal (exporting line). This study was carried out on site by using two types of demulsifiers, where bottle test method was used. The two demulsifiers were screened at different concentrations to determine the most effective demulsifier as discussed in section 4.2.2.

4.2.1 Bottle-Testing History

In November-2008, a survey carried out in Mabruk field by the chemical contractor company, and the efficiency of the current chemical used in the field as emulsion breaker has been verified. The current emulsion breaker CH 2137-T is a product formulated for Mabruk field and used as demulsifier. This chemical is giving high performances, allowing the complete water separation according to operating conditions. The efficiency was found to be very high. The good results have been compared to some newly developed products with the aim of determining further improvements to its performance. CH-2137-T remains efficient among all tested products. The parameters monitored to evaluate the efficiency of the emulsion breakers for the crude oil, have been:

- Volume of separated water;
- Water separation rate;
- Sharp interface;
- Quality of separated water (oil in water);
- No over-dosage effects encountered.

According to the system characteristics, such as short residence time (approx. 4 min.) and high turbulence, 2137-T has been chosen. To evaluate the performance of the chemicals during the first 10 minutes, all the products selected and fit on the Figure 4.1 have reached at least the 70% of the theoretical performance where the test crude has 32-33% water cut at that time (Laura et al., 2009).

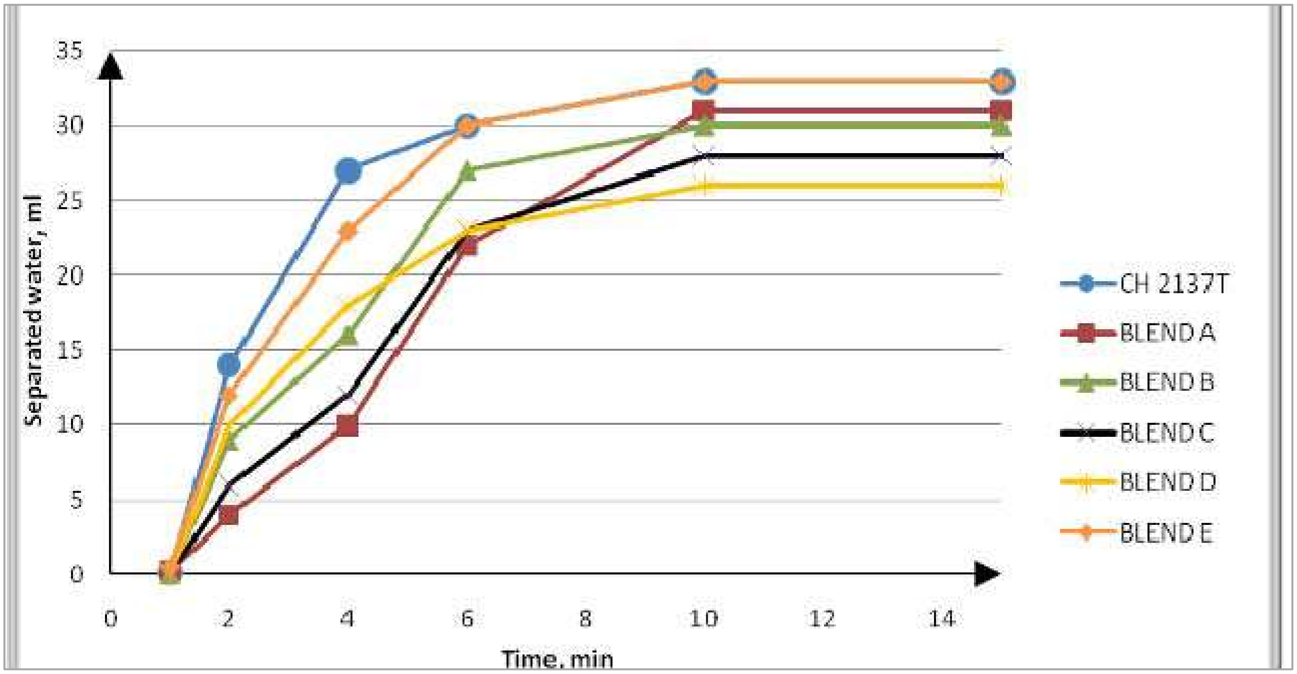


Figure 4.1 Previous bottle-test results performed in Mabruk field dated November-2008 (Laura et al., 2009).

Laura et al. (2009) explained, in the figure 4.1, each curve is relative to a different chemical, including the incumbent 2137T. Further, a rank has been coupled to each of the main parameters using a number between 0 and 6. Figure 4.2 describes the overall performance of the tested demulsifiers.

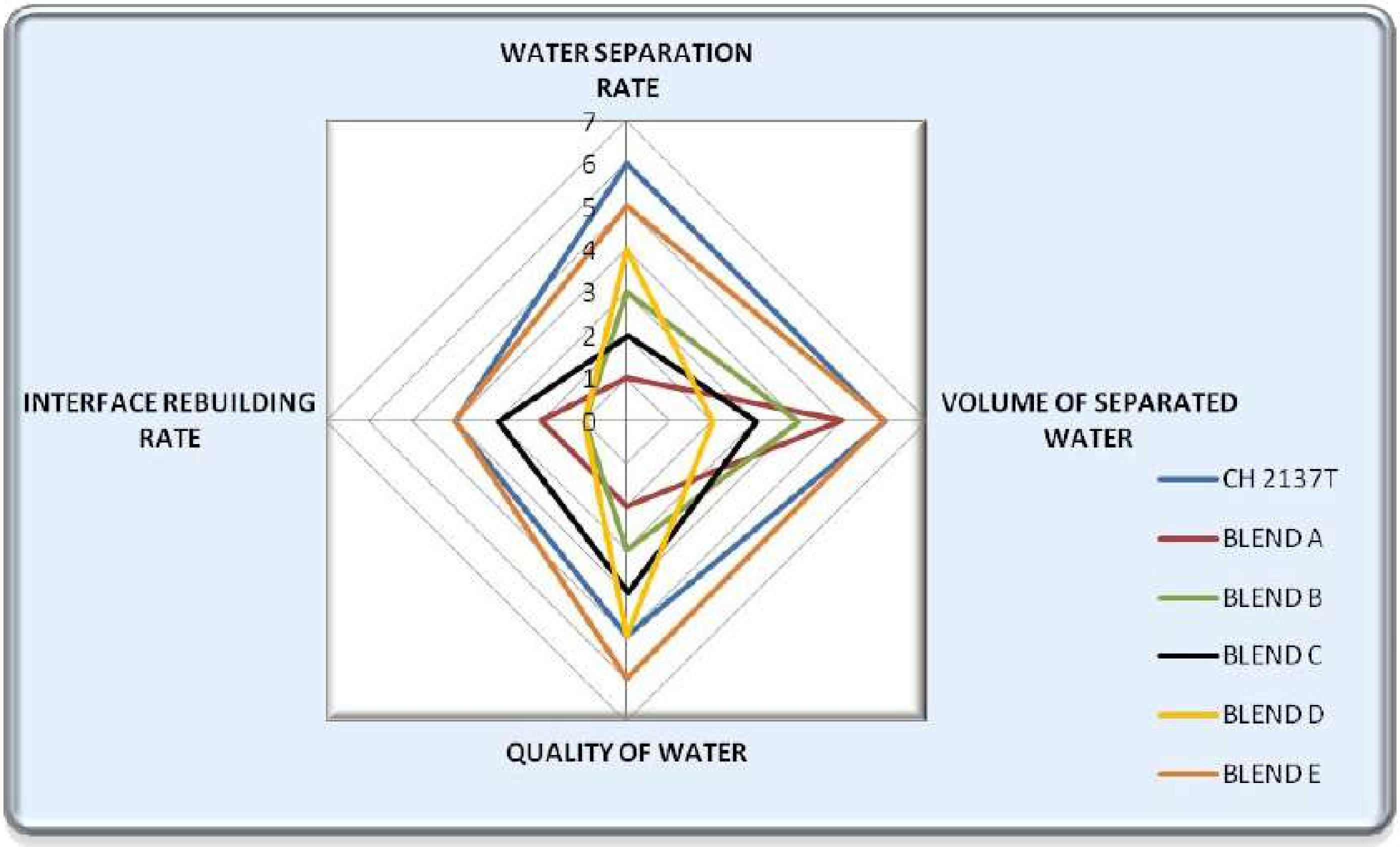


Figure 4.2 The main parameters monitored to evaluate the efficiency of the emulsion breakers (Laura et al., 2009).

Laura et al. (2009) concluded, considering all the parameters monitored to evaluate the efficiency of the tested potential blends against 2137-T, **2137 T** is a really good product for the Mabruk field plant, giving the largest polygon area. Hence, it has been confirmed that 2137 T is a good choice for the Mabruk crude oil.

4.2.2 Bottle-Test

The bottle test is the basic tool used in most of the demulsifier screening work performed in the field. It is based on the comparison between demulsifier products with a known standard, in this case 2137-T. The new potential blend (Blend-X) is prepared at the central laboratories of the chemical contractor company. These two products, 2137-T and Blend-x, were tested against each other using bottle test procedure to validate the current product used in the field (2137-T).

