T.R.
YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING DEPARTMENT

STUDY OF EFFECT OF SALT CONTENT OVER ESTABLISHMENT OF CHEMICAL CORROSION MECHANISM IN KHURMALA CRUDE OIL. CASE: DESALTER UNIT AT CPS (CENTRAL PROCESS SECTION)

M. Sc. THESIS

PREPARED BY: Sherko Yousif M.AMEEN
SUPERVISOR : Prof. Dr. Nahit AKTAŞ

VAN-2017

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled "**STUDY OF EFFECT OF SALT CONTENT OVER ESTABLISHMENT OF CHEMICAL CORROSION MECHANISM IN KHURMALA CRUDE OIL. CASE: DESALTER UNIT AT CPS (CENTRAL PROCESS SECTION)**" presented by Sherko Yousif M.AMEEN under supervision of Prof. Dr. Nahit AKTAŞ in the department of Chemical Engineering has been accepted as a M. Sc. / Ph.D. thesis according to Legislations of Graduate Higher Education on 17.../03./2017. with unanimity / majority of votes members of jury.

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Member:Assist. Prof. Dr. Özgül GÖK Signature:

This thesis has been approved by the committee of The Institute of Natural and Applied Science on 24.../03./2017. with decision number 2017./16-I

Prof. Dr. Suat ŞENSOY
Enstitü Müdürü

Signature
....
Director of Institute

THESIS STATEMENT

It is stated that all the information in the thesis is presented in the frame of ethical behavior and academic rules and also in this study prepared in accordance with the thesis writing rules, all references and sources of information that do not belong to me are fully cited and marked at references.

Signature

Sherko Yousif M.AMEEN

ABSTRACT

STUDY OF EFFECT OF SALT CONTENT OVER ESTABLISHMENT OF CHEMICAL CORROSION MECHANISM IN KHURMALA CRUDE OIL. CASE: DESALTER UNIT AT CPS (CENTRAL PROCESS SECTION)

M.AMEEN, Sherko Yousif
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Supervisor: Prof. Dr. Nahit AKTAŞ
March 2017, 67 pages

In the present study experimental nature of field level evaluation design have the object to study the effect of salt content over establishment of chemical corrosion over metallurgical pipelines ocurring in desalter units at CPS-KAR installations. The purpose of this study was to discover the right mechanism of corrosion based on in/out method. The applied methodology had four parts: a) Diagnosis of actual situation and determining the corrosion mechanism, b) determine the concentration of salts in different conditions of affection over pipelines, c) develop the right process to manage corrosion and disminish salt content, d) evaluation of effect and present a proposal to the operational manager staff. After experimental determinations the mains results were: a) Is present 2 mechanisms of corrosion the first: Deposits corrosion mecanism based on main process of desalation and second: electrochemical corrosion produced by third mixture of electrolyte, anode and cathode reactions. b) the best demulsifier was A with 99.96% of salt removal at 42 ppm of concentration emulsion less than 0.001mL. the perdominant mechanism is electrochemical based on fact of spontaneus reaction of corrosion with high potential (E0: +0.193V).

Keywords: Corrosion mechanism, Crude oil, Demulsifier, Desalter, Salt content.

ÖZET

KHURMALA HAM PETROLÜNÜN KIMYASAL KOROZYON SÜRECININ BELIRLENMESI İÇIN TUZ MIKTARI ETKISI ÇALIŞMASI: MERKEZI SÜREÇ BÖLÜMÜNDEKI TUZ UZAKLAŞTIRMA ÜNITESI

M.AMEEN, Sherko Yousif
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Tez Danışmanı : Prof. Dr. Nahit AKTAŞ
Mart 2017, 67 sayfa

Bu çalışmada alan düzeyinde değerlendirme tasarımının deneysel niteliği, CPS-KAR GRUP ŞİRKETİ kurulumlarında tuz giderme birimlerinde meydana gelen metalürjik boru hatları üzerindeki kimyasal korozyonun oluşmasına yönelik tuz içeriğinin etkisini incelemek amacı ile hazırlanmıştır. Bu çalışmanın amacı, giriş / çıkış yöntemine dayalı doğru korozyon mekanizmasını bulmaktır. Uygulanmış metodoloji dört bölümden oluşmaktadır: A) Gerçek durumun teşhisi ve korozyon mekanizmasının belirlenmesi B) boru hatları üzerindeki farklı koşullarda tuz konsantrasyonunun belirlenmesi C) korozyonu yönetmek ve tuz içeriğini tahliye etmek için doğru prosesi geliştirmek D) Etkinin değerlendirilmesi ve operasyonel yönetici personeline teklif sunulması. Deneysel saptamalardan sonra şebeke sonuçları şöyledir: A) İlk olarak korozyon mekanizmaları, bunlar 2 tanedir: Birincisi Korozyon mekaniğini ana tuz giderme işlemine dayandırır, ikincisi elektrolit, anot ve katot reaksiyonlarının üçüncü karışımının ürettiği elektrokimyasal korozyondur. B) en iyi emülsüzleştirici A, 0.001 mL'den az 42 ppm konsantrasyon emülsiyonunda % 99.96 tuz giderme ile A idi. Perdominant mekanizma, korozyonun yüksek potansiyele (E0: + 0.193V) spontan reaksiyonu nedeniyle elektrokimyasal bir yöntemdir.

Anahtar kelimeler: Demulsifier, Desalter, Ham Petrol, Korozyon mekanizma, Tuz miktarı.

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2017

M.AMEEN, Sherko Yousif

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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	**Description**
Conc.	Concentraion
g	Gram
kg	Kilogram
m	Metre
cm	Centimetre
mm	Millimetre
l	Litre
ml	Millimetre
C°	Celsius
%	Percentage
ppm	Part per milion
ppt	Part per thousand
PTB	Part per thousands barrel
“	Symole for second in time
‘	Symbole for minutes in time
µs	micro siemens
mpy	Mils per year
N	Normality
M	Molality
Vol	volume
W/V	Wáter per volume
V/V	Volume per volume

Abbreviations	**Description**
DMF A	Demulsifier from baker Hughes company
DMF B	Demulsifier from chimec company
DMF C	Demulsifier from tekkon company
DMF D	Demulsifier from petrofann company
ASTM	American Society for Testing and Materials
NACE	National Association of Corrosion Engineers
API	American Petroleum Institute
EBT	Erichrome Black T
EDTA	Ethanol Diamine Tetra Acetic acid
DMF	Demulsifier
Ksp	Constant Solubility Product
NC	No Change
EM	Emulsion
Wt.	Water

1. INTRODUCTION

Iraqi government decided around 10 years ago to develop oil and gas fields at Khormala site as results of geological research of strategic wells with high reservoirs of gas.

By that way, Central Process Station (CPS) began construction; commissioning and start up, and now together with south, middle and north stations produce crude oil sent to Erbil refinery and tukey by pipline and natural gas sent to Khormala Power Plant to produce electricity.

This study was developed in CPS, motivated by try to support solving some corrosion problems.

Metallic materials, pure metals and their alloys tend to enter into chemical union with the elements of a corrosive medium to form stable compounds similar to those found in nature. When metal loss occurs in this way, the compound formed is referred to as the corrosion product and the metal surface is spoken of as being corroded. (Perry, 1997) In this way, in the Khurmala region (25 km north Erbil) it is carried out an important project of oil and gas. among the projects being carried out there is one that stands out for crude oil extraction and purification process to export to Erbil KAR called Central Process Station (CPS).

During the extraction process is natural that oil is accompanied of water and salts from the site, for that, CPS has three stations: the south, north and middle stations.

From the time of its operation, it has been proved the high amount of salts present in the oil. To try to reduce the amount of salt in the water emulsified crude accompany, desalination plants were installed to break the emulsion and decant salts.

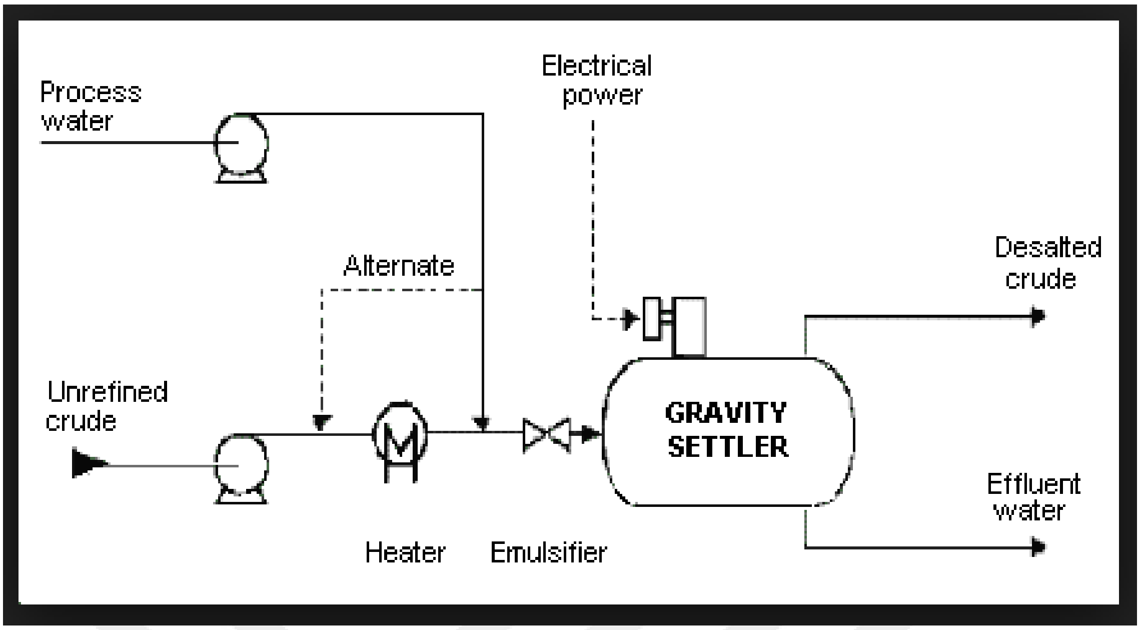


Figure 1.1. Desalter scheme.

In order to increase the efficiency of the separation water / oil, demulsifiers additives are applied to streams to desalt but this process have created high salt content that problems causing significant corrosion in pipelines and chemical disturbance in Erbil Refinery receiving crude oil with high level of free water.

Figure 1.2. Examples of observable corrosion condition at CPS Desalator.

Because the desalter units are newly installed and that the group of qualified staff in the area of corrosion recently established not counted so far with the relevant experience and processes to define clearly the corrosion mechanism occurring at CPS.

This research aims to study the effect of salts present in the oil on the corrosion mechanism, in order to implement the actions necessary to reduce the corrosion rate and in turn improve the effectiveness of the separation of the water phase / crude allowing this, meet the following specific objectives:

1. Establish a strategy for monitoring corrosion in order to obtain sufficient information to determine the current condition of the corrosion process.
2. Apply corrosion study in order to determine the predominant corrosion mechanism., Following the recommendations of the techniques employed by the ASTM and ASME.
3. To determine the optimal dose of demulsifier to apply around trying to reduce the salt content in the oil and thereby reducing corrosion as directed by international standards and references available.
4. Evaluate the effect on corrosion mechanism to implement the new dose of demulsifier in the desalter.

1.1. Goals and Objectives of Research

1.1.1. Main goals

1. Removing salts from crude oil for better marketing and transportation.
2. Prevention of corrosion from pipelines and all other devices and units that crude oil is passed through for more safety.
3. Define type of corrosion protection to desalter based on knowledge of main corrosion mechanism.
4. Determination the right type of demulsifier.

1.1.2. Specific objectives

1. Establish a strategy for monitoring corrosion in order to obtain sufficient information to determine the current condition of the corrosion process.
2. Apply corrosion study in order to determine the predominant corrosion mechanism., Following the recommendations of the techniques employed by the ASTM and ASME.
3. To determine the optimal dose of demulsifier to apply around trying to reduce the salt content in the oil and thereby reducing corrosion as directed by international standards and references available.
4. Evaluate the effect on corrosion mechanism to implement the new dose of demulsifier in the desalter.

1.2. Thesis Outline

This experimental research proposal with evaluative level is composed of five chapters.

The following describes the most important aspects:

Chapter 1: consists of a review of the desalination process, corrosion levels found, dose demulsifier as well as the importance of determining the corrosion mechanism is exposed, which are the mainstay of this research, later setting objectives, benefits and the contribution of this study, through its justification, also including the scope and limitations of the same.

Chapter 2: consists in literature review of the Background of the research, due to the limited information of this type of corrosion both in Iraq and in the Kurdistan region, turned to studies of international character, which founded and closely connected as methods, techniques and procedures used, as well as contributions concerning the type of corrosion under study. The theoretical bases are intended to describe the most important aspects of the desalination process, types of corrosion found, the corrosion mechanisms and methods used to determine them. Note that the definition of basic terms the most important words, which are of little use in the chemical field of corrosion explained. The matrix explains operationalization of variables according to specific objectives, analysis variables, dimensions and indicators;

and finally, the statistical parameters for the validation of the methods used.

Chapter 3: the applied methodological framework described, for it being an experimental research, evaluation level, consisting in non-experimental design and within it a transactional study since this investigation was limited only to determine the optimal concentrations the demulsifier and its relation to the mechanism of corrosion.

Chapter 4: consisting the results and datas with explanations for each recorded results after and before applied demulsifiers and then calculating the existing cations for deposits as a factor of occurring corrosion mechanism.

Finally; Chapter 5: provides a general Conclusion and Recommendation

2. LITERATURE REVIEWS

2.1. Corrosion in Desalter Units

Scattergood (2015) was studied a method of optimizing system parameters in a crude unit to reduce corrosion and corrosion byproduct deposition in the crude unit is disclosed and claimed. The method includes measuring or predicting properties associated with the system parameters and using an automated controller to analyze the properties to cause adjustments in the chemical program to optimize the system parameters. Adjusting the system parameters effectively controls corrosion in the crude unit by reducing the corrosiveness of a fluid in the process stream and/or by protecting the system from a potentially corrosive substance. System parameter sensing probes are arranged at one or more locations in the process stream to allow accurate monitoring of the system parameters in the crude unit.

2.2. Methods Used to Measuring Corrosion in Crude Oil

Stern (1958) was applyed a method for determining corrosion rate from electrochemical polarization data obtained in the region of the corrosion potential is described. The technique has foundation in theory, is supported by experimental evidence, and appears to have widespread application. The advantages and limitations of the method are discussed.It would appear that the use of linear polarization measurements can supply valuable information regarding: (1.) Studies of the effect of environment variables on corrosion rate. These include changes in composition, velocity, and temperature, (2.) Evaluations of inhibitors in controlling corrosion, (3.) Comparison of the corrosion rates of various alloys of similar composition in a given environment, and (4.) Determination of changes in corrosion rate with time, including studies of underground structures as well as materials in aqueous solutions.

2.3. Demulsifiers Used in Desalter Units

Al-Otaibi (2003) was studied that oil produced in most oil fields is accompanied by water in the form of an salts, principally chlorides of sodium, calcium, and magnesium. If crude oil is left untreated, when emulsion that must be treated. In addition, this water normally contains dissolved it is processed in a refinery the salt can cause various operating problems. This paper investigates experimentally the effect of five factors (gravity settling, chemical treatment, freshwater injection, heating, and mixing) on the efficiency of the dehydration/desalting process for a Kuwaiti crude oil and a commercial demulsifier (Servo CC 3408).

Kokal (1999) discussed problems related to emulsion that have been encountered in a large Saudi Arabian field. This is a unique field lying both onshore and offshore and is producing from seven different reservoirs. These oils range in viscosities from 2 cP to over 10 cP (@ 22°C) and API gravities range from 28 to 40. The n-pentane asphaltene content varies from 0.2% to over 7% and watercut for producing wells ranges from dry wells (0% watercut) to over 70%. These properties provide an interesting case of operational problems in oil-water separation. The problems include increased incidents of shorting in the separator, tripping of equipment and increased demulsifier consumption.

2.4. Equilibrium in Heterogeneous Systems

A closed system containing at least two phases is called a heterogeneous system. Reactions (changes) between or among phases are driven by energy manifested in temperature of chemical potentials. When there is no net change in a closed system among the phases, the system is said to have reached an equilibrium condition.

At a definite temperature, a phase in a closed system has a certain tendency to change. Such a tendency is called the ACTIVITY of the phase. As long as such a phase exists, its tendency or activity remains constant. However, the activities of substances in a gas phase are proportional to their partial pressures or concentrations. For a solution, their activities are proportional to their concentrations. Thus, their partial pressures or concentrations are indicators of their tendency to change.

At equilibrium, these tendencies of changes reach certain proportion such that the forward and reverse changes are balanced. Similar to the equilibrium conditions of homogeneous systems, heterogeneous systems also tend to reach equilibrium conditions. EQUILIBRIUM CONSTANTS can also be assigned to describe equilibrium conditions of heterogeneous systems.

We shall look at several types of heterogeneous systems to illustrate how we deal with their behavior or change (Kokal, 1999).

2.5. Electrochemical Corrosion

Electrochemical corrosion of metals occurs when electrons from atoms at the surface of the metal are transferred to a suitable electron acceptor or depolarizer. Water must be present to serve as a medium for the transport of ions.

The most common depolarizers are oxygen, acids, and the cations of less active metals. Because the electrons flow through the metallic object itself, the anodic and cathodic regions (the two halves of the electrochemical cell) can be at widely separated locations. Anodic regions tend to develop at locations where the metal is stressed or is protected from oxygen.

Contact with a different kind of metal, either direct or indirect, can lead to corrosion of the more active one.

Corrosion of steel can be inhibited by galvanizing, that is, by coating it with zinc, a more active metal whose dissolution leaves a negative charge on the metal which inhibits the further dissolution of Fe^{2+}.

Cathodic protection using an external voltage source is widely used to protect underground structures such as tanks, pipelines and piers. The source can be a sacrificial anode of zinc or aluminum, or a line-operated or photovoltaic power supply.

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^{+} + e^{-}$

Is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a depolarizer (Hill and Colb, 2013).

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes. The economic aspects of corrosion are far greater than most people realize; the estimated cost of corrosion in the U.S. alone was $276 billion per year. Of this, about $121 billion was spent to control corrosion, leaving the difference of $155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact, with motor vehicles and transportation being a close second.

2.6. Corrosion Cells and Reactions

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like this reactions examples:

$$\mathrm{Fe_{(s)} + Fe^{+2}_{(aq)} + 2_{e-}} \qquad (1)$$

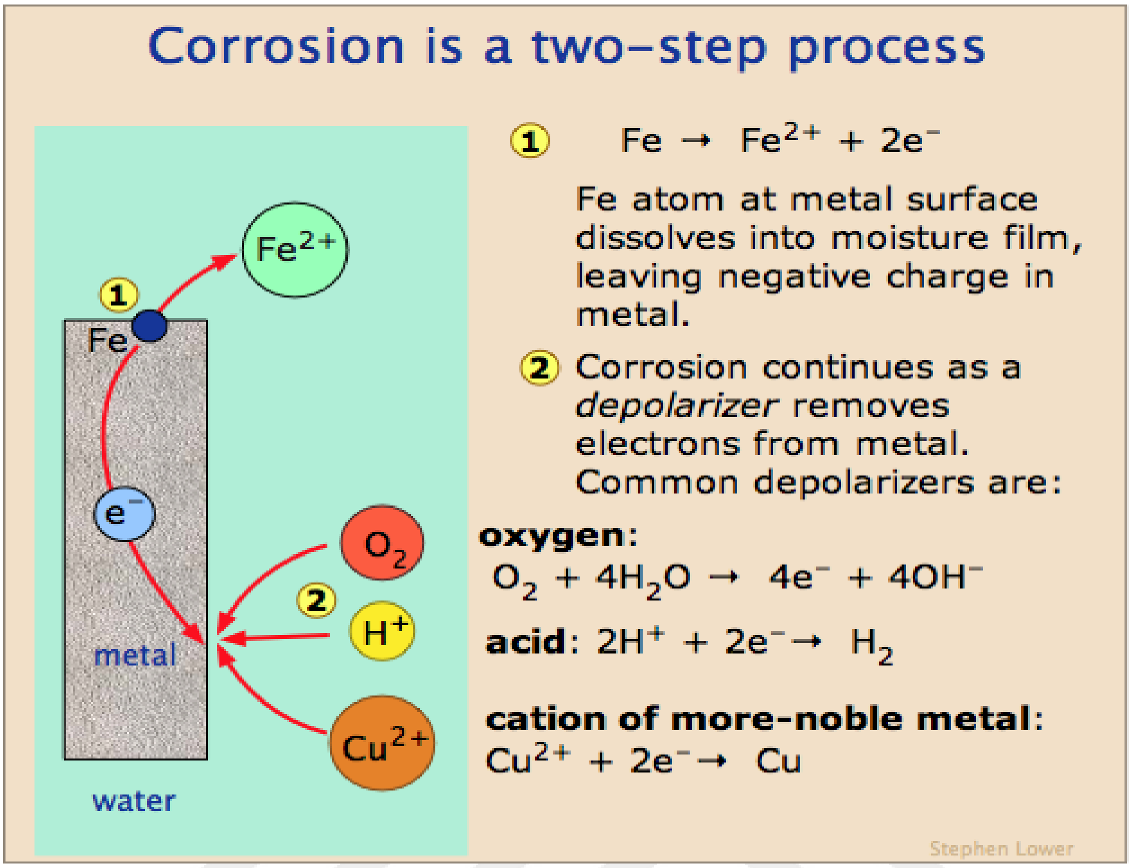
and the cathodic steps can be any of:

$$\mathrm{O_2 + 2H_2O + 4_{e-} \rightarrow 4OH^-} \qquad (2)$$

$$\mathrm{H^+ + e^- \rightarrow \tfrac{1}{2}H_{2(g)}} \qquad (3)$$

$$\mathrm{M^{+2}} + 2e^- \rightarrow \mathrm{M_{(s)}} \qquad (4)$$

where M is a metal.



Corrosion is a two-step process

① $Fe \rightarrow Fe^{2+} + 2e^-$

Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

② Corrosion continues as a *depolarizer* removes electrons from metal. Common depolarizers are:

oxygen: $O_2 + 4H_2O \rightarrow 4e^- + 4OH^-$

acid: $2H^+ + 2e^- \rightarrow H_2$

cation of more-noble metal: $Cu^{2+} + 2e^- \rightarrow Cu$

Figure 2.1. This corrosion proceess named Chemical Corrosion is ilustrated.

This type of corrosion is named electrochemical corrosion of iron. Corrosion often begins at a location where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.) The metal ions dissolve in the moisture film and the electrons migrate to another location where they are taken up by a depolarizer. Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as rust.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

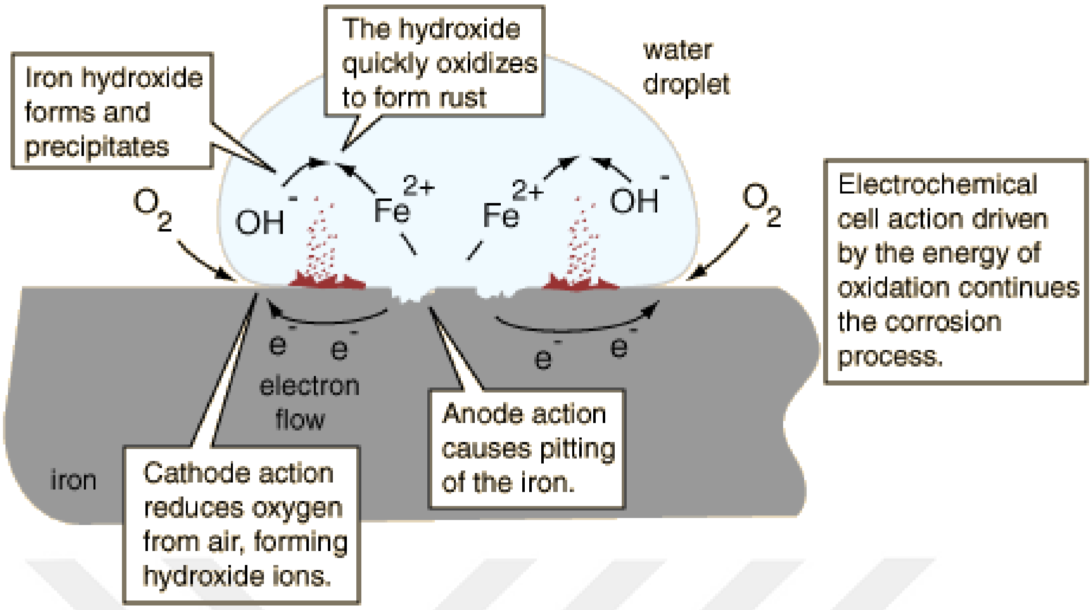


Figure 2.2. Corrosion of iron cast Alloy.

2.7. Schematic Diagram of Corrosion Cells on Iron

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" region will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

2.8. Desalter

Is a process unit in an oil refinery that removes salt from the crude oil. The salt is dissolved in the water in the crude oil, not in the crude oil itself. The desalting is usually the first process in crude oil refining.

The salts that are most frequently present in crude oil are calcium, sodium and magnesium chlorides. If these compounds are not removed from the oil several problems arise in the refining process. The high temperatures that occur downstream in the process could cause water hydrolysis, which in turn allows the formation of corrosive hydrochloric acid. Sand, silts and salt cause deposits and foul heat exchangers. The need to supply heat to vaporize water reduces crude pre-heat capacity. Sodium, arsenic and other metals can poison catalysts. By removing the suspended solids, they are not carried into the burner and eventually flue gas, where they would cause problems with environmental compliance such as flue gas opacity norms.

Most produced water contains salts that can cause problems in production and refining, when solids precipitate to form scale on process equipment. The salts also accelerate corrosion in piping and equipment. The salt content of crude oil almost always consists of salt dissolved in small droplets of water that are dispersed in the crude. Sometimes the produced oil contains crystalline salt, which forms because of pressure and temperature changes and because of stripping of water vapor as the fluid flows up the wellbore and through the production equipment.

crude oil desalter is a device used in petroleum refineries to remove inorganic salts, water and sediment from the incoming petroleum crude oil feedstock before it is refined. This article focuses on the use of electrostatic desalters to produce a dehydrated, desalted crude oil with a low sediment content. Almost all refineries now use electrostatic desalters. However, there may still be a few refineries employing the older, less efficient method that utilizes chemicals and settling tanks.