In general, a bottle test is conducted by placing an emulsion sample in a bottle and adding a measured amount of a demulsifier chemical. The bottle is capped and then shaken for a specified time in order to mix the contents. The bottle is set aside and the water drop is observed for few minutes (1, 2, 3, 5, 10 &15 min). A sample of the oil layer is then obtained and centrifuged to determine the quantity of water, emulsion and solids (in case) remaining. In this experimental work the water drop has been observed at 1, 3, 5, 7 minutes that it is been noticed that after 7 minutes, the oil/water level is stabilized (Korosoglou et al., 2010).

4.2.3 Bottle-Test Procedure

The bottle test is the basic tool used in most of the demulsifier screening work performed in the field. It is based on the comparison of demulsifier products with a known standard, in this case 2137-T.

A- Ratio Test

Bottle test the candidate demulsifier (2137-T) over a range of concentrations to obtain optimum volume.

B- Elimination Test

- Prepare the new blend that will be tested against the existing demulsifier. In this work, Blend-X is the new blend which has been already prepared at the central laboratory and ready to be tested against 2137-T (Allegrucci, personal communication, June, 2012).
- The two blends are ready to be tested at the chemistry Mabruk field laboratory.
- Test the new product at the same dosages that the candidate demulsifier was tested on and record your observations.
- Make a comparison and decide which one is the best.

C- Confirmation Test

Test the optimum blend over a range of treatment rates to identify any over or under treatment characteristics (Korosoglou et al., 2010).

4.2.4 Establishing Test Conditions

The conditions of the individual bottle test are modified according to the individual system. The following test conditions and variables were investigated:

- Representativeness of sample

  The samples were taken from the GOSP inlet trunk line where all the production lines gather and the sample point was 15:00 o'clock positioned (0^{o} degree angle).
- Treating temperature(s) effects

  The tests were carried out at the system temperature ($60^{O}C$).
- Agitation/shake time effects

The prescription bottles were shaken 100 times (at least), which is usually enough to disperse the chemical into the crude oil.

- Settling time required

  The time given was similar to the residence time in the system (2-5 min at the 3-phase separator), where 4 minutes was considered for this test (Allegrucci, personal communication, June, 2012).

- Sample ageing effects

  Fresh emulsion samples were taken for the test.

Taking the above criteria into consideration, the following method was used:

- Tests run at 60ºC, the temperature in the system.
- Demulsifier added to each bottle at required dosage.
- Bottles agitated to disperse demulsifier and replicate shear in the system (simulation).
- Water drop rate (volume versus time) recorded for each bottle.
- At the end of each test, a sub-sample of the top oil is taken and centrifuged to determine the BS&W. This corresponds to the expected BS&W going from the 3-phase separator to the to the next treatment unit which is the de-salter, where further water separated from the crude oil. A composite BS&W was not taken because the water/emulsion interface was not there (no emulsion observed and clear interface for 2137-T) (Allegrucci, personal communication, June, 2012).

4.3 Preparation for the Bottle Test

Prepare the chemistry Laboratory; materials, machines, and tools needed for the test, such as;

- Packers 100, 200, 500, 1000 ml
- Pipettes (±20)
- Microliter syringes (adjustable)
- Centrifuge (adjustable speed RPM, temperature & timing)
- Crude oil sampling bottles (potable water bottles, 1.5 liters)
- Water bath (adjustable temperature)
- Standard bottle-test kit (4 prescription bottles, 100 ml each, test tube rack)

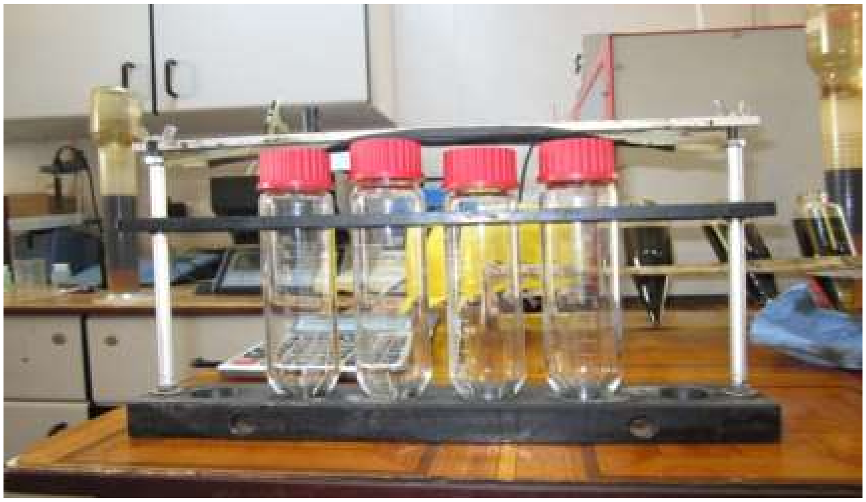


Figure 4.3 Standard bottle-test kit.

- Fume hood

Figure 4.4 Fume hood.

- Emulsion Breaker (Demulsifiers) samples;

  100 ml 2137 T and 100 ml Blend-X
- A standard demulsifier bottle (1 liter)

Figure 4.5 Standard demulsifier bottle.

- Clock timer.
- Personal safety gears (PPE), coverall, H_2S detector, chemical gloves, safety shoes and escape mask
- Prepare the Emulsion breaker samples (demulsifiers) a day before the experiment 2137 T (100 ml), Blend-X (100 ml).

Figure 4.6 Preparing the demulsifiers samples.

Figure 4.7 Preparing 2137-T demulsifier sample.

- Prepare the laboratory/ machines/ tools and materials a day before.

Figure 4.8 Mabruk field's laboratory.

4.4 The Experiment

1- Collect chemical free samples of the crude (located at the plant inlet) 4-5 bottles, 1500 ml each.

Figure 4.9 Collecting fresh crude oil samples.

2- Submerge 1 bottle of fresh crude oil into water bath (60^{O}C, 15 min)

Figure 4.10 Heating up the fresh crude oil samples.

3- Submerge the bottle-test kit (empty) into the water bath (60 ^{O}C, 15 min.)

Figure 4.11 Heating up empty bottle-test kit.

4- Take the fresh sample out of the bath. If you can see easily the water-oil interface and some water is already separated at the bottom, this means, the emulsion is easy to resolve. Therefore, this crude emulsion is easy or moderate type (Allegrucci, personal communication, June, 2012).

Figure 4.12 Fresh crude oil sample after heating up.

5- Shake the sample bottle to free the gas (shake, open the cap repeatedly) until the total dissolved gas is freed.

Figure 4.13 Freeing the gases out of crude oil sample.

6- Shake the sampling bottle then fill the prescription bottles (100 ml mark).

Figure 4.14 Filling the prescription bottles with fresh crude oil.

7- Put the bottles inside the water bath for 2-3 minutes.

Figure 4.15 Heating up the 4 prescription bottles using the water bath.

8- Take the bottles out of water bath and remove the lids.

Figure 4.16 The 4 prescription bottles out of the water bath.

9- Calculate the demulsifier dosage (to be added to each bottle). What is the equivalent amount of 10 ppm (demulsifier) in 100 ml crude oil sample?

$(10\times 10^\wedge-6)/(100\times 10^\wedge-3)=1\times 10^\wedge-4$ Liter

So, 10 ppm = 100 μl.

Therefore, a volume of the stock 2137-T was added to the crude oil sample to achieve the desired demulsifier concentration dose. Table 4.1 provides the volumes of the 2137-T (or Blend-X) added to the crude oil to provide the desired demulsifier concentration dose.

Table 4.1 Equivalent concentrations (μl) in a 100 ml crude oil sample to provide the desired equivalent demulsifier dose concentration in units of ppm.

Equivalent volume per 100 ml crude, μl	Equivalent demulsifier concentration in crude oil sample, ppm
50	5
100	10
150	15
200	20
250	25

10- Add 10 ppm of 2137 T to 3 bottles using the syringes (very quick & keep one bottle blank).

Figure 4.17 Adding 10 ppm dosage of 2137-T to 3 prescription bottles.

11- Lid the bottles and shake them hard (100 times). This simulates the agitation occurring inside the 3-phase separator.

Figure 4.18 Shaking the treated prescription bottles.

12- Put-back the bottles in the water bath (2-3 min.)

Figure 4.19 The treated prescription bottles in the water bath.

13- Take the bottles out of the bath, put them on the table and observe the water dropping speed (start the timer clock immediately). Record the interface level versus time at 1, 3, 5, & 7 minutes.

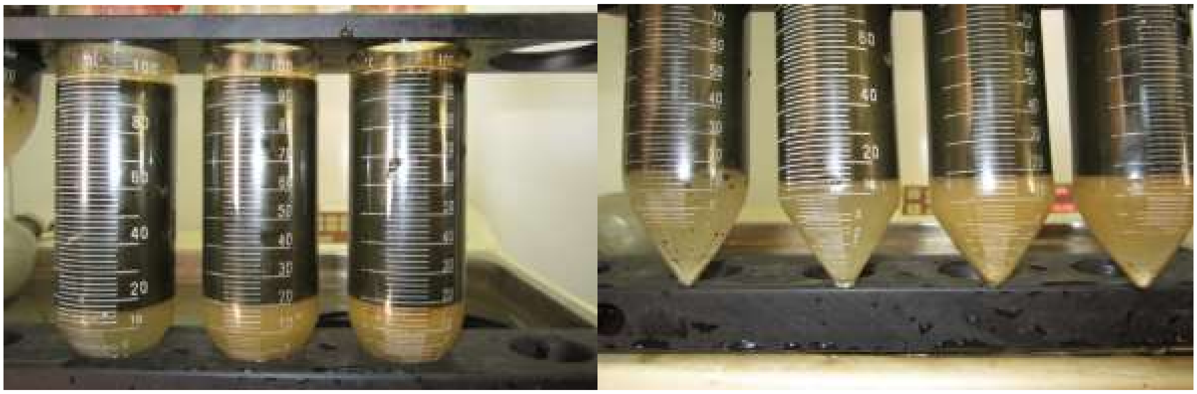


Figure 4.20 The treated prescription bottles out of the water bath for monitoring.