Removal of the salts, water and sediment is necessary to avoid excessive fouling of equipment as well as corrosion from the generation of hydrochloric acid (HCl) by the hydrolysis of the chloride salts present in the incoming crude oil, in particular magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). Any salts that are not removed represent a source of metals that can "poison" expensive catalysts used in various petroleum refinery processes.

2.9. Contaminants in Crude Oil as Received by Refineries

The amount of water, salts and sediment in the crude oil as received at petroleum refineries varies widely with the source of the crude oil, the prior processing of the crude oil at the source sites and with the mode of transporting the crude oil from its source to the refineries.

Typically, the raw crude oil produced by oil wells drilled into underground petroleum oil reservoirs is accompanied by brine (i.e., water containing inorganic chloride salts). The amount of chloride salts in the brine may be as high as 20 % by weight. Some of that brine is emulsified with the crude oil. The salts present in raw crude oil may be in the form of crystals dispersed in the oil and some of the salts are dissolved in the brine in their ionized form.

The salts present in petroleum crude oils are mainly chlorides with following approximate breakdown:

75 weight percent Sodium chloride ($NaCl$)
15 weight percent Magnesium chloride ($MgCl_2$)
10 weight percent Calcium chloride ($CaCl_2$)

The sediment present in petroleum crude oils include clay, rust, iron sulfide (FeS), asphaltenes and various other water-insoluble particles.

The raw crude is usually subjected to processing at or very near to the oil field production sites in order to separate the oil from the brine before the oil is transported to petroleum refineries via pipeline, railway tank cars, tanker trucks or sea-going crude oil tankers. Such oilfield processing typically involves washing the oil with water to remove salts, some heating, use of demulsifying chemicals and simple settling vessels and tanks. In some cases, the oilfield processing includes electrostatic desalting as well. In general, the oilfield processing facilities strive to remove enough water, sediment and salts so that the transported crude oil contains less that 1 to 2 % by volume of sediment and water (BS&W) and less than 10 to 20 pounds of salts per 1000 barrels (PTB) of clean, water-free crude oil (which is equivalent to a salt content of 34 to 68 ppm by weight). Nevertheless, the crude oils as received at petroleum refineries have a salt content that ranges from a PTB of 10 to 300 (34 to 1,020 ppm by weight), based on spot samples of many different crude oils as delivered to refineries. Transportation by sea-going crude oil tankers is vulnerable to salt water pickup by the crude oil cargo.

Crude oil also contains trace elements such as vanadium (V), nickel (Ni), copper (Cu), cadmium (Cd), lead (Pb) and arsenic (As), all of which can cause problems in some of the various processing units in the petroleum refineries. They may be present in the form of oil-soluble organo-metallic compounds or as water-soluble salts.

2.10. Terms and Definitions

Centrifuge: a machine with a rapidly rotating container that applies centrifugal force to its contents,typically to separate fluids of different densities or liquids from solids.

Copper strip corrosion:this is a qualitative method that is used to determine the level of corrosion of petroleum products.in this test,a polished copper strip is suspended in the product and its effect observed.

Emulsion or emulsibility: the ability to be demulsified being sometimes expressed as the rate at which a liquid (as an oil) separates from an emulsion.

PH meter: a simple and speedy device to measure the acidity and alkalinity of a fluid.a PH meter acts as a volt meter that measures the electrical potencial difference between a PH electrode and a reference electrode and displays the result in terms of the PH value of the solution in which they are immersed.

Salt meter or salinometer:it is a device to measure the salinity,or dissolved salt content,of a solution.

3. MATERIAL AND METHODS

3.1. Type of Research

The corrosion process, who involves salt content and its mechanism, is an experimental research and to be proposed to design a process that is carried out on a laboratory scale for determining dosage of demulsified additive. The parameters do regard this experimental research it is based on the view that under Arias (2004), is defined as:

The process of subjecting an object or group of individuals to certain conditions or stimuli (independent variable), to observe the effects or reactions (dependent variable) occur. Regarding the level, it is purely explanatory, because its purpose is to demonstrate the changes in the dependent variable that were caused by the independent variable. That is, it aims to establish a cause precisely - effect.

The characteristics of the research for which is justified as an experimental research developed in field study, it is because, the independent chemical variables studied are: a) experimental parameters of: corrosion rate, dosage level and salt content. These will be investigated in order to determine the degree of physical and chemical relationships with the mechanism of corrosion follow in desalter unit. And its conformity with international specifications of performance (dependent variable - or response variable). Optimization and validation of the research will take place at different experimental conditions using factorial designs.

This research presents a level of descriptive depth, because it is characterized as a fact for the reason that there are already indications of how that corrosion process takes action over metallurgy.

3.2. Research Design

This work focuses as an experimental factorial design study, as this method allows to study the experimental variables with a minimum number of trials. Whereas the intention of the research is to get the right corrosion mechanism over pipeline material using the official methods for determining corrosion rate, the indicator or dependent variable more convenient was defined as the level of corrosion velocity obtained before and after applying right demulsified additive. The specification of corrosion control process to be achieve is shown in table 3.1.

Table 3.1. Specification Control of corrosiveness in KAR/CPS complex.

Parameter	Official Ranges
Corrosion rate, max	2 mpy
Water content, Max	2 %
Salt content in crude, max	20 PTB
pH	< 10.5

Source: (KAR Process Handbook, 2010)

Application of factorial design of experiments applied research stages require that once optimized the process determine the right dossage of demulsifier to apply.

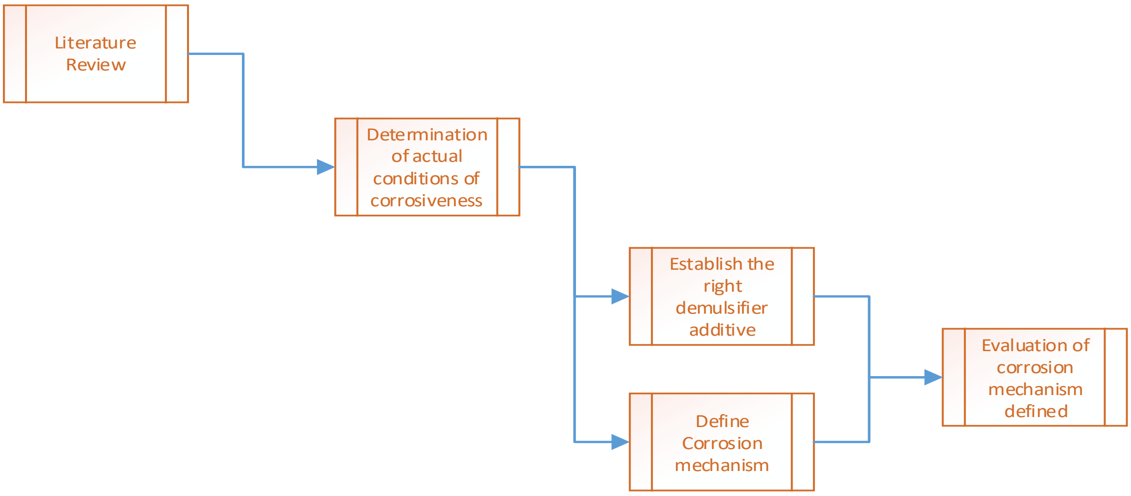


Figure 3.1. Experimental design.

3.2.1. Stage one: Document reviewed

It aims conducted a review of the topic under study concerning technical information.

This stage consisted of the following activities:

1. Research centers, libraries, Internet sources visited: for the importance of this research the following sources were consulted: Egyptian Journal of Petroleum, International journal of Industrial Chemistry and papers from Department of chemical Engineering College at Basrah University. Iraq.
2. Selection of information based on the level of relevance: based on fact that researches selected were identified because all of the emulsion gives next important information about: modelling of corrosion on system over this study and assessment of localized corrosion to give information about how clear can be the mechanism of corrosion studied by this research and the content of select bibliography.
3. The scientific articles and reference books about type of corrosion mechanism developed in desalators were used to define the experimental part of this research and give guidance to understand why in a desalter can coexist more than one type of corrosion.
4. Finally, methods for evaluating the effectiveness associated with demulsifier additives, this activity gave the theorical orientation about to define the range of dosage to be used.

3.2.2. Stage two: Established a strategy for monitoring corrosion in order to obtain sufficient information to determine the current condition of the corrosion process.

In this step, the protocol of tests used was established to know the actual mechanism details without intervention, meanwhile in the actual conditions. For that, the most important test and official methods used are mentioned in table 3.2 shown.

Table 3.2. Protocol to obtain actual conditions.

Parameter	Official Method And Procedure
Iron	ASTM D 1193
Water content, Max	NACE/ASTM D1796
Demulsibility	ASTM D2711
pH	ASTM G51/SP0285
Salt content	ASTM/NACE D 3230
Magnesium, Calcium and Total Hardness	ASTM D 2340
Alkalinity in wáter	ASTM D1067-02
Total disolved solids	SM-2540
Disolved Oxygen	ASTM D 888-87
Total Disolved Salts (TDS)	SM-2540
Conductivity	BC 3020
Chloride	ASTM D 4458-05
Density and API	ASTM D 1298
Bottle test	ASTM D 4007

Among the tasks applied at this stage done following:

1. All test methods were tested in a recognition laboratory at Amine Plan in Khurmala oil and gas field at KAR Company, the list of methods available for mentioned laboratory is in appendix 1.

All methods were checked with right standards before and after analysis of samples of this research to give satisfactory results before they could be putted into use and get enough certainty developing mechanism of corrosion. Is Important to say, that more accuracy on result more accuracy on definition of steps in mechanism of corrosion.

2. Representative samples and determination of the current state of corrosion of the desalter unit: in this activity at least a defined samples were taken to assure that results did not affected by unrepresentative samples. The samples taken were as mentioned in the table above:

Table 3.3. Date and time of sampling.

Date and time of sampling		Types of samples
25/11/2015	8:00 AM	Crude oil before entering into desalter
8/2/2016	1:00 PM	Water from outlet of desalter/first time
10/2/2016	1:00 PM	Water from outlet of desalter/second time
2/12/2015	8:00 AM	Demulsifier/BAKER HUGHES
18/12/2015	8:00 AM	Demulsifier/CHEMIC
5/1/2016	8:00 AM	Demulsifier/TEKKON
15/1/2016	8:00 AM	Demulsifier/PETROFANN

3. Analyze the results so that these form the basis for determining the protocol corrosion mechanism and the optimal dosage of demulsifier. This part will be explained detailed at chapter Four (Results and Discussion).

3.2.3. Stage three: Determination of optimal dose of demulsifier to apply around trying to reduce the salt content in the oil and thereby reducing corrosion as directed by international standards and references available.

The indicator used to determine the optimal dose of demulsifier must meet the following conditions:

1. The lower salt content of the desalter outlet.
2. The lower emulsion value.
3. The higher water content and decanted separate.

For this experiment between 17 ppm and 72 ppm of the current dose they were held and salt content, and the behavior of phases and characterization of organic and water layer were determined. Once know this ratio the more suitable corrosion mechanism will determine and conforming to this chemical and mathematical simulation in order to confirm the chemical species responsible for fixed corrosion mechanism. The official methods for NACE and ASTM were used constantly.

3.2.4. Stage four: Evaluation of the effect on corrosion mechanism to implement the new dose of demulsifier in the desalter.

At this stage, with the results obtained by mathematical models and applying the mechanism defined were validated by the corrosion and specialist staff in among CPS Site Manager. The validation were conducted by professional KAR staff from corrosion section and comparing the corrosion mechanism modeled vs. preexisting models at available literature, the results of this is presented at Results and Discussion Chapter and the evidence of this technical Validation at site in Appendix 2.

3.3. Methods and Equipments.

The list of methods and equipments used in this research were:

Table 3.4. List of Methods and equipments in KAR used in this research.

Parameter	**Equipments**
Water content, Max	Centrifugal Model koehler Instrument company.inc.
Demulsibility	Water bath PMT est.1878 Instrument. HOLLAND
pH	HANNA HI 2211 Ph/ORP meter
Salt content	SALTMETER, STANHOPE-SETA Salt-in-crude analyzer
Iron	Spectrophotometer ECLAB
Magnesium, Calcium and Total Hardness	Volumetric glassware
Alkalinity in water	Volumetric glassware
Total disolved solids	Oven GX-45BE

Table 3.5. List of Methods and equipments in KAR used in this research (continued).

Parameter	Equipments
Disolved Oxygen	Dissolved oxygen test kit, visual colorometric analysis, 1-12 ppm
Total Disolved Salts (TDS)	Volumetric glassware
Conductivity	conductivity meter TRANS BC3020
Chloride	Volumetric glassware
Density and API	Hydrometer and sensitive balance
Bottle test	Water bath PMT est.1878 Instrument. HOLLAND

3.4. Procedures of Applied Tests for This Research.

3.4.1 Procedure of bottle test (Method ASTM D 4007)

A. Taking 100 ml of crude oil in a special test tube of centrifuge (centrifuge tube).

B. Add 50-100 ppm of diluted demulsifier (note: diluted demulsifier by it's solvent (diesel), 1:1000 demulsifier ratio).

C. Add dilute demulsifiers are depends on the actual dosage of demulsifier into the desaltor at the following dosage: 17, 22, 27, 32, 37, 42, 47, 52, 57, 62, 67 and 72 ppm of diluted demulsifier into the tube. Shake frequently about 200-400 times vigorously then introduce the tube into the water bath for about 120 minutes and reading all phases every each 5 minutes to read the separated amount of water and emulsion layers.after that introduce it into the centrifuge setting at 60C° for about 15 minutes.

D. Remove test tubes from centrifuge and record the levels of water ,emulsion and crude oil. Make a table of data obtained.

3.4.2 Procedure of salt content (Method ASTM D 3230)

A. Taking 15 ml of xylene in to a 100 mL cylinder add 10 ml of crude oil and complete it to 50 ml with xylene.
B. Shake for about 1 minute vigorously then complete it to 100 ml with mixed alcohol (63% ml of butanol+37% ml of ethanol) and shake for about 30 seconds.
C. Let settle down for about 5 minutes.
D. Introduce the mixture into electrode and read directly result of salt content in PTB.

3.4.3 Procedure of hydrometer (Method ASTM D 1298)

A. Hydrometer is used to measuring the density of liquids to knowing the API gravity.
B. Take 500 ml of crude oil and introduce hydrometer into he liquid and record the level.
C. Read the density and temperature at hydrometer and calculate API gravity using this equation:

$$API = \frac{141.5}{S.G} - 131.5 \qquad (5)$$

3.4.4 Procedure of pH

Rinse the electrode tip with distilled water. Immerse the tip (bottom 4 cm /1½”) into the sample and stir gently for a few seconds For a faster response and to avoid cross-contamination of the samples, rinse the electrode tip with a few drops of the solution to be tested, before taking measurement.

3.4.5. Electrical conductivity (Trans Instruments BC 3020)

A. Switch on the unit.
B. Note on the bottom right side display ATC should appear. Otherwise, it may have been set off.

C. Rinse the prove witch distilled-Water then dip into the test liquid and stir and tap on the prove to remove bubbles. Tiny bubble in the sensor cell can affect measurements and gives erroneous reading.

D. Keep still and wait a while for temperature compensation to take place.

E. When the READY sign appear on the left side of display, it indicates a stabilized endpoint reading has been reach. you can take the measurements.

F. Report the result in the Daily Report.

3.4.6. Procedure for total, calcium and magnesium hardness (Method ASTM 2340)

A. Measure 50 ml of sample(separated water from desalter)in to a clear colorless container utilizing white background.

B. Then add 0.4 ml of buffer solution and approximately 0.4 g of indicator powder erio chrome black T(EBT).

C. after that, add standard EDTA disodium salt solution slowly from a burette with the continuous stirring until the color changes from red to blue.

D. Complete the titration within 5 minutes after the buffer addition.

E. For Calcium Hardness: Measure 100 ml of sample of water in a volumetric flask and place in a 250 ml Erlenmeyer flask. Then add 2-3 drops of triethanolamine solution 30%(V/V) and also add approximately 4ml of solution of KOH 20%(W/V).stirring and adjusting the PH of the solution between 12 and 13 with the KOH solution. Add about 0.1 g of murexide indicator (a spatula tip).after that titrate with the EDTA solution until the color of the solution changes from pale pink to violet.then calculate the hardness due to calcium as the average of two tests which do not differ by more than 0.2 ml.

F. Record the volume of EDTA consumed to calculate the amount of total hardness.

$$hardness = \frac{(\mathrm{A}-\mathrm{B})*1000}{\mathrm{C}} \tag{6}$$

A=volume of EDTA consumed.

B=volume of EDTA for blank.

C=volume of sample.

3.4.7. Procedure for alkalinity (Method ASTM D 1067-02)

A. Take 50 ml of sample in to a volumetric flask 250 ml and add 2 drop of sodium thiosulphate.
B. For alkalinity P (partial Alkalinity) add 3 drop of phenolphthalene indicator and for total alkalinity (M alkalinity) use methyl orange indicator (same amount).
C. After that, titrate with standard sulphuric acid 0.02024N with continuous stirring until the color is changing from violet to pink.
D. Record the volume of H_2SO_4 consumed for calculating the alkalinity of water taken from desalter.
E. Calculate results using this equation:

$$alkalinity = \frac{\mathrm{A*N\,H2SO4*50000}}{\mathrm{B}} \tag{7}$$

A=volume of H2SO4 consumed.
N H2SO4=0.02024
B= volume of sample.

3.4.8. Procedure for total dissolved solids (T.D.S)

This value is calculated from reading of total conductivity, by Debye Hunkel Law of corrosive electrolytic species the conductivity is related directly from conductivity then it will multiplied from 0.47001 to 0.504500 depending of how much conductance is the species involves.

3.4.9. Procedure of dissolved oxygen (Method ASTM D 888-87)

A. Fill the sample special cup to the 25 ml.
B. Place the ampoule in the sample cup.
C. Snap the tip by pressing the ampoule against the side of the cup.
D. The ampoule will fill,leaving a small bubble to facilitate mixing.
E. Then mix the contents of the ampoule by inverting at several times,

F. Allowing the bubble to travel from end to end.
G. Dry the ampoule and wait for color development.
H. Hold the comparator in a nearly horizontal position while standing directly beneath a source of light.
I. Place the ampoule between the color standards moving it from left to right along the comparator until the best color match is found if the color of the ampoule is between two color standards.
J. A concentration estimate can be made.

3.4.10. Procedure of total solid

A. Washing the crucible and set in to oven to drying and cool it in desiccator then weight.
B. After that, 100 ml of water sample and putting in oven about 1 hour at 105C° .
C. To evaporate water completely then weight the crucible by sensitive balance to knowing how much solid is remained.

$$total\ solid = \frac{(\mathrm{W2-W1})*1000}{\mathrm{vol.of\ sample(mL)}} \tag{8}$$

W2=weight of crucible+residue(gm)
W1=weight of crucible(gm)

3.4.11. Procedure of chloride test

A. Rinse the titration flask or vessel with plenty of softened water sample.
B. Measure out 50 ml of water sample to the flask and add 1 ml of potassium chromate 5%.
C. After that titrate with AgNO3 until the first light steady red color appears.
D. Calculate the amount of Chloride using this equation:

$$chloride\ ppm = \frac{(V\ Agno3 - V\ Blank) * T\ AgNO3 * 1000}{V\ sample\ ml} \tag{9}$$

V AgNO3=Vol. AgNO3 used to titrate the sample.
V Blank=0.15ml of sample.
T AgNO3=1.08 mg Cl^- /ml.

3.4.12. Procedure of calcium hardness

A. Measure 100ml of sample of water in a volumetric flask and place in a 250 ml Erlenmeyer flask.
B. Then add 2-3 drops of triethanolamine solution 30%(V/V) and also add approximately 4ml of solution of KOH 20%(W/V).
C. Stirring and adjusting the PH of the solution between 12 and 13 with the KOH solution.
D. Add about 0.1 gm of murexide indicator (a patula tip) or double amount of EBT used in total hardness.after that titrate with the EDTA solution until the color of the solution changes from pale pink to violet.
E. Then calculate the hardness due to calcium as the average of two tests which do not differ by more than 0.2 ml.

4. RESULTS AND DISCUSSION

In this section of the research results and explanations concerning how the corrosion mechanisms involved in the desalter are presented.
The results are presented for each objective achieved in research.

4.1. Results Related to Determine Right Dosage of Demulsifier

The correct dose of demulsifier is one that produces a particular time as separation of water, with little or no presence of emulsion and the largest displacement of dissolved salts from the crude oil to the aqueous phase desalter background.

After the time of operation and the application of the conditions established operations both phases (crude oil and water) are separated, meaning that this phenomenon has highly effect on the definition of the mechanisms of corrosion are presented below the tables and graphs of results evaluated for each demulsifier.
Criteria to be used to select the correct demulsifier:

a) The greater amount of water removed.
b) The highest percentage of salt removal from the organic phase to the aqueous phase.
c) The lower and more stable emulsion value.

Table 4.1. Bottle test and salt content for BAKER HUGHES Demulsifier RI35 .

DMF(Vol.)		**Time for each 5 minutes inside the water bath (50 c°)**															
PPM	**ML**	**5‘**	**10‘**	**15‘**	**20‘**	**25‘**	**30‘**	**35‘**	**40‘**	**45‘**	**50‘**	**55‘**	**60‘**	**65‘**	**70‘**	**75‘**	**80‘**
17	1.7	0	0	0	0	0	0	start	Same	EM	EM	EM	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt
22	2.2	0	0	0	0	0	0	Start	Same	EM	EM	EM	EM	EM	EM	EM	EM
27	2.7	0	0	0	0	0	0	start	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt	0-0.05 wt
32	3.2	0	0	0	0	0	0	start	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM	0-0.75 EM
37	3.7	0	0	0	0	0	0	Start	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM	0-0.25 EM
42	4.2	0	0	0	0	0	0	start	1ML EM	1ML EM	1ML EM	0.1 wt	0.1 wt	0.1 wt	0.1 wt	0.1 wt	0.1 wt
47	4.7	0	0	0	0	0	0	start	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM	0-0.1 EM
52	5.2	0	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC
57	5.7	0	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC
62	6.2	0	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC
67	6.7	0	0	0	0	0	0	start	NC	NC	NC	NC	NC	NC	NC	NC	NC
72	7.2	0	0	0	0	0	0	start	NC	NC	NC	NC	NC	NC	NC	NC	NC

In that table can be observed layout of all data collected by methodology applied to each demulsifier to crude oil in order to simulate at laboratory scale process at desalter.

At time pass, can be observed change of volumes of phases, where, at initial stage all is one phase and then phase began to separate water, appear emulsion and free water.

That’s the behavior spected caused use of demulsifier.

Table 4.2. Centrifugational test for BAKER HUGHES Demulsifier RI35 .

Separated layers by centrifuge/15 min.			Salt Content/PTB
Water	**Emulsion**	**Crude**	
0-0.4	0.4-0.45	0.45-100	9.7
0-0.4	0.4-0.55	0.55-100	7.3
0-0.5	0.5-0.55	0.55-100	3.8
0-0.55	0.55-0.6	0.6-100	2.0
0-0.5	0.5-0.6	0.6-100	1.4
0-0.75	0.75-0.9	0.9-100	1.3
0-0.3	0.3-0.45	0.45-100	7.7
0-0.3	0.3-0.45	0.45-100	5.2
0-0.3	0.3-0.5	0.5-100	9.5
0-0.35	0.35-0.55	0.55-100	12.4
0	0-0.1	0.1-100	3.5
0	0-1	1-100	3.5

After separation of phases, centrifugation was applied to get the final value of each phase, on results 0-0.75 ml of separated water is indicates high changes and 1.3 PTB is best result (lowest PTB as salt content) at fixed dosage.

In next figure will be shown emulsion vs. time, this is to know operational time to decant water and release crude oil form desalter.

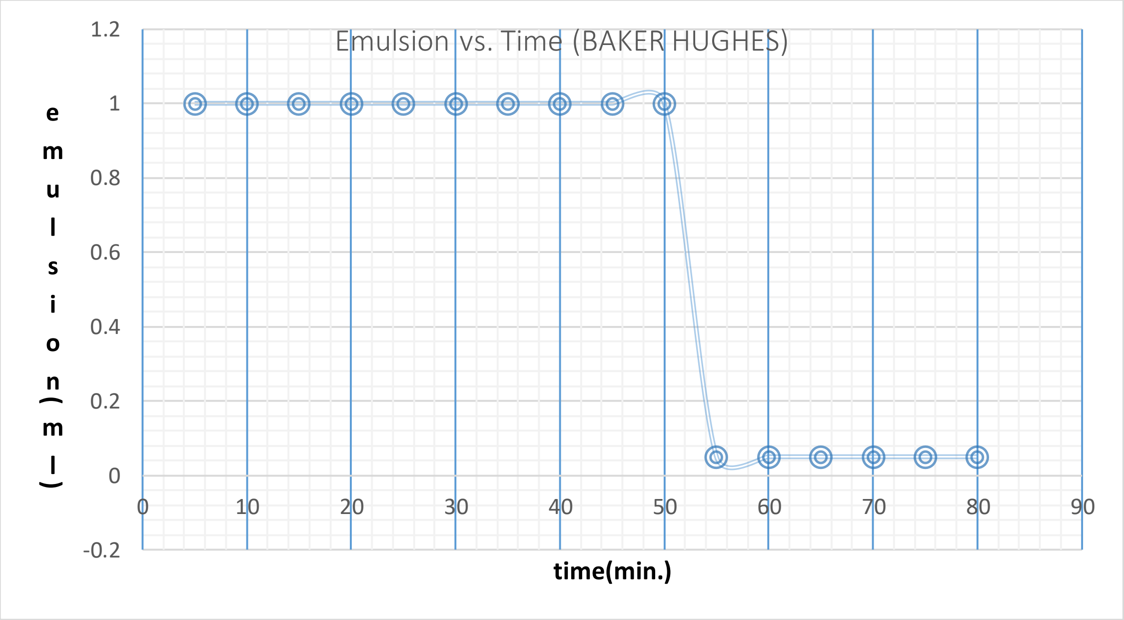


Figure 4.1. Emulsion vs. Time for BAKER HUGHES Demulsifier RI35 .

In last Figure, can be observe that Demulsifier BAKER gives a time optimal time of separation at nearly 55 min, so more time of residence of crude oil on desalter in not necessary and give no significant changes over phases separated.