14- Repeat the previous steps from 7 to 15 with different dosages 15 ppm & 20 ppm (2137 T). Record the water dropping speed (interface level versus time).

Table 4.2 Water dropping rates for 2137-T

2137- T Dosage, ppm	1min.	3min.	5min.	7min.
Blank	18*	19**	19.5*	19.5*
10	18*	19	19.5	19.5
15	20	22	22	22
20	19	20	20	20
Notes: *Bad interface and there is no sharp level **Bad interface with oil bubbles in the water layer (1st bottle on the left)				

Figure 4.21 The 3- prescription bottles treated with 10 ppm dosage of 2137-T, after 7 minutes (blank sample-left).

Figure 4.22 The 3-prescription bottles treated with 15 ppm dosage of 2137-T, after 7 minutes (blank sample-left).

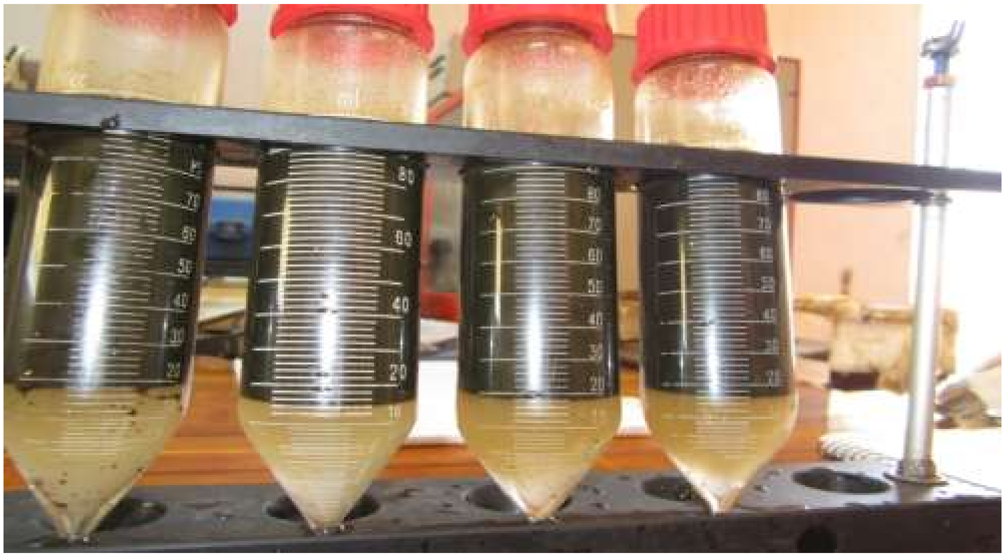


Figure 4.23 The 3-prescription bottles treated with 20 ppm dosage of 2137-T, after 7 minutes (blank sample-left).

15- By repeating the same steps from 7 to 15 with the 2nd demulsifier (Blend-X). The following results were obtained (interface level, volume % versus time, minutes);

Table 4.3 Water dropping rates for Blend-X.

Blend-X Dosage, ppm	1min.	3min.	5min.	7min.
Blank	18**	19**	19.5**	19.5**
10	18*	18.5*	19.5*	19.5*
15	18*	19*	19.5*	19.5*
20	18*	19*	19.5*	19.5*
Notes: *No clear interface & poor water clarity **Bad interface with bubbles (oil in water)				

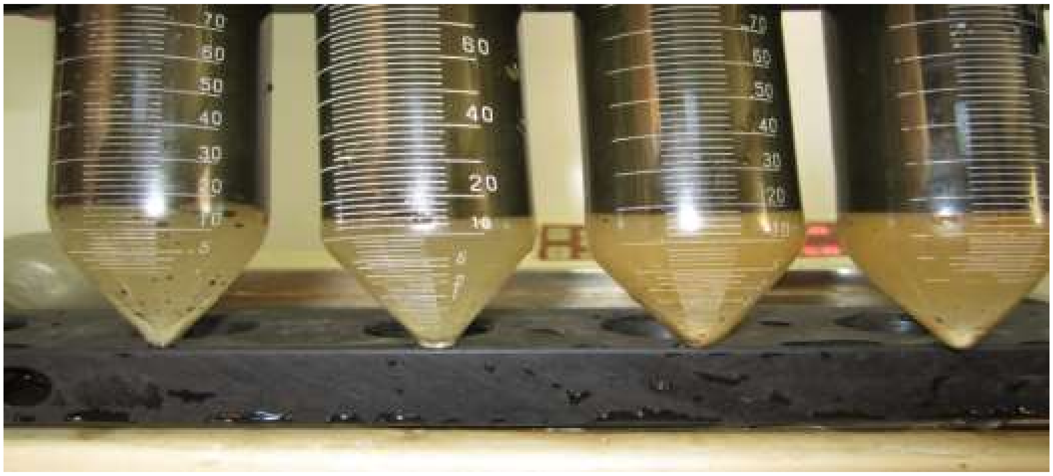


Figure 4.24 3-prescription bottles treated with 10 ppm of Blend-X after 7 minutes (blank sample-left).

Figure 4.25 3-prescription bottles treated with 15 ppm dosage of Blend-X, after 7 minutes (blank sample-left).

16- In a comparison between the two demulsifiers 2137 T and Blend-X, and based on the previous results, as well as some other parameters have been considered during the analysis. Visual methods have been applied to determine the performances of the two different chemicals in terms of the quality of interface, water and oil. The following is my conclusion:

The Emulsion Breaker 2137 T has shown a faster water dropping, much better water clarity, gives a sharp oil-water interface and better separation performance. The water clarity is very important issue when it comes to the oily water processing. The oily water separation is usually the last processing stage in the plant. The oily water separation unit is fed by the produced water gathered from the different separation facilities such as the 3-phase separator and the desalter (dehydrator). At this stage, the new Blend-X could be eliminated and the dosage optimization for 2137 T demulsifier starts here.

17- Referring to 2137 T results, 10 ppm dosage gave good interface but it might be not enough. So, 15 ppm dosage gave more water separated (22 versus 19.5%). The 20 ppm dosage did not give any improvement compared to 15 ppm dosage performance. Therefore, the optimization now is being between 10 and 15 ppm dosages of 2137 T demulsifier.

18- Take 1.5 liters fresh crude oil sample and fill the test bottles (100 ml , 4 bottles)

Figure 4.26 Fresh crude oil samples.

19- Add 10, 12.5, & 20 ppm dosages of 2137 T to the bottles (keep the 1st one left blank).

Figure 4.27 Adding different dosages of 2137-T to fresh crude oil samples (blank sample-left).

20- Put the bottles in the water bath (60^{O}C for 15 min.).

Figure 4.28 Heating up the treated and blank samples.

21- Take the bottles out of the bath then shake them for 100 times.

Figure 4.29 The heated bottles out of the water bath for shaking.

22- Put the bottles back in the bath (2-3min.).

Figure 4.30 After shaking, the bottles again in the water bath for heating.

23- Take the bottles out of the bath and record the results (interface level, volume % versus time, minutes)

Table 4.4 Water dropping rates for (2137-T) at selected concentrations

2137- T Dosage, ppm	1min.	3min.	5min.	7min.
Blank	-	-	-	-
10	18	19	20	20
12.5	20	20	20	20
15	19	20	20	20

The previous results show that there are no important effects on the test response due to the increase of the dosage. So, all the dosages gave the same result after 5 minutes. Hence, the dosage of 15 ppm could be eliminated. Now, the optimization is between 10 & 12.5 ppm dosages. At this stage, it is recommended to test the two remaining bottles (10 & 12.5 ppm) with the centrifuge. Furthermore, 10 ml of oil should be extracted out of the bottle for each bottle by removing the oil at approximately 10 cm. higher than the interface level.

Figure 4.31 Adding 10, 12.5 and 15 ppm dosages of 2137-T to fresh crude oil samples (blank sample-left).

24- Upon extracting 10 ml. (just oil) from the upper part (10 cm above the interface level) from each bottle 10, 12.5 ppm and the blank, pour into the centrifuge con-bottles as shown in Figure 4.33.

Figure 4.32 Sub-sampling the treated bottles (10, and 12.5 ppm. of 2137-T).

25- Put the con-bottles (full of oil) in the centrifuge (use one extra to balance the centrifuge).

Figure 4.33 Centrifuging the sub-samples (10, 12.5 ppm. of 2137-T and blank sample).