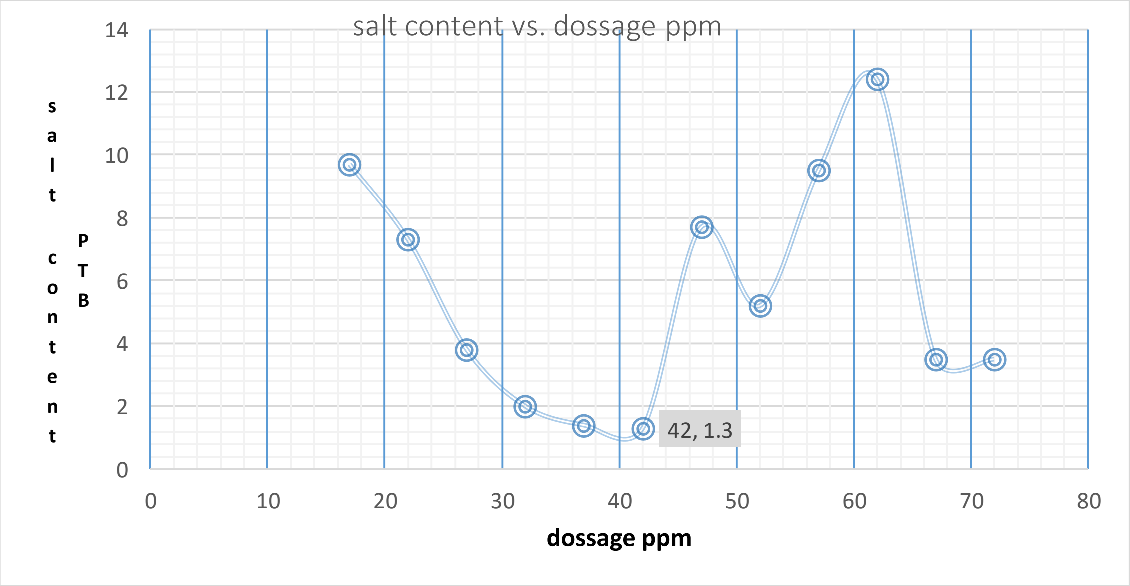


Figure 4.2. Salt Content vs. Dossage (ppm) for BAKER HUGHES Demulsifier RI35 .

In this figure it clearly seen that 42 ppm of dossage with 1.3 PTB of salt is the optimal point for desalter with this demulsifier.

Table 4.3. Bottle Tests data for CHIMEC demulsifier 2722 .

DMF(vol.)		**Time for each 5 minutes inside the watert bath (50 c°)**															
PPM	**ML**	**5'**	**10'**	**15'**	**20'**	**25'**	**30'**	**35'**	**40'**	**45'**	**50'**	**55'**	**60'**	**65'**	**70'**	**75'**	**80'**
17	1.7	0	0	0	start	trace	trace	trace	trace	trace	0.05	0.05	0.1	0.1	0.15	0.155	0.2
22	2.2	0	0	start	0.1	0.1	0.2	0.2	0.3	0.3	0.35	0.35	0.4	0.4	0.4	0.4	0.4
27	2.7	0	0	start	0.05	0.05	0.1	0.1	0.15	0.15	0.25	0.25	0.25	0.25	0.3	0.3	0.3
32	3.2	0	0	0	start	trace	trace	trace	0.05	0.05	0.055	0.055	0.1	0.15	0.2	0.2	0.225
37	3.7	0	0	0	0	0	0	0	0	0	start	trace	trace	trace	trace	trace	trace
42	**4.2**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**start**	**trace**	**trace**	**trace**	**trace**	**0.05**	**0.05**
47	4.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	start	trace
52	5.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	start	trace
57	5.7	0	start	0.1	0.2	0.3	0.3	0.35	0.4	0.4	0.4	0.4	0.4	0.45	0.45	0.45	0.45
62	6.2	0	start	0.1	0.2	0.2	0.2	0.25	0.25	0.3	0.3	0.3	0.3	0.35	0.35	0.35	0.35
67	6.7	0	start	0.1	0.3	0.3	0.3	0.35	0.4	0.4	0.4	0.4	0.45	0.45	0.45	0.45	0.45
72	7.2	0	0	0	0	0	start	trace	trace	trace	trace	trace	trace	0.05	0.05	0.055	0.1

At this table can be observed that at 42 ppm of dossage, demulsifier show it best perfomance with very low value of emulsion and salt content.

Table 4.4. Centrifugal test for CHIMEC Demulsifier 2722 .

Separated layers by Centrifuge/15 Min.			**Salt Content/PTB**
Water	**Emulsion**	**Crude**	
0-0.55	0	0.55-100	15.1
0-0.6	0	0.6-100	11.5
0-0.5	0	0.5-100	22.4
0-0.6	0	0.6-100	16
0-0.6	0	0.6-100	2.1

Table 4.5. Centrifugal test for CHIMEC Demulsifier 2722 (Continued).

Separated layers by Centrifuge/15 Min.			Salt Content/PTB
Water	**Emulsion**	**Crude**	
0-0.65	**0**	**0.65-100**	**1.8**
0-0.6	0	0.6-100	2.1
0-0.6	0	0.6-100	5.6
0-0.6	0	0.6-100	2.3
0-0.6	0	0.6-100	2.3
0-0.65	0	0.65-100	2.2
0-0.65	0	0.65-100	3.4

In the Table 4.4 can be observed that dossage can be getting a very low value of salt content 1.8 PTB will be at 0.65 ml of water as better dossage.

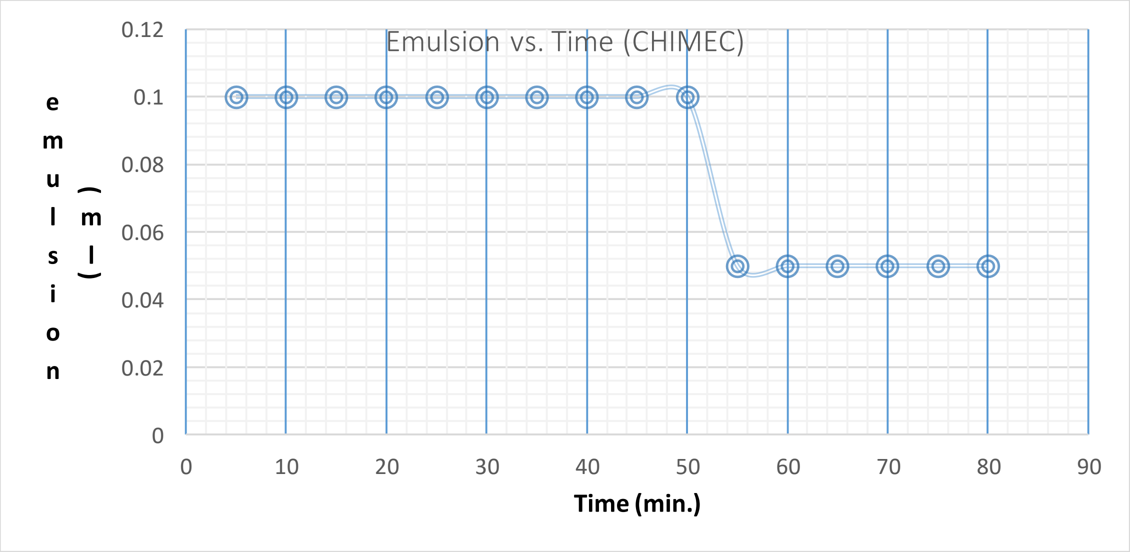


Figure 4.3. Emulsion vs. Time for CHIMEC Demulsifier 2722 .

In last figure can be mentioned that best dosage will be get around at gamp of 0,1 to 0,005 mL.

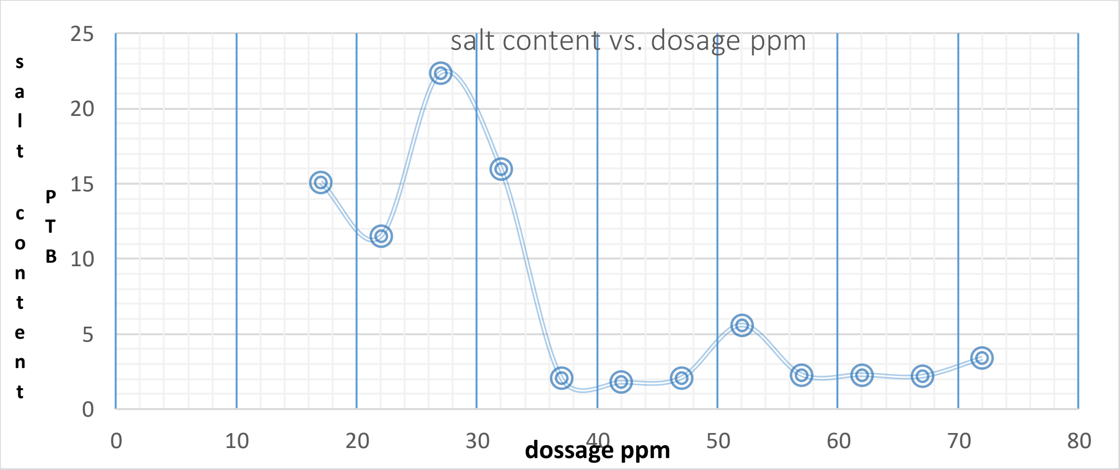


Figure 4.4. Salt Content vs. Dossage (ppm) for CHIMEC Demulsifier 2722 .

As can be observed, CHIMEC demulsifier actuates at 50 mintures and 2.8 PTB of salt as better point of separation.

Table 4.6. Bottle Tests datas for TEKKON Demulsifier CT-C18/17

DMF(Vol.)		**Time for each 5 minutes inside the water bath (50 c°)**															
PPM	**ML**	**5‘**	**10‘**	**15‘**	**20‘**	**25‘**	**30‘**	**35‘**	**40‘**	**45‘**	**50‘**	**55‘**	**60‘**	**65‘**	**70‘**	**75‘**	**80‘**
17	1.7	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
22	2.2	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
27	2.7	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
32	3.2	0	0	0	0	0	0	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
37	3.7	0	0	0	0	0	start	0.05	0.05	0.05	0.05	0.05	0.1	0.15	0.2	0.3	0.3
42	**4.2**	**0**	**0**	**0**	**0**	**0**	**0**	**Start**	**start**	**0.05**	**0.05**	**0.05**	**0.1**	**0.1**	**0.15**	**0.25**	**0.25**
47	4.7	0	0	0	0	0	0	0	0	start	0.05	0.05	0.05	0.05	0.15	0.2	0.2
52	5.2	0	0	0	0	0	0	0	0	0	start	0.05	0.05	0.1	0.1	0.15	0.15
57	5.7	0	0	0	0	start	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM
62	6.2	0	0	0	0	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM
67	6.7	0	0	0	0	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM
72	7.2	0	0	0	0	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM	EM

In previous table step at 42 ppm shows the best separated value of crude oil from emulsion and free water 0.25 ml for this additive.

Table 4.7. Centrifugational test for TEKKON Demulsifier CT-C18/17 .

Separated layers by centrifuge/15 min.			**Salt content/PTB**
Water	**Emulsion**	**Crude**	
0-0.0.5	0.5-0.7	0.7-100	12.5
0-0.5	0.5-0.65	0.65-100	24.6
0-0.5	0.5-0.6	0.6-100	17.4
0-0.55	0.55-0.7	0.7-100	7.6
0-0.7	0	0.7-100	1.6
0-0.65	**0**	**0.65-100**	**1.2**
0-0.7	0.7-0.75	0.75-100	1.9
0-0.7	0.7-0.75	0.75-100	1.4
0-0.5	0.5-0.6	0.6-100	5.6
0-0.55	0.55-0.7	0.7-100	3.1
0-0.55	0	0.55-100	4.6
0-0.55	0.55-0.7	0.7-100	6.3

In previous table step six is the best point of dosage for TEKKON additive, and the best value of salt content is 1.2 PTB.

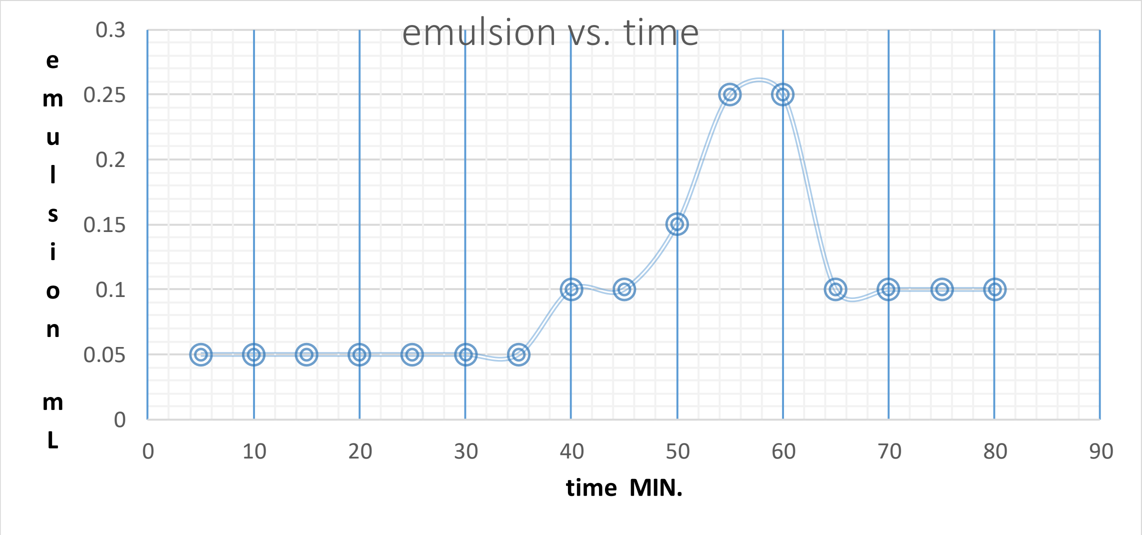


Figure 4.5. Emulsion vs. Time for TEKKON Demulsifier CT-C18/17 .