After putting inside the centrifuge for 5 min. at (1300 RPM, 60^{O}C), the following results were obtained:

Table 4.5 Water cut results out of the cetrifuge for (2137-T)

2137 T Dosage, ppm	Water percentage %
Blank	9
10	3.5
12.5	3.5

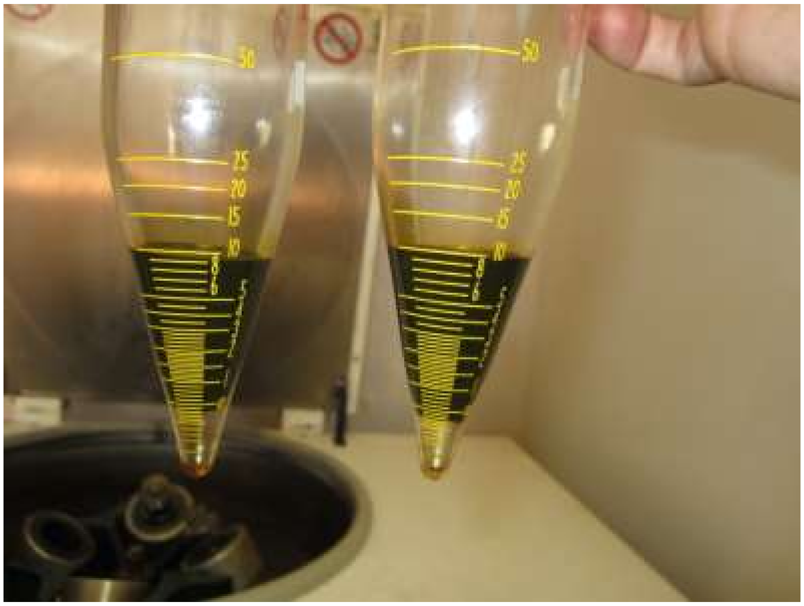


Figure 4.34 The centrifuged sub-samples treated with 2137-T (10 ppm-right versus 12.5 ppm-left).

Both centrifuged sub-samples, 10 and 12.5 ppm show that the water cut resulted is less than 4% as shown in picture 4.36. This result has to be compared to the maximum water cut that the de-salter could handle, which is 6% (inlet) according to the operational philosophy of Mabruk plant (GOSP) (Aubourg, 2005). Therefore, both dosages gave water level less than 4% which is still acceptable as the output of the three-phase separator (D-05) and the inlet water cut entering the de-salter (D06). At the end of the test, a sub-sample of the top oil is taken out of 10 ppm and 12.5 ppm samples and centrifuged. The sub-samples give < 4% BS&W, which corresponds to the expected BS&W going to the de-salter (out of the 3-phase separator).

Chapter 5

Results and Discussions

5.1 Introduction

The chemical contractor company has been asked by the owner to provide other potential chemicals which can provide same or improved separation compared to the candidate demulsifier (2137-T). A new demulsifier product (Blend-X) has been tested and compared to the candidate one. The bottle test was performed on site using the two products. So, the following are the final results obtained.

5.2 Effects of Various Concentrations

Both demulsifiers, the candidate 2137-T and the new potential Blend-X were tested over the same ranges of concentrations 10, 15 and 20 ppm. The interface levels were recorded versus time, where the interface level represents the separated water volume (%).

Table 4.1 Bottle-test results with 2137 T versus Blend-X:

Chemical	**Dosage (ppm)**	**Water-drop (%)**				**Interface thief**		**Composite grind-out**	
		1’	**3’**	**5’**	**7’**	**Water (%)**	**Emuls. (%)**	**Water (%)**	**Emuls. (%)**
Blank	-	18*	19*	19.5*	19.5*	-	-	-	-
2137 T	**10**	**18**	**18.5**	**19.5**	**19.5**	**-**	**-**	**-**	**-**
Blend-X	10	18**	19	19.5	19.5**	-	-	-	-
2137 T	**15**	**20**	**22**	**22**	**22**	**-**	**-**	**-**	**-**
Blend-X	15	18**	19	19.5	19.5**	-	-	-	-
2137 T	**20**	**19**	**20**	**20**	**20**	**-**	**-**	**-**	**-**
Blend-X	20	18**	19	19.5	19.5**	-	-	-	-

*Bad interface level with bubbles & no sharp interface level

**Poor water clarity, bubbles & no clear interface.

Notes about Table 4.1:

- The interface thief was taken just for 10 ppm, 12.5 ppm & the blank bottles.
- No composite grind-out test was needed (Allegrucci, personal communication, June, 2012).

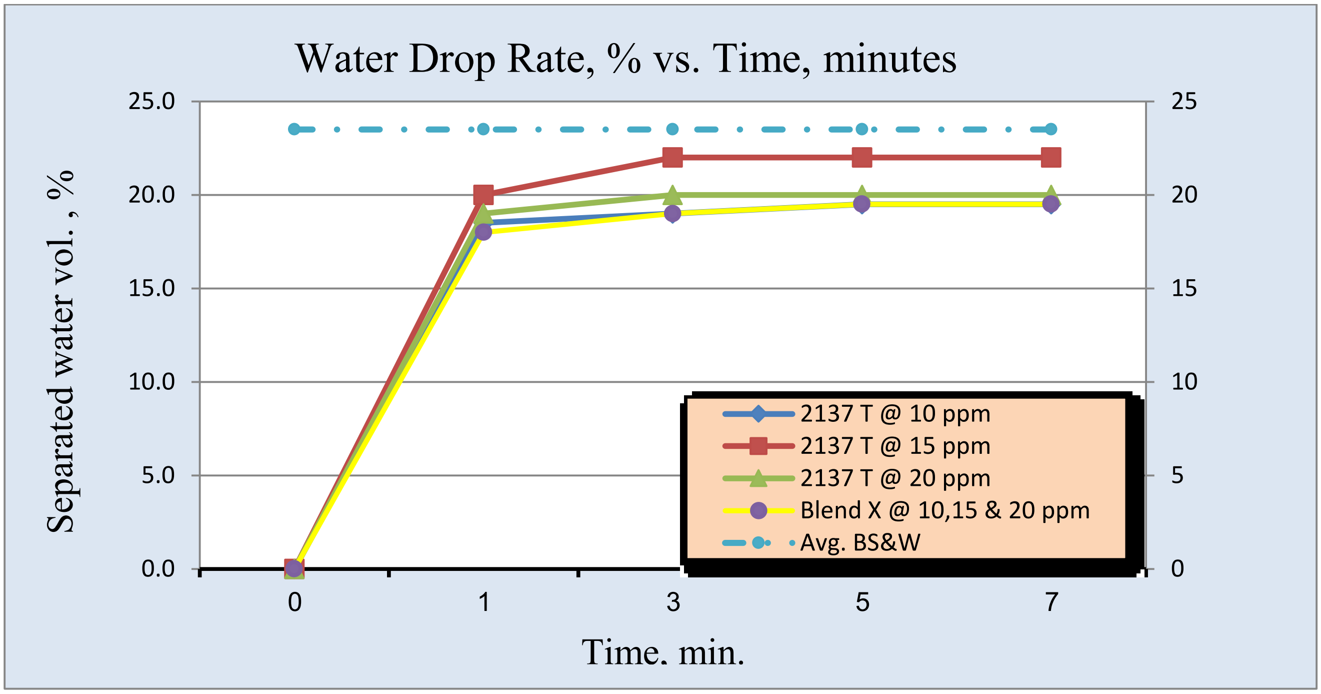


Figure 5.1 Separated water volumes (ml) versus time at different demulsifiers and dosages.

At the bottle-testing day, 23.38 % average BS& W (Base Sediments & Water) was recorded for the fresh crude sample. The rate of separation between oil and water has been determined on site, focusing on the attention on the volumes measured after the first minutes of the bottle tests. The choice has been to evaluate the water separation rate after 4 minutes from the beginning of the analysis. The slope of the initial points of the curves in Figure 5.1 is linked to the water separation rate.

5.3 Demulsifiers Screening Process

The chemical performance achieved at the laboratory using the bottle-test was compared to the actual performance of the 3-phase separator. The performance of 3-phase separator is calculated based on measured water cut of the inlet and the outlet streams. The results obtained from the bottle test are representing the simulated performance of 3-phase separator. Some other parameters have been considered during the analysis of the bottle test in order to evaluate the two different demulsifiers. At the bottle test, the interface rebuilding rate has been measured by volume readings. Visual methods have been applied to determine the performances of the different demulsifiers in terms of the quality of interface, water and oil.

5.3.1 3-Phase Separator Actual Performance

The performance of the 3-phase separator is affected by several factors, where each factor should be optimized in order to achieve the maximum performance as designed. These factors are; vessel design, temperature, flow rate, oil level, oil-water interface level, retention time and demulsifier (dosage/type). Given the inlet and outlet BS&W of a separator, it is possible to calculate the separator efficiency.