In last figure, range of 50 to 60 minutes represents better range of dosage.

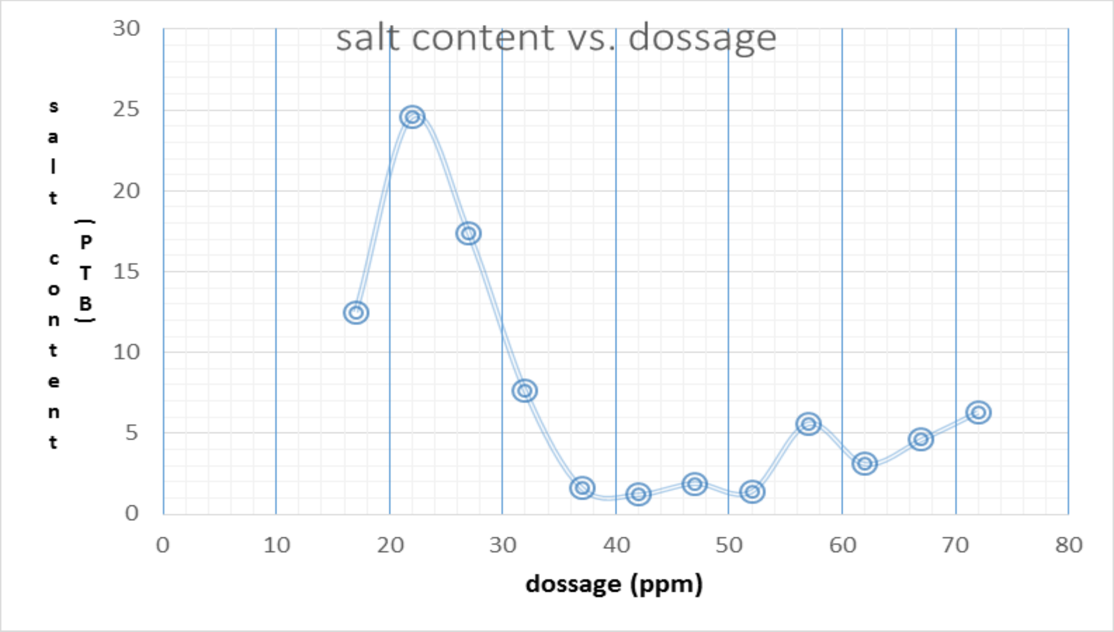


Figure 4.6. Salt Content vs. dossage for TEKKON Demulsifier CT-C18/17 .

In table 4.5 and figures associated can be observed that the best point of dossage is 0.65 ml of separated water and 55 min with lowest concentration of salts.

Table 4.8. Bottle Test datas for PETROFANN Demulsifier KD-3300 .

DMF(Vol.)		**Time for each 5 minutes inside the wt bath (50 c°)**															
PPM	**ML**	**5‘**	**10‘**	**15‘**	**20‘**	**25‘**	**30‘**	**35‘**	**40‘**	**45‘**	**50‘**	**55‘**	**60‘**	**65‘**	**70‘**	**75‘**	**80‘**
17	1.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
22	2.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
27	2.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	start	0.05
32	3.2	0	0	0	0	0	start	trace	trace	trace	trace	trace	trace	trace	trace	start	0.05
37	3.7	0	0	0	0	start	trace	trace	trace	trace	trace	trace	trace	trace	0.05	0.05	0.05
42	**4.2**	**0**	**0**	**0**	**0**	**start**	**trace**	**trace**	**trace**	**trace**	**trace**	**trace**	**trace**	**trace**	**start**	**trace**	**trace**
47	4.7	0	0	start	trace	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.055	0.055	0.055
52	5.2	0	0	0	0	start	trace	trace	trace	trace	trace	trace	trace	trace	start	trace	trace
57	5.7	0	0	0	0	0	0	0	Start	trace	trace	trace	trace	trace	trace	trace	trace

Table 4.9. Bottle Test datas for PETROFANN Demulsifier Kd-3300 (continued).

DMF(Vol.)		**Time for each 5 minutes inside the wt bath (50 c°)**															
PPM	**ML**	**5‘**	**10‘**	**15‘**	**20‘**	**25‘**	**30‘**	**35‘**	**40‘**	**45‘**	**50‘**	**55‘**	**60‘**	**65‘**	**70‘**	**75‘**	**80‘**
62	6.2	0	0	0	0	0	0	0	0	start	trace	trace	trace	trace	trace	trace	
67	6.7	0	0	0	0	0	0	0	Start	trace	trace	trace	trace	trace	trace	trace	trace
72	7.2	0	0	0	0	0	0	0	Start	trace	trace	trace	trace	trace	trace	trace	trace

PETROFAN additive shows better performance at 42 ppm of dossage with traces of emulsion and it is not acceptable for applying into desalter.

Table 4.10. Centrifugational test for PETROFANN Demulsifier KD-3300 .

Separated layers by centrifuge/15 min.			**Salt Content/PTB**
Water	**Emulsion**	**Crude**	
0-0.25	0.25-0.3	0.3-100	38.9
0-0.25	0	0.25-100	44.8
0-0.35	0	0.35-100	39.4
0-0.35	0	0.35-100	34.3
0-0.25	0.25-0.45	0.45-100	13.6
0-0.2	**0.2-0.35**	**0.35-100**	**11.8**
0-0.25	0.25-0.5	0.5-100	8.4
0-0.2	0.2-0.45	0.45-100	9.9
0-0.2	0.2-0.55	0.55-100	2.9
0-0.3	0.3-0.55	0.55-100	2.6
0-0.4	0.4-0.5	0.5-100	2.6
0-0.45	0.45-0.5	0.5-100	2.1

As shown in previous table, best salt content recorded is 2.9 PTB in step 9, but at the same dose of previews demulsifiers 42 ppm the recorded salt content is 11.8 PTB so it is not acceptable value.

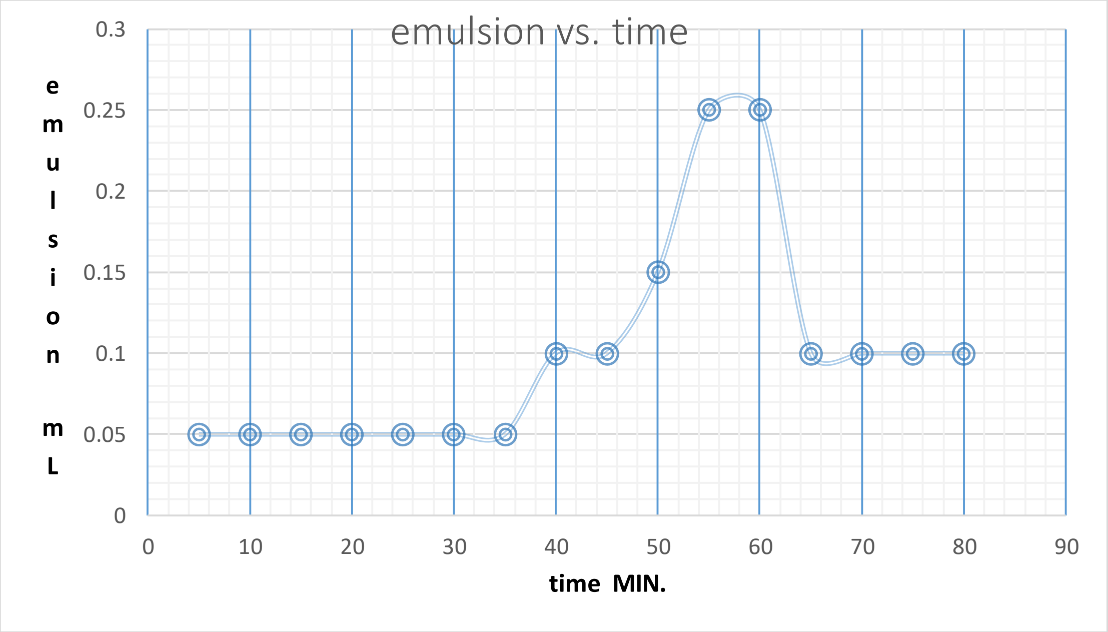


Figure 4.7. Emulsion vs. Time for PETROFANN Demulsifier KD-3300.

In last representation, best result is obtained at 2.9 PTB of salt content and 42 ppm of dosage.

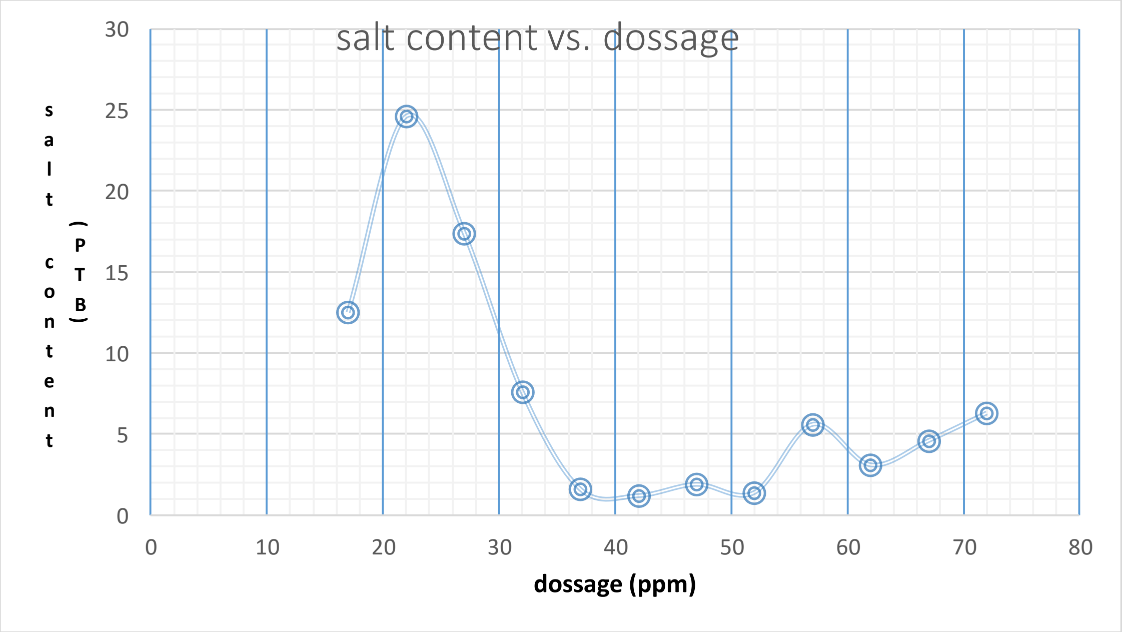


Figure 4.8. Salt Content vs. dosage (ppm) for PETROFANN Demulsifier KD-3300.

With PETROFANN demulsifier the optimal dosage was obtained at 42 ppm with 0.2 ml of separated water and less than 11.8 PTB of salt. This additive compared to rest is worst behavior.

4.2. Calculations of Corrosion Species Formed During Desalter Process

4.2.1. Conditions before desalination process

Determining whether a corrosion mechanism is present is necessary to identify and confirm the presence of the products formed by side reactions of corrosion.

Were based on this condition, a series of calculations were performed to confirm whether certain corrosion mechanisms are present, to achieve this, samples of liquids after the separation were taken and proceeded to chemical characterization. The results of the characterization of the phases are as follows.

Table 4.11. Some characteristics of KHURMALA crude oil before desalter.

Tests	**Results**
Water	0-0.055 mL
Sediment	0.055-0.75 mL
Bitumen	Zero
API	34.9
Salt Content	123.5 PTB

In previus table can be resalted that salt content is very high. Can not processing by Erbil refinery without pretreatment.

Table 4.12. Some characteristics of KHURMALA water before desalter.

Tests	Results
pH at 20 C°	7.9
Conductivity	574 µs
Total disolved salt TDS	269.78 µs
Total hardness	275.1 ppm
Ca+2 hardness	8.3 ppm
Mg+2 hardness	266.8 ppm
Disolved oxygen	8 ppm
Alkalinity	178.11ppm
Total solid	0.0289 gm
Chloride	4.8 ppm
Iron	0.94 ppm

After the desalination process occurs sampled and results are as follow:

Table 4.13. Some characteristics of KHURMALA crude oil after desalter.

Tests	Results
Water	0-0.15 ml
Sediment	Zero
Bitumen	Zero
API	34.9
Salt Content	8-16 PTB (depends)

Table 4.14. Some characteristics of KHURMALA water after desalter.

Tests	Results
pH at 24.1 C°	6.44
Conductivity	9.06 µs
Total disolved salt TDS	4.258 µs
Total hardness	1053 ppm
Ca+2 hardness	11.1 ppm

Table 4.15. Some characteristics of KHURMALA water after desalter (continued).