Separator efficiency (actual) = ((Inlet BS&W - Outlet BS&W actual) / (Inlet BS&W) x 100%

Specifically, for the bottle-test date, June the 22nd, 2012, where 2137-T was injected at 8 ppm concentration, here are the BS&W values:

Inlet BS&W = 23.38 %
Outlet BS&W (actual) = 2.8 %

Separator efficiency = ((23.38-2.8) / 23.38) x 100

= 88.02 %

5.3.2 3-Phase Separator Simulated Performance

Referring to Table (4.4), the separated water volumes are equivalent to BS&W values of the 3-phase separator outlet. The following are the results of the optimized dosages:

2137 T Dosage, ppm	1min.	3min.	5min.	7min.
Blank	-	-	-	
10	18	19	20	20
12.5	20	20	20	20
15	19	20	20	20

The separated water volume after 5 minutes for 10 ppm dosage (T-2137) is considered;

BS&W remaining (centrifuged) =3.5 %

Inlet BS&W = 23.38 %

The outlet BS&W obtained by using bottle-test (simulated @10ppm) = 3.5%

Separator efficiency (simulated) = ((Inlet BS&W - Outlet BS&W simulated) / (Inlet BS&W) x 100%

Separator efficiency (simulated) = ((23.38 -3.5) / 23.38) x100

= 85.03 %

In a comparison between the two efficiencies, the actual (88.02%) and the simulated (85.03%), there is about 3% difference. The reason behind this could be because of an error in measuring the inlet BS&W or the actual outlet BS&W. At this stage, I would argue that there is a margin of 5-10 % error factor in calculating the separator efficiency should be taken into consideration.

The comparison between the two efficiencies should be based on the same dosing rates however, at the bottle testing day, regulating the actual dosing rate of 2137-T from 8 to 10 ppm was not possible. Such a change in the injection rate needs to be approved by the operation department prior to implement, which was not possible at that time. Therefore, the comparison between the actual and the simulated efficiency might not be totally logic.

5.3.3 Visual Methods

Four visual parameters have been considered to evaluate the two tested demulsifiers, 2137-T versus Blend-X. These parameters are volume of separated water, water separation rate, sharp interface and quality of separated water (oil-in-water). A rank of 0-6 was coupled to each parameter, where the higher number, the better performance. All the main parameters involved in the choice of a demulsifier, have been linked together building the 4 axes graphic as shown in the Figure 5.2. Each parameter is described by a point on the axis, from 0 to 6. Then, these points were linked to build a polygon. Polygons with a higher surface correspond to a chemical with a better overall behavior. The following is a rank of the four visual parameters ranging from 0 to 6 for each demulsifier (Allegrucci, personal communication, June, 2012):

For 2137-T;

T1	6
T2	6
T3	4
T4	4

T1 = water separation rate
T2 = volume of separated water
T3 = quality of water
T4 = Interface rebuilding rate

For Blend-X;

X1	3
X2	4
X3	1
X4	3

X1 = water separation rate
X2 = volume of separated water
X3 = quality of water
X4 = Interface rebuilding rate

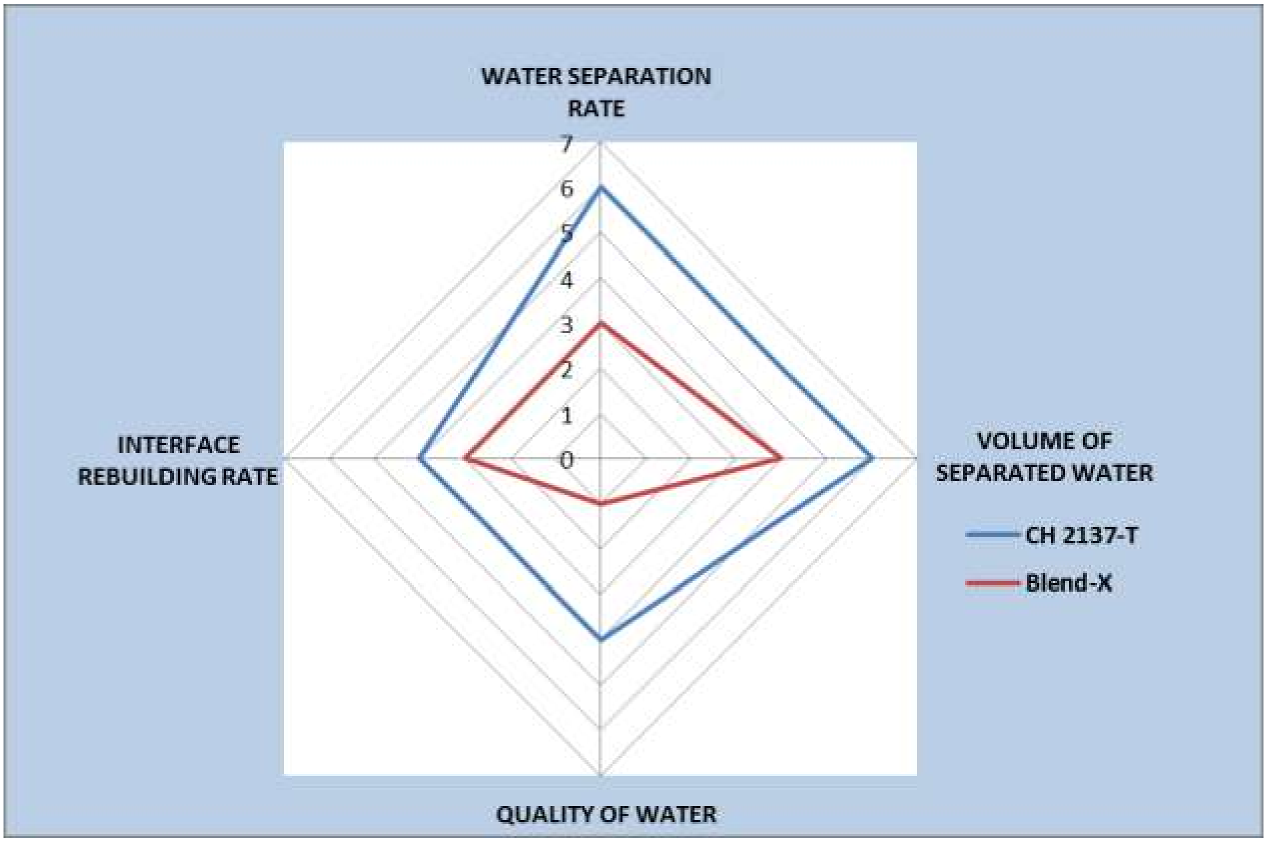


Figure 5.2 Polygons of the main visual parameters for both demulsifiers (2137-T and Blend-X).

Referring to the previous analyses, it is possibly to argue that, the demulsifier **2137-T** gives very good performance giving: faster water drop, more efficient dehydration, much better water clarity (oily water quality) and sharp oil-water interface compared to Blend-X demulsifier. Therefore, 2137-T is still recommended for Mabruk's water-in-oil emulsion treatment.

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

In conclusion, the bottle-test has been carried out on two kinds of demulsifiers, the new demusifier Blend-X against the candidate 2137-T. Based on the results obtained, it is confirmed that the demulsifier 2137 T is working and giving very good interface quality, fast water dropping and very good water clarity. At the laboratory dosage 10 ppm, there is 3.5% residual of water, which is good for the de-salter (dehydrator) that there is no fresh water added. If a decision is made to inject fresh water, it is possible to increase the dosage between 10 and 12.5 ppm, which is good to be injected at GOSP plant inlet.

The candidate 2137-T was validated as the most suitable demulsifier using a bottle-test, and the minimum ratio has been determined for Mabruk treatment plant which is 10 ppm (total liquid). Upon completing the bottle-test, the field trial might be started by injecting the selected demulsifier into the plant inlet stream, where the optimum dosage would be possibly determined.

6.2 Recommendation for Future Study

The field trails are usually performed during the start-up of oil field however it is recommended to implement bottle testing and field trials once every 2-3 years. In case, there is a major change in crude oil properties or any substantive operational parameter such as, the retention time in 3-phase separator, bottle testing and field trials are highly recommended (Ben Mahmoud, personal communication, June, 2012). Further, increasing the demulsifier dosage might be needed or sometimes even replacing the demulsifier by another potential demulsifier.

As soon as the bottle-test is completed, the field trial could be possibly started. The field trials usually take up to 2-4 weeks, keeping in mind that the starting injection rate should be a bit lower than the lowest bottle test treating ratio (10 ppm). In the light of this, in order to ensure a gradual decrease and system stability throughout the plant test, it is recommended to reduce the chemical injection rate by about 10% each time and check the system stability simultaneously. Continue reducing the chemical rate following this procedure until the minimum amount of the chemical required has been determined (Shirley, 2008). For Mabruk oil field, it is recommended to tailor different demulsifier for each reservoir whenever that is possible. In addition, the injection points could possibly be relocated at the satellites instead of the plant inlet. Extensive chemical injection facilities could be provided at each oil wellhead and GOSP process train that will probably overcome any potential emulsion problem in the future.

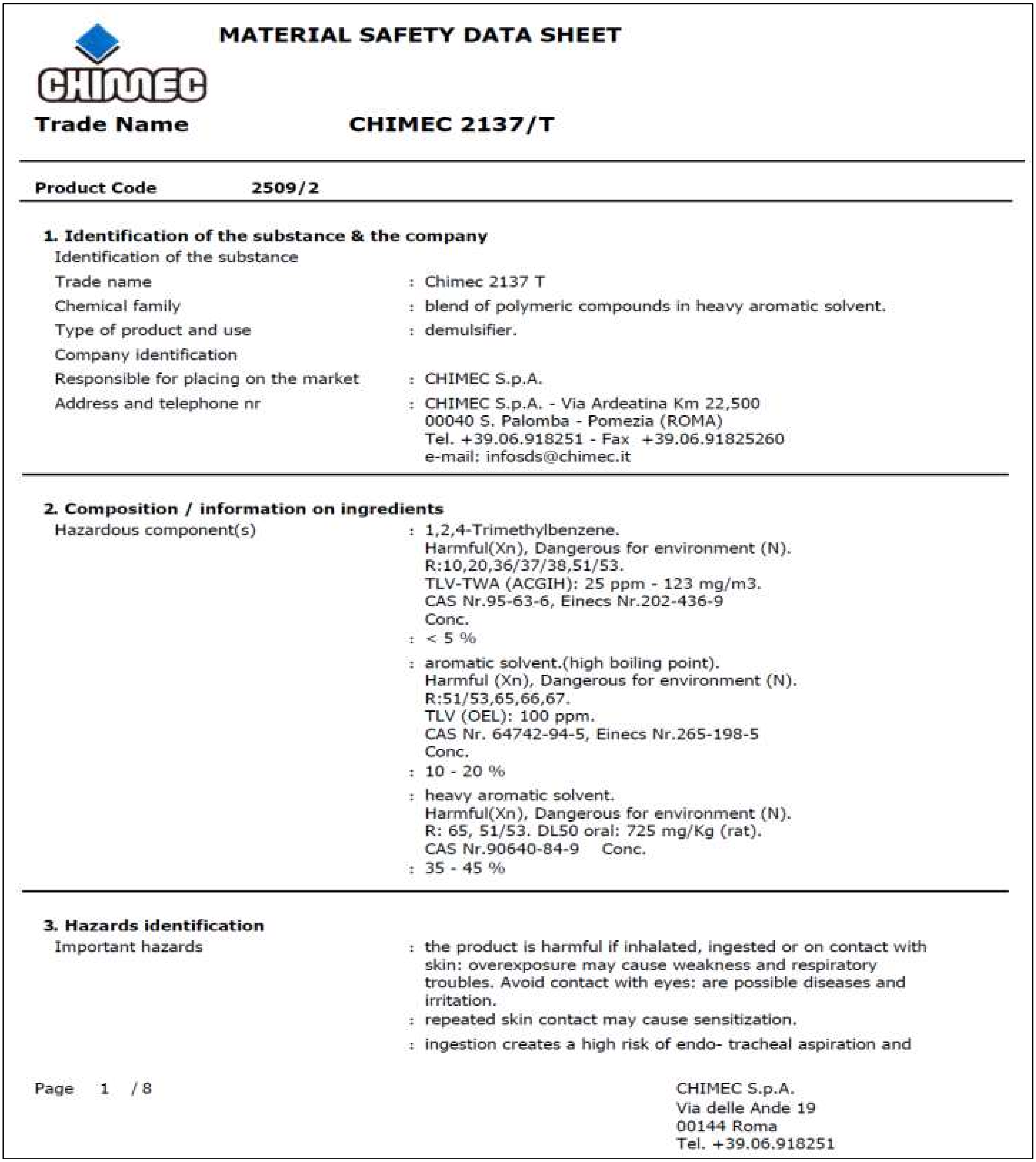
There were some challenges encountered my thesis approach, such as the confidential nature of some information and the availability of oily-water analyzer instrument. Firstly, the confidential nature of the information related to demulsifier blend(s) formulation(s) was one of the most serious challenges encountered the experimental work of this thesis. To overcome this challenge, there are two ways to know the unknown formulation(s), either by using certain software to prepare such a blend(s) or by using chemical analysis to analyze these unknown blends, e.g. by using a gas-chromatography-mass spectrometry (GC-MS). GC-MS analysis of the demulsifier would have provided further insight into its chemical composition which would have enriched the thesis data analysis, discussion and conclusions.

Secondly, the oil in water analyzer used in Mabruk field was Horiba, Model (OCMA-310), Oil Content Analyzer which is an infra-red absorbance analyzer. This analyzer used to measure the free and separable oil content existing in the produced oily water. The results obtained compared to the standard value of the allowed oil in water according to the Libyan environmental regulations. At the bottle-test day, Horiba instrument was out of service due to a technical problem. Further, the calibration trial for this machine was not success at that time. As a result, the oily water resulted from bottle-testing the Blend-X was not tested by Horiba analyzer. For further studies, it is highly recommended to prepare and calibrate Horiba analyzer days before the planned bottle-test day.

Appendix A

Material Safety Data Sheet

Material Safety Data Sheet (MSDS) for Demulsifier CH 2137-T



MATERIAL SAFETY DATA SHEET

Trade Name **CHIMEC 2137/T**

Product Code **2509/2**

1. Identification of the substance & the company

Identification of the substance

Trade name : Chimec 2137 T

Chemical family : blend of polymeric compounds in heavy aromatic solvent.

Type of product and use : demulsifier.

Company identification

Responsible for placing on the market : CHIMEC S.p.A.

Address and telephone nr : CHIMEC S.p.A. - Via Ardeatina Km 22,500
00040 S. Palomba - Pomezia (ROMA)
Tel. +39.06.918251 - Fax +39.06.91825260
e-mail: infosds@chimec.it

2. Composition / information on ingredients

Hazardous component(s) : 1,2,4-Trimethylbenzene.
Harmful(Xn), Dangerous for environment (N).
R:10,20,36/37/38,51/53.
TLV-TWA (ACGIH): 25 ppm - 123 mg/m3.
CAS Nr.95-63-6, Einecs Nr.202-436-9
Conc.
: < 5 %

: aromatic solvent.(high boiling point).
Harmful (Xn), Dangerous for environment (N).
R:51/53,65,66,67.
TLV (OEL): 100 ppm.
CAS Nr. 64742-94-5, Einecs Nr.265-198-5
Conc.
: 10 - 20 %

: heavy aromatic solvent.
Harmful(Xn), Dangerous for environment (N).
R: 65, 51/53. DL50 oral: 725 mg/Kg (rat).
CAS Nr.90640-84-9 Conc.
: 35 - 45 %

3. Hazards identification

Important hazards : the product is harmful if inhaled, ingested or on contact with skin: overexposure may cause weakness and respiratory troubles. Avoid contact with eyes: are possible diseases and irritation.

: repeated skin contact may cause sensitization.

: ingestion creates a high risk of endo- tracheal aspiration and

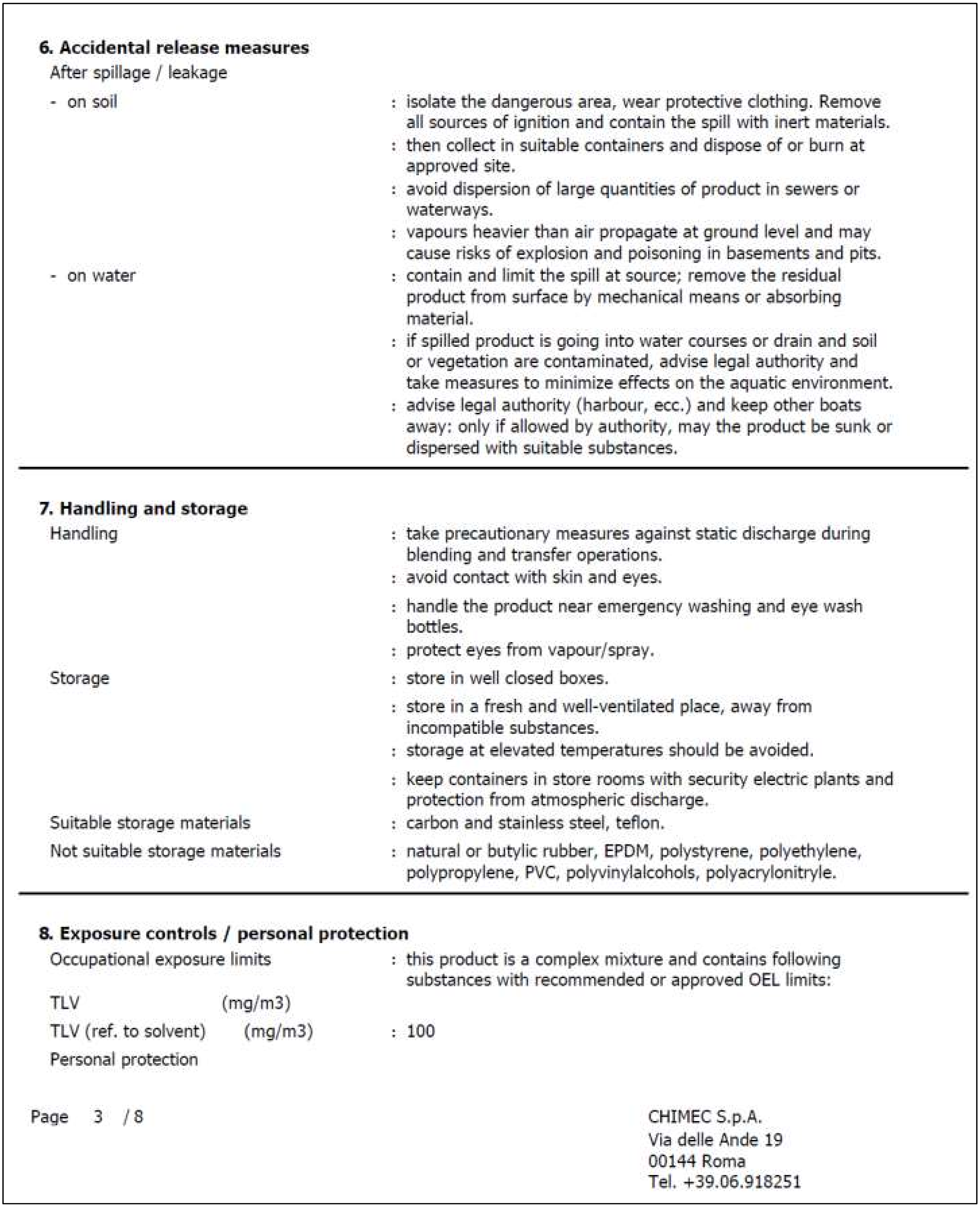
	when product drops reaching the lungs, cause chemical pneumonia, pulmonary edema and hemorrhage.
	: the product is toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

4. First-aid measures

First aid	
- Inhalation	: remove the exposed person from contaminated area; keep warm and in fresh air. : if not breathing, give artificial respiration and seek immediate medical attention.
- Skin contact	: take off immediately all contaminated clothing. : wash thoroughly with soapy water. : if irritation persists, seek medical advice.
- Eye contact	: wash with plenty of water,for at least 15 minutes, keeping the lids well open. : seek medical advice.
- Ingestion	: do not induce vomiting. : rinse the mouth with clean water; give plenty of water, seek medical advice. : do not give anything by mouth to an unconscious or convulsing person. : if aspiration is suspected (during spontaneous vomiting,for instance),seek medical advice urgently.