Tests	Results
Ca+2 hardness	11.1 ppm
Mg+2 hardness	1041.9 ppm
Disolved oxygen	2 ppm
Alkalinity	317.768 ppm
Total solid	0.2258 gm
Chloride	2230 ppm
Iron	8.61 ppm

4.2.2. Identification and determination of the corrosive species in the process

The identification of chemical species was through knowledge of the chemical and electrochemical equilibrium occurs in chemistry desalter. In this regard they will be applied to:

1. Heterogeneous equilibrium (Constant Solubility Product Ksp).
2. Electrochemical equilibria and presence of corrosion cells.

Criteria Applied:

1. Heterogeneous equilibrium: when a chemical is present in one phase and can cause corrosion by fouling species need to achive or higher solubility factor or solubility constant of equilibria, for this, comparison of Ksp (experimental) Vs. Kps (theorical) will give the clue to identify if chemical corrosion specie is formed and present.
2. Electrochemical equilibria: if a cell corrosion potential is positive, so corrosion is possible. For that in here need to apply the law of Hess.

Calculations for each cation:

Calcium:

$\mathbf{Ca(OH)_2 \leftrightarrow Ca^{+2} + 2OH^-}$

$Ksp=5.5*10^{-6}$

$S=1.11*10^{-2}$

$Keq=4*S^3$

$Keq=4[\ Ca^{+2}\ ]^3$

11.1 ppm=11.1 ppm Ca^{+2}

11.1 ppm Ca^{+2}= 11.1mg/l Ca^{+2}

mg/l → mol/l

Ca^{+2}=40g/mol

11.1 mg/l*1g/1000mg*1 mol/40 g

=0.000278 mol/l

Ksp (Exp.) $=4*(0.000278)^3$

Ksp (Exp.) $=8.78*10^{-11}$

If Ksp (Exp.) ≤ Ksp(Theo.)

So: $Ca(OH)_2$ is no present as deposits so corrosion by $Ca(OH)_2$ deposits is not happening.

$$\mathbf{CaCO_3 \leftrightarrow Ca^{+2} + CO^{-2}}$$

$Ksp=2.8*10^{-9}$

$S=5.29*10^{-5}$

[Ca+2] $=2.78x10^{-4}$ mol/l

$Ksp= S^2$

$Ksp =(2.78.10^{-4})^2$

$Ksp=7.73x10^{-8}$

So: $CaCO_3$ is present as deposits and corrosion is happening.

$$\mathbf{CaSO_4 \leftrightarrow Ca^{+2} + SO_4^{-2}}$$

Ksp (Exp.) $=7.73x10^{-8}$

Ksp (Theo.) $=9.1x10^{-6}$

$S=3x10^{-3}$ (Theo.)

So $CaSO_4$ is no presents as deposits for corrosion mechanism.

Magnesium:

$\mathbf{MgCO_3 \leftrightarrow Mg^{+2} + CO_3^{-2}}$

Ksp=$3.5\text{x}10^{-8}$

S=$1.87\text{x}10^{-4}$

Ksp=$[Mg^{+2}]^2$

1041.9ppm=1041.9 ppm Mg^{+2}

1041.9ppm Mg^{+2}=1041.9 g/l Mg^{+2}

Mg/l → mol/l

Mg^{+2}=24.305 g/mol

1041.9 mg/l Mg^{+2}*1g/1000mg*1mol/24.305 g

=0.04286 mol/l

Ksp (Exp.) =$(0.04286)^2$ =0.001837=$1.837\text{x}10^{-3}$

Ksp (Exp.) ≥Ksp (Theo.)

So $MgCO_3$ is present as deposits.

$\mathbf{Mg(OH)_2 \leftrightarrow Mg^{+2} + 2OH^-}$

Ksp (Theo.) =$1.8\text{x}10^{-11}$

S=0.000165=$1.65\text{x}10^{-4}$

Ksp=$4S^3$

Ksp=$4(0.001837)^3$

=2.48x10-8 mol/l

$Mg(OH)_2$ is present as deposits.

Iron:

$\mathbf{Fe(OH)_2 \leftrightarrow Fe^{+2} + 2OH^-}$

Ksp=$8\text{x}10^{-16}$

Ksp=$4S^3$

S=$\sqrt[3]{\mathbf{Ksp/4}}$ =$1.41\text{x}10^{-32}$

8.61 ppm Fe^{+2} to Mg/l Fe^{+2}

Mg/l to mol/l

M.wt=55.56g/mol

8.61mg/l Fe^{+2}*1g/1000mg*1mol/55.56 gm=0.001549 mol/l=$1.549x10^{-3}$ mol/l

Ksp(Exp.) =4($1.549x10^{-3}$)3 =$1.487x10^{-2}$ mol/l

So $Fe(OH)_2$ is present as deposits

$$\mathbf{Fe(OH)_3 \leftrightarrow Fe^{+3} + 3OH^-}$$

Ksp(Theo.) =$4x10^{-38}$

S=$\sqrt[4]{\mathbf{Ksp/27}}$

S=$1.96189x10^{-10}$

Ksp=27($1.549x10^{-3})^4$

Ksp=$1.5544x10^{-4}$ mol/l

So $Fe(OH)_3$ is present as deposits

$$\mathbf{FeS \leftrightarrow Fe^{+2} + S^{-2}}$$

Ksp=6*10-19

S=$\sqrt{\mathbf{Ksp}}$ = $3.6x10^{-37}$

Ksp(Exp.) =($1.549x10^{-3})^2$

Ksp(Exp.) =$2.399x10^{-6}$

so FeS is present as deposits

$$\mathbf{FePO_4 \leftrightarrow Fe^{+3} + PO_4^{-3}}$$

Ksp= $1.3x10^{-22}$

Ksp=S2

S=$\sqrt{\mathbf{Ksp}}$ =$1.69x10^{-58}$

Ksp(Exp.) =($1.549x10^{-3})^2$

Ksp(Exp.) =$2.399x10^{-6}$ mol/l

So $FePO_4$ is present as deposits

$\mathbf{FeCO3} \leftrightarrow \mathbf{Fe}^{+2} + \mathbf{CO3}^{-2}$

Ksp=$3.2\text{x}10^{-11}$

S=$\sqrt{\mathbf{Ksp}}$ = $5.65\text{x}10^{-11}$

Ksp(Exp.) =$(1.549\text{x}10^{-3})^2$

Ksp(Exp.) =$2.399*10^{-6}$ mol

So: $FeCO_3$ is present as deposit by corrosion.

Table 4.16. List of Cations, Solubilities and Ksp.

Cation	S Exp.	S Theo.	Ksp Exp.	Ksp Theo.	Compound production of corrosion phenomena
Calcium(Ca+2)					
Ca(oH)2	$2.78*10^{-4}$	$1.11*10^{-10}$	$8.78*10^{-11}$	$5.5*10^{-6}$	NO
CaCO3	$2.78*10^{-4}$	$5.29*10^{-5}$	$7.78*10^{-8}$	$2.8*10^{-9}$	YES
CaSO4	$2.78*10^{-4}$	$3.0*10^{-3}$	$7.73*10^{-8}$	$9.1*10^{-6}$	NO
Magnesium(Mg+2)					
MgCO3	$4.28*10^{-2}$	$1.87*10^{-4}$	$1.837*10^{-3}$	$3.5*10^{-8}$	YES
Mg(OH)2	$1.837*10^{-3}$	$1.65*10^{-4}$	$2.48*10^{-8}$	$1.8*10^{-11}$	YES
Iron(Fe+2 & Fe+3)					
Fe(OH)2	$1.54*10^{-3}$	$1.41*10^{-32}$	$1.487*10^{-2}$	$8.0*10^{-16}$	YES
Fe(OH)3	$1.54*10^{-3}$	$1.96*10^{-10}$	$1.55*10^{-4}$	$4.0*10^{-38}$	YES
FeS	$1.54*10^{-3}$	$3.6*10^{-37}$	$2.34*10^{-6}$	$6.0*10^{-19}$	YES
FePO4	$1.54*10^{-3}$	$1.69*10^{-58}$	$2.34*10^{-6}$	$1.3*10^{-22}$	YES
FeCO3	$1.54*10^{-3}$	$5.65*10^{-6}$	$2.399*10^{-6}$	$3.2*10^{-11}$	YES

4.2.3. Mechanism of corrosion (Electrochemical theory) of rusting

The overall rusting involves the following steps:

1. Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidised to ferrous ions.

At anode:

$$Fe_{(s)} + Fe^{+2}_{(aq)} + 2e^{-} \tag{10}$$

Thus the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.

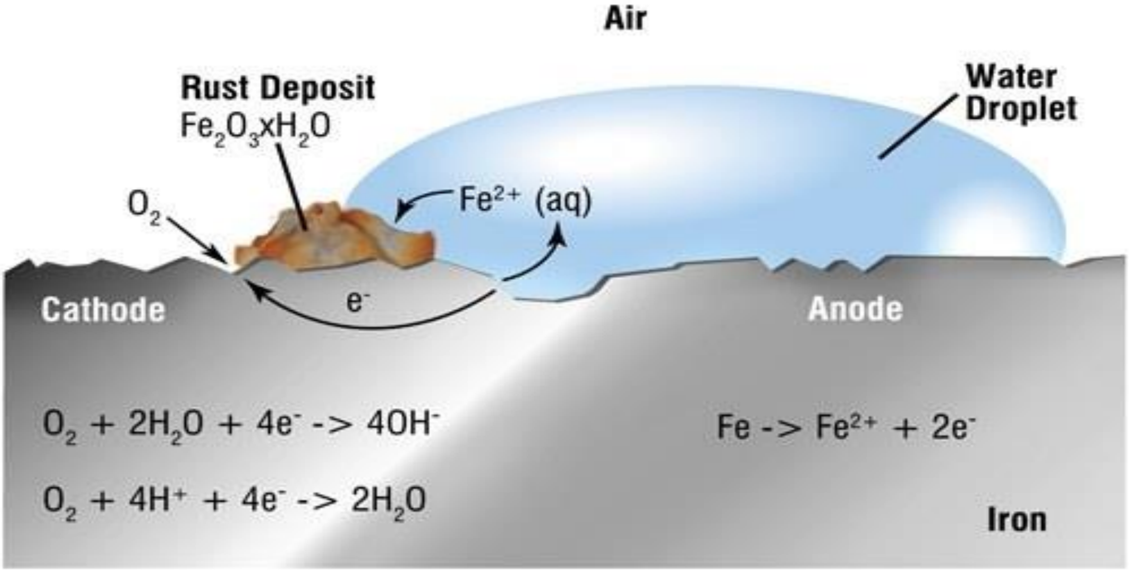


Figure 4.9. Mechanism of rusting.

2. At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The ions are obtained either from water or from acidic substances (e.g. in water:

$$H_2O \rightarrow H^{+} + OH^{-} \tag{11}$$

$$CO_2 + H_2O \rightarrow H^{+} + HCO_3^{-} \tag{12}$$

At cathode:

$$H^+ + e^- \rightarrow H \tag{13}$$

The hydrogen atoms on the iron surface reduce dissolved oxygen.

$$4H + O_2 \rightarrow 2H_2O \tag{14}$$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \tag{15}$$

3. The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalise number of electrons lost and gained i.e.

Oxi. Half reaction: $\mathrm{Fe}_{(s)} \rightarrow \mathrm{Fe}^{2+}_{(aq)} + 2\mathrm{e}^-] \times 2 \;\; (\mathrm{E} = -0.44\ \mathrm{V})$ (16)

Red. Half reaction: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O \;\; (E = 1.23\ V)$ (17)

Overall cell reaction: $2Fe_{(s)} + 4H^+ + O_2 \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O \;\; (E_{cell}) = 1.67\ V$ (18)

The ferrous ions are oxidised further by atmospheric oxygen to form rust.

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+ \tag{19}$$

And

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.xH_2O \;\; (rust) \tag{20}$$

It may be noted that salt water accelerates corrosion. This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.

5. CONCLUSIONS

The apply corrosion study in order to determine the predominant corrosion mechanism is electrochemical mechanism combined with forming deposits, research exhibit high spontaneous corrosion phenomena that must be attended as soon as possible by improving operational conditions or applying cathode protection (best option for electrochemical mechanism prevention), in Khormala CPS case is positive 0.018V promoting corrosion process.

The corrosion produced by deposits formation is due to a presence of: iron compound ($FeCO_3$, $FePO_4$, $Fe(OH)_3$, $Fe(OH)_2$, FeS, $Mg(OH)_2$, $CaCO_3$, $MgCO_3$). Those components separated from water after desalination will increase corrosion rate so, best option will be a neutral demulsifier and implement quality control of water feeding desalters units. In other hand, best will be stable media to avoid capacity of desalter to produce salts in solid forms, better dissolved,By the results obtained, best demulsifier is Baker with the optimal dose of 42 ppm, giving as much less salt content about 1.8 PTB with this demulsifier to apply around trying to reduce the salt content in the oil and thereby reducing corrosion as directed by international standards and references available.

5.1. Future Work And Recommendations

1. Based on dominion of corrosion mechanism by electrochemical process combined with salt deposits would be convenient to establish a cleaning and maintenance program to protect desalter equipment from deeply corrosion.
2. Update type of demulsifier and diminished rate of dosage to optimal value,obtaining with this less production of HCl in refinery process and elevating marketing prices.
3. Emprove metalorgical for desalter to be strnger for this kind of separation process for using lower dosage and a friendly demulsifier can help environment.
4. It is highly recommended not give further use for drained water at desalter unit (after treatment) to any other application.
5. Based on results of this research, the best behavior will be adding additive for demulsifing at crude oil inlet,not during separation process.