5. Fire - fighting measures

Extinguishing media	
- Suitable	: carbon dioxide, dry chemicals, foam, water spray (or fog).
- Not suitable	: water jets.
Fire/explosion hazards	: avoid static build up; must be earthed. : avoid vapours contact with sources of flame (open flames, sparks, very hot surface).
Fire-fighting procedures	: fire fighters and others who may be exposed to the products of combustion, should be equipped with NIOSH approved positive pressure self-contained breathing apparatus and full protective clothing. : when exposed to flames or high temperatures encountered during fire conditions, sealed containers may rupture because of the build up of internal pressure: cool containers with water and remove. : the contaminated water used for extinguishing must be disposed of in accordance with local legislation.



6. Accidental release measures

After spillage / leakage

- on soil : isolate the dangerous area, wear protective clothing. Remove all sources of ignition and contain the spill with inert materials.
: then collect in suitable containers and dispose of or burn at approved site.
: avoid dispersion of large quantities of product in sewers or waterways.
: vapours heavier than air propagate at ground level and may cause risks of explosion and poisoning in basements and pits.

- on water : contain and limit the spill at source; remove the residual product from surface by mechanical means or absorbing material.
: if spilled product is going into water courses or drain and soil or vegetation are contaminated, advise legal authority and take measures to minimize effects on the aquatic environment.
: advise legal authority (harbour, ecc.) and keep other boats away: only if allowed by authority, may the product be sunk or dispersed with suitable substances.

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7. Handling and storage

Handling : take precautionary measures against static discharge during blending and transfer operations.
: avoid contact with skin and eyes.
: handle the product near emergency washing and eye wash bottles.
: protect eyes from vapour/spray.

Storage : store in well closed boxes.
: store in a fresh and well-ventilated place, away from incompatible substances.
: storage at elevated temperatures should be avoided.
: keep containers in store rooms with security electric plants and protection from atmospheric discharge.

Suitable storage materials : carbon and stainless steel, teflon.

Not suitable storage materials : natural or butylic rubber, EPDM, polystyrene, polyethylene, polypropylene, PVC, polyvinylalcohols, polyacrylonitryle.

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8. Exposure controls / personal protection

Occupational exposure limits : this product is a complex mixture and contains following substances with recommended or approved OEL limits:

TLV (mg/m3)

TLV (ref. to solvent) (mg/m3) : 100

Personal protection

- Respiratory protection : a localized aspiration is necessary if the warmed product forms vapours.
  : none under normal conditions.
  : ensure good ventilation.
  : in closed premises or in case of insufficient ventilation, use protective mask with filter for organic vapours.
- Skin protection : protective gloves made of nitrile or PVA, approved for protection against chemical substances (EC seal - Directives 89/686 and 93/68).
- Eye protection : goggles or face shield with safety glasses.
- Others : appropriated protective clothing.
  : eyewash bottle with clean water.

Industrial hygiene : keep away from sources of ignition - no smoking.
: ventilate thoroughly the working place.
: do not eat or drink when handling this product.
: remove all contaminated clothing and remove protective clothing when the work is completed.
: handle in accordance with good industrial hygiene and safety procedures.

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9. Physical and chemical properties

Appearance
Physical state at 20°C : liquid.
Colour : brown.
Odour : characteristic.
Change in physical state -760 mm Hg
- Freezing point (°C) : n.d.
- Boiling point (°C) : ca. 180 °C
- Pour point (ASTM D97) (°C) : < - 12

Density at 20°C (gr/cm3) : 0.98 ± 0.02
Viscosity at 20°C (cP) : < 100
Solubility in water (% weight) : insoluble.
Soluble in : aromatic and aliphatic hydrocarbons.
: organic solvents.
pH value in distilled water : n.d.
Flash point (ASTM D 93) (°C) : > 61
Auto-ignition temperature (°C) : > 450
Explosion limits
- Lower (% vol) : 0.6

- Upper	(% vol)	: 7.0
Thermal decomposition	(°C)	: stable if utilized under normal conditions.
Further information		: The information reported in this Material Safety Data Sheet are not to be considered as a guarantee on any specific properties of the product.

10. Stability and reactivity

Conditions to avoid	: the product is incompatible with concentrated acids and strong oxidizing agents.
Substances to avoid	: avoid contact with strong oxidizers.
On combustion forms	: may release oxides of carbon and other toxic gases and vapours.
Hazardous decomposition products	: no hazardous decomposition products.
Hazardous reactions	: none to our knowledge.

11. Toxicological information

Rat oral LD50	(mg/kg)	
Inhalation		: vapour overexposure: irritation of eyes, of nose and threat, headache, dizziness and drowsiness. : repeated and prolonged exposure: possible depressant effect on the central nervous system. : may cause anesthetic and/or narcotic effects.
Dermal toxicity		: the vapours may cause irritation.
Ingestion		: ingestion creates a high risk of aspiration and subsequent chemical pneumonia.
Corrosivity / Irritating capacity		
- skin		: direct contact may cause irritation and dermatitis, produced by its defatting effect.
- eyes		: direct contact: medium irritation, without corneal damage.
Sensitization		: repeated skin contact may cause sensitization.
Carcinogenicity		: this product contains an aromatic solvent not listed in XXX Adaptation to Technical Progress (ATP) of Dangerous Substances Directive 67/548 EEC, note H. benzene < 1 mg/Kg alpha-benzopyrene < 5 mg/Kg.
Mutagenicity		: no evidence of this effect is shown.
Teragenicity		: no evidence of this effect is shown.

12. Ecological information

Information on ecological effects	: utilize in accordance with good working practice and avoid to disperse the product in the environment. : the product is toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Mobility : with a correct disposal in biological treatment system, are not expected problems for the degradation activity of activated sludge.

96 Hour-LC50-fish (mg/l) : n.d.

Persistence and degradability : the product is rapidly eliminated from the aquatic medium through irreversible adsorption onto suspended matter and dissolved organics.

Biodegradation (%) : this product is not water-soluble and is therefore slowly degraded by micro- organisms.

Bioaccumulative potential : the product has been shown to present no bioaccumulation hazard in aquatic plants or fish.

WGK class (Germany) : 2 - hazardous.

AOX : the product does not contain organic halons.

13. Disposal considerations

Disposal : dispose in a safe manner in accordance with local/national regulations.

: do not dispose in a sink, drain or in the immediate environment.

: of the methods of disposal currently available, it is recommended that an alternative be selected according to the following order of preference, based upon environmental acceptability:

: 1 - recycle or rework if at all feasible;
2 - incinerate at an authorized facility;
3 - treat at an acceptable waste treatment facility.

Disposal of packaging : dirty containers of product must be recycled or disposed by an authorized facility.

: empty containers can retain product residues and may be hazardous: do not use heat, sparks, open flames, or cigarettes on near empty container.

14. Transportation information

- ADR/RID/IATA

Proper shipping name : Environmentally hazardous substances, liquid, n.o.s.

ADR Class : 9 - Miscellaneous dangerous substances and articles

Packaging group : III

Risk Label(s) : 9 - Dangers other than those covered by the other classes.

Subsidiary Risk Label(s) : Marine pollutant (P).

Danger identification number (upper) : 90

Substance identification number (lower) : 3082

Tremcard type : P

UN Number. : 3082

IMO-IMDG

IMO class : 9 - Miscellaneous dangerous substances and articles

Risk Label : 9 - Dangers other than those covered by the other classes.

Subsidiary Risk Label : Marine pollutant (P).

Proper shipping name : Environmentally hazardous substances, liquid, n.o.s.

Contains : heavy aromatic solvent

Packaging group : III

Emergency Schedule (EmS) : F-A, S-F

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15. Regulatory information

UE

- Symbol(s) : Harmful:Xn
  : Dangerous for environment: N
- Contains : heavy aromatic solvent
- R Phrase(s) : R 51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
  : R 20/21 :Harmful by inhalation and in contact with skin.
  : R 43 :May cause sensitization by skin contact.
  : R 65 :Harmful: may cause lung damage if swallowed.
  : R 66: Repeated exposure may cause skin dryness or cracking
  : R 67: Vapours may cause sleepiness or giddiness
- S Phrase(s) : S 23 :Do not breathe gas/fumes/vapour/ spray
  : S 24 :Avoid contact with skin.
  : S 62 : if swallowed do not induce vomiting: seek medical advice immediately and show this container or label.
  : S 60: This material and its container must be disposed of as hazardous waste.

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16. Other information

Further information : R 50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

: R 10 :Flammable.

: R 20 :Harmful by inhalation.

: R 36/37/38 :Irritating to eyes, respiratory system and skin.

: R 20/21 :Harmful by inhalation and in contact with skin.

: R 43 :May cause sensitization by skin contact.

: R 51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

: R 65 :Harmful: may cause lung damage if swallowed.

	: R 66: Repeated exposure may cause skin dryness or cracking
	: R 67: Vapours may cause sleepiness or giddiness
Sources of key data used	: N.Irving SAX - Dangerous properties of Industrial Materials (Sixth edition) - Edited by Van Nostrand Reinhold Company - 1984
	: TLV - Threshold Limit Values for Chemical Substances in Work Environment - Adopted by ACGIH - 2000
	: A.D.R. - European Agreement concerning the international carriage of Dangerous Goods by Road - United Nation Publication
	: Karel VERSCHUEREN - Handbook of Environmental data on organic chemicals - 1977
Information for medical staff	
Revised chapters	: The chapters indicated by " ********** " have been modified with the present version of this MSDS.

Issue Date: 03/07/2007

Preparata da: C.SCALAMANDRE
This MSDS complies with Directives 91/155/EC, 93/112/EC, 2001/58/EC, 2001/59/EC, 2001/60/EC and their amendments.

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Appendix B

Mabruk/Dahra/Garian Process Train Design Cases

Table 1: Mabruk Process Train Design Cases

Stream name		Feedstock	Feedstock	Feedstock
Description		Year 2005	Year 2013	Year 2027
Stream phase		Liquid	Liquid	Liquid
Total stream				
Temperature ****	°C	56	56	56
Pressure	bar g	12,0**	12,0**	12,0**
Total Molar Rate	kmol/h	5 960	9 802	11 207
Total Mass Rate	kg/h	236 021	266 125	253 159
Molecular Weight		39,6	27,2	22,6
Enthalpy	M*kcal/h	8,157	11,375	12,152
Total Molar Comp, Percents				
H_2O		88,34	95,05	97,51
N_2		0,04	0,02	0,01
CO_2		0,01	0,01	0,00
H_2S		0,05***	0,03***	0,02***
C1		0,26	0,11	0,06
C2		0,20	0,08	0,04
C3		0,38	0,16	0,08
iC4		0,15	0,07	0,03
nC4		0,41	0,17	0,09
iC5		0,31	0,13	0,07
nC5		0,31	0,13	0,07
C6		0,52	0,22	0,11
C7		0,80	0,34	0,17
C8		0,97	0,41	0,21
C9		0,72	0,31	0,15
C10		0,66	0,28	0,14
C11		0,53	0,22	0,11
C12		0,46	0,20	0,10
C13		0,48	0,20	0,10
C14		0,42	0,18	0,09
C15		0,40	0,17	0,08
C16		0,31	0,13	0,07
C17		0,29	0,12	0,06
C18		0,30	0,13	0,06
C19		0,27	0,11	0,06
C20+		2,41	1,02	0,51

Continued Table-1,

Vapor				
Molar Rate	kmol/h	n/a	n/a	n/a
Mass Rate	kg/h	n/a	n/a	n/a
Volumetric Rate	ACTm^3/h	n/a	n/a	n/a
Molecular Weight		n/a	n/a	n/a
Mass Heat Capacity	kcal/kg.°C	n/a	n/a	n/a
Cp/Cv		n/a	n/a	n/a
Density	kg/ACTm^3	n/a	n/a	n/a
Thermal conductivity	kcal/h.m.°C	n/a	n/a	n/a
Viscosity	cP	n/a	n/a	n/a
Z factor (from density)		n/a	n/a	n/a
Liquid				
Molar Rate	kmol/h	5 960	9 802	11 207
Mass Rate	kg/h	236 021	266 125	253 159
Volumetric Rate	ACTm^3/h	273,0	293,4	270,3
Molecular Weight		39,6	27,2	22,6
Mass Heat Capacity	kcal/kg.°C	0,69	0,81	0,89
Density	kg/ACTm^3	865	907	936
Thermal conductivity	kcal/h.m.°C	0,113	0,142	0,179
Viscosity *	cP	2,7	2,7	2,7
Surface tension	dynes/cm	62,1	65,0	66,0

Notice:

*Viscosity corresponds to oil only

** Fluid data given at 12 barg for liquid stream – Operating pressure at inlet of GOSP will be controlled at 4 barg and therefore the stream will be partially vaporized.

*** The global H2S content in the production stream is such that the free water phase H2S content reaches 200 mg/l at the reservoir conditions (1200 psia & 135°F).

**** The inlet temperature refers to summer conditions.

Table 2: Dahra / Garian Process Train Design Cases

Stream Name		**Feedstock**	**Feedstock**	**Feedstock**
Description		Year 2004/2005	Year 2010	Year 2026
Phase		Mixed	Mixed	Mixed
Total Stream Properties				
Temperature ***	C	68.4	66.9	56.8
Pressure	BAR(GA)	8.5	8.5	8.5
Molar Rate	KG-MOL/HR	7322.112	10276.8	7568.900
Mass Rate	KG/HR	259670.6	220553.7	146966.1
Molecular Weight		35.46	21.46	19.42
Enthalpy	M*KCAL/HR	12.052	13.191	7.934
Vapour Fraction		0.0000	0.0000	0.0000
Total Molar Composition, percent				
H2O		89.2137	97.8477	99.0979
N2		0.0299	0.0059	0.0024
CO2		0.0854	0.0168	0.0068
H2S		0.0345**	0.0153**	0.0125**
C1		0.1614	0.0338	0.0164
C2		0.1080	0.0227	0.0113
C3		0.3363	0.0709	0.0352
IC4		0.1049	0.0220	0.0108
NC4		0.2056	0.0433	0.0215
IC5		0.1910	0.0392	0.0181
NC5		0.1653	0.0341	0.0160
C6		0.1487	0.0314	0.0156
C7		0.2084	0.0439	0.0219
C8		0.2101	0.0443	0.0220
C9		0.1465	0.0309	0.0154
C10		0.1115	0.0235	0.0117
C11		0.0655	0.0138	0.0069
C12		0.0518	0.0109	0.0054
C13		0.0475	0.0100	0.0050
C14		0.0314	0.0066	0.0033
C15		0.0266	0.0056	0.0028
C16		0.0177	0.0037	0.0019
C17		0.0158	0.0033	0.0017
C18		0.0127	0.0027	0.0013
C19		0.0098	0.0021	0.0010
C20+ (MABRUK)				
CNDAH		0.1530	0.0323	0.0160
GC6		0.3627	0.0708	0.0277
GC7		0.6084	0.1188	0.0465
GC8		0.9326	0.1822	0.0712
GC9		0.7805	0.1524	0.0596
GC10		0.6694	0.1307	0.0511
GC11		0.5474	0.1069	0.0418
GC12+		4.2060	0.8215	0.3213

Continued Table-2,

Vapor Phase Properties				
Molar Rate	KG-MOL/HR	n/a	n/a	n/a
Mass Rate	KG/HR	n/a	n/a	n/a
Actual Volume Rate	M3/HR	n/a	n/a	n/a
NPT Vapor Rate	NM3/HR	n/a	n/a	n/a
Specific Gravity (Air=1.0)		n/a	n/a	n/a
Molecular Weight		28.017	28.017	28.502
Enthalpy	KCAL/KG	n/a	n/a	n/a
CP	KCAL/KG-C	n/a	n/a	n/a
Actual Density	KG/M3	n/a	n/a	n/a
Thermal Conductivity	KCAL/HR-M-C	n/a	n/a	n/a
Viscosity	CP	n/a	n/a	n/a
Vapor Z (from K-value)				
Liquid Phase Properties				
Molar Rate	KG-MOL/HR	7322.112	10276.813	7568.900
Mass Rate	KG/HR	259670.6	220553.7	146966.1
Actual Volume Rate	M3/HR	304.333	236.029	152.500
Std. Liquid Rate	M3/HR	293.684	230.266	150.067
Std. Specific Gravity		0.8851	0.9588	0.9803
Molecular Weight		35.464	21.461	19.417
Enthalpy	KCAL/KG	46.413	59.810	53.988
CP	KCAL/KG-C	0.728	0.911	0.958
Actual Density	KG/M3	853.246	934.434	963.711
Surface Tension	DYNE/CM	60.2921	64.3588	66.5803
Thermal Conductivity	KCAL/HR-M-C	0.10311	0.17509	0.25019
Viscosity *	CP	1.11516	1.16406	1.58452
H2S Content	ppmw	331.4986	242.9322	219.36821

Notice:

G: stands for Garian Reservoir, NDAH: stands for North Dahra Reservoir

*Viscosity corresponds to oil only

** The global H2S content in the production stream is such that the free water phase H2S content reaches 200 mg/l at the reservoir condition.

*** The inlet temperature refers to summer conditions.

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