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APPENDIX

Appendix 1: List of Methods

Method name	Code of method
Iron	ASTM D 1193
Water content, Max	NACE/ASTM D 1796
Demulsibility	ASTM D 2711
pH	KAR-GTP-T-03-INS-012
Salt content	ASTM/NACE D 3230
Magnesium, Calcium and Total Hardness	KAR-GTP-T-03-INS-010
Alkalinity in wáter	KAR-GTP-T-03-INS-001
Total disolved solids	SM-2540
Disolved Oxygen	ASTM D 888-87
Total Disolved Salts (TDS)	KAR-GTP-T-03-INS-005
Conductivity	KAR-GTP-T-03-INS-005
Chloride	KAR-GTP-T-03-INS-011
Density and API	ASTM D 1298
Bottle test	ASTM D 4007

Appendix 2: Repeatability of Methods

Method name	Precision
Iron	$0.25.\overline{X}$
Water content, Max	Max. 0.02% between readings
Demulsibility	≤ 0.01 ml between readings
pH	0.1 between readings
Salt content	$0,3401.X^{0.75}$
Magnesium, Calcium and Total Hardness	$0,13.X^{0.8}$
Alkalinity in water	$0,25.X^{0.5}$
Total disolved solids	$0,20.X^{0.25}$
Disolved Oxygen	Max. 2 ppm
Total Disolved Salts (TDS)	$0,3401.X^{0.75}$
Conductivity	2.1µs max. Between readings
Chloride	4% of average
Density and API	≤ 0.2 API
Bottle test	≤ 0.01 ml between readings

EXTENDED TURKISH SUMMARY
(GENİŞLETİLMİŞ TÜRKÇE ÖZET)

KHURMALA HAM PETROLÜNÜN KIMYASAL KOROZYON SÜRECININ BELIRLENMESI İÇIN TUZ MIKTARI ETKISI ÇALIŞMASI: MERKEZI SÜREÇ BÖLÜMÜNDEKI TUZ UZAKLAŞTIRMA ÜNITESI

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1. ÖZET

Bu çalışmada alan düzeyinde değerlendirme tasarımının deneysel niteliği, CPS-KAR GRUP ŞİRKETİ kurulumlarında tuz giderme birimlerinde meydana gelen metalürjik boru hatları üzerindeki kimyasal korozyonun oluşmasına yönelik tuz içeriğinin etkisini incelemek amacı ile hazırlanmıştır. Bu çalışmanın amacı, giriş / çıkış yöntemine dayalı doğru korozyon mekanizmasını bulmaktır. Uygulanmış metodoloji dört bölümden oluşmaktadır: A) Gerçek durumun teşhisi ve korozyon mekanizmasının belirlenmesi B) boru hatları üzerindeki farklı koşullarda tuz konsantrasyonunun belirlenmesi C) korozyonu yönetmek ve tuz içeriğini tahliye etmek için doğru prosesi geliştirmek D) Etkinin değerlendirilmesi ve operasyonel yönetici personeline teklif sunulması. Deneysel saptamalardan sonra şebeke sonuçları şöyledir: A) İlk olarak korozyon mekanizmaları, bunlar 2 tanedir: Birincisi Korozyon mekaniğini ana tuz giderme işlemine dayandırır, ikincisi elektrolit, anot ve katot reaksiyonlarının üçüncü karışımının ürettiği elektrokimyasal korozyondur. B) en iyi emülsüzleştirici A, 0.001 mL'den az 42 ppm konsantrasyon emülsiyonunda % 99,96 tuz giderme ile A idi. Perdominant mekanizma, korozyonun yüksek potansiyele (E0: + 0.193V) spontan reaksiyonu nedeniyle elektrokimyasal bir yöntemdir.

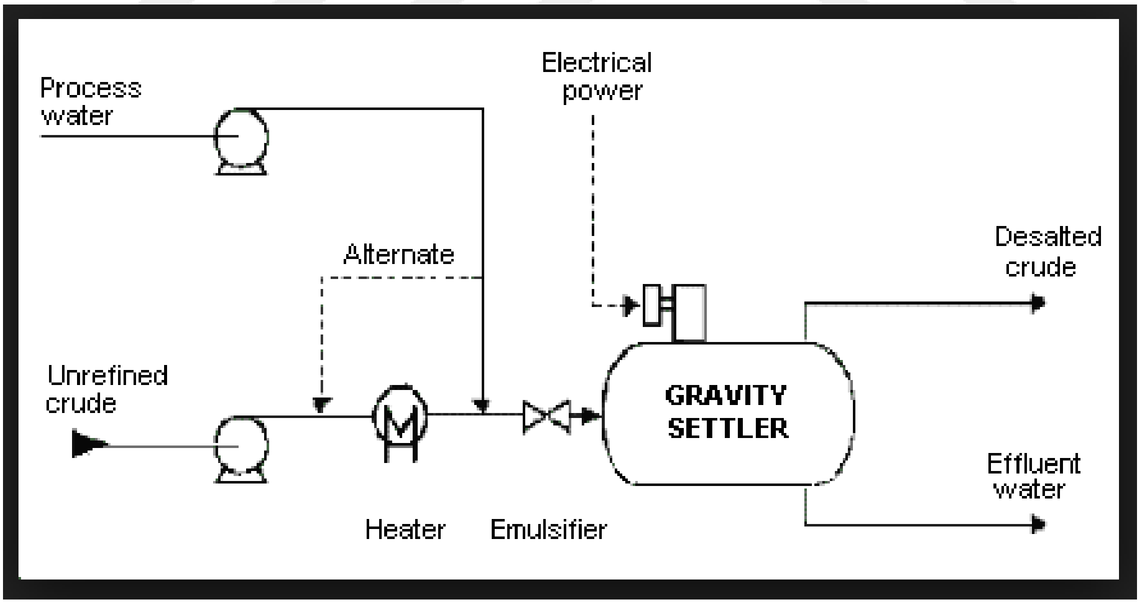
Anahtar kelimeler: Demulsifier, Desalter, Ham Petrol, Korozyon mekanizma, Tuz miktarı.

2. GİRİŞ

Metalik materyaller, saf metaller ve alaşımları doğada bulunanlara benzer sağlam bileşikler oluşturmak amacıyla aşındırıcı bir ortamın unsurlarıyla beraber kimyasal bileşim yapmaya yönelirler. Bu şekilde metal kaybı yaşandığında oluşan bileşim "yenim ürünü" olarak adlandırılır ve metal yüzeyin "yenime uğradığı" söylenir. (Perry, 1997)

Bu suretle Khurmala bölgesinde (Erbil'in 25 km kuzeyinde), petrol ve gaz ile ilgili önemli bir çalışma yürütülmektedir. Bu çalışma, Merkezi İşlem İstasyonunda (CPS) Erbil'e gönderilecek olan ham petrolün çıkarımı ve arıtımı ile ilgilidir.

Ham petrolün çıkarımı esnasında petrolün içerisinde su ve tuz içeriklerinin bulunması gayet doğaldır. CPS'nin üç istasyonu bulunmaktadır: güney, kuzey ve orta istasyon. İşlemlerin başından itibaren petrolün içerisinde yüksek miktarda tuz bulunduğu görülmüştür. Emülsiyonu çözmek ve tuz miktarını azaltmak amacıyla desalinasyon tesisleri kurulmuştur.



Şekil 1.1 Desalter şeması .

Su- petrol ayrımının etkililiğini arttırmak ve tuz miktarını azaltmak amacıyla emülsiyon çözücülerin katkı maddeleri kullanılmış ancak bu işlem yüksek miktarda tuz içeriğine sebep olmuş ve susuz ham petrol alan Erbil rafinerisinin boru hatları ve kimyasal işlemlerinde önemli problemlere neden olmuştur.

Şekil 1.2 CPS Desalator de gözlemlenebilir korozyon durumun örnekleri .

Bu çalışma tuzlu içeriğin korozyon mekanizması üzerindeki etkisini incelemektedir. Korozyon oranını azaltmak ve su \petrol ayrımını etkililiğini arttırmak için çeşitli işlemler gereklidir.

Bu deneysel çalışma planı üç bölümden oluşmaktadır. Belirtiler bölümler çalışmanın en önemli açılarını açıklamaktadır.

Birinci bölüm, bu çalışmanın dayanak noktası olan korozyon mekanizmasının etkisini belirlemenin yanı sıra desalinasyon işlemi, bulunan korozyon seviyeleri, çalışmanın hedefleri, yararları, katkıları, alanı, sınırları ve gerekçeleriyle ilgilidir.

İkinci bölüm, literatür bildirişlerinde belirtildiği gibi hem Irak hem Kürdistan bölgesindeki korozyon tipleriyle ilgili sınırlı bilgiden dolayı çeşitli metod, teknik ve prosedürleri kullanan uluslararası çalışmalarla ilgilidir. Teorik dayanaklar; desalinasyon işleminin en önemli açıları bulunan korozyon tipleri, korozyon mekanizmaları ve bunları belirlemek için kullanılan metodları açıklamaktadır. Ayrıca en önemli olan ve kimyasal korozyon alanında çok az kullanılan terimsel ifadeler belirtilmiştir. Matris; analiz değişkenleri, boyutları, göstergeleri ve kullanılan metodların geçerliliği için istatiski parameterleri belirtmektedir.

Üçüncü bölüm; metodlar, materyaller, uygulanan metodolojik sistemler ile ilgilidir. Bu araştırma, emulsiyon çözücünün optimal konsantrasyonunu belirleme ve korozyon mekanizmasıyla sınırlı olduğu için deneysel olmayan bir çalışmayla transaksiyonel analizi üzerine dayalıdır.

3. AMAÇLAR

3.1. Temel Hedef

Khurmala ham petrolünde tuzlu içeriğin kimyasal korozyon mekanizması üzerindeki etkisinin incelenmesi ve değerlendirilmesi.

3.2. Spesifik hedefler

1. Korozyon işleminin mevcut durumunu belirleyip yeterli bilgi edinmek amacıyla bir strateji geliştirmek.
2. ASTM ve ASME tarafından kullanılan tekniklerin sonuçlarını takiben ana korozyon mekanizmasını belirlemek amacıyla bir çalışma yapmak.
3. Petroldeki tuz içeriğini azaltmak amacıyla emülsiyon çözücünün optimal dozunu belirlemek ve böylece uluslararası standart ve reteransların belirttiği şekilde korozyonu azaltmak.
4. Tuz giderici de emulsiyon çözücünün yeni dozunu uygulamak amacıyla korozyon mekanizmasının etkisini değerlendirmek.

4. KAYNAK BİLDİRİŞLERİ

4.1. Tuz Giderici Bölümlerde Korozyon

Scattergood (2015), bir ham petrol ünitesinde korozyon ve yan ürünlerin çöküntüsünü azaltmak amacıyla sistem parameterlerin optimizasyonuyla ilgili bir metodu incelenmiştir. Bu metod, sistem parameterleriyle ilgili olan özellikleri ölçmekte ve bunları analiz etmek için otomatik bir kontrolör kullanılmaktadır. Herhangi bir akışkanın korozifliğini azaltarak veya sistemi muhtemel korozif bir maddeden koruyarak ham petrol ünitesindeki korozyonu etkili bir şekilde kontrol etmektedir. Ham petrol ünitesinde sistem parameterleriyle ilgili doğru bilgi vermek için incelemeler birkaç yerde yapılmıştır.

4.2. Ham Petrolünde Korozyonu Ölçmek İçin Kullanılan Metodlar

Stern (1958), elektro kimyasal polarizasyondan gelen korozyon oranlarını belirlemek amacıyla bir metod uygulamıştır. Bu tekniğin teorik olarak dayanakları bulunmakta, deneysel çalışmalarla desteklenmekte ve geniş uygulama alanı bulduğu görünmektedir. Bu metodun avantajları ve sınırlılıkları açıklanmıştır.

Doğrusal kutuplanma ölçümlerini kullanmanın birçok değerli bilgiyi sağladığı görünmektedir:

1. Çevresel değişkenlerin korozyon oranı üzerindeki etkisi. Bunlar kompozisyon, hız ve sıcaklık ile ilgili değişkenlerdir.
2. Korozyonu kontrol etmede engelleyicilerin değerlendirilmesi.
3. Benzer kompozisyondaki çeşitli alaşımların korozyon oranlarının karşılaştırılması.
4. Sulu çözeltideki materyallerin yanı sıra yeraltı yapıları da dahil korozyon arasındaki değişikliklerin belirlenmesi.

4.3. Tuz Giderici Bölümlerde Kullanılan Emülsiyon Çözücüler

M. Al- Otaibi (2003), birçok petrol sahasında üretilen petrolün başta sodyum klorür, kalsiyum ve magnezyum olmak üzere tuzlu içerikleri barındırdığını söylemiştir. Ham petrol işlenmezse rafineride çeşitli problemlere sebep olabilir. Bu çalışma deneysel olarak beş faktörün (yerçekimi, kimyasal işlem, tatlı su püskürtmesi, ısıtma ve karıştırma) Kuwaiti ham petrolünde piyasada satılan bir emülsiyon çözücüyü (Servo CC 3408) kullanarak dehidrasyon/Tuz giderme işlemi üzerindeki etkisini incelemektedir.

Kokal (1999) Suudi Arabistan'da büyük bir petrol sahasında karşılaşılan emülsiyon problemlerini incelemiştir. Bu petrol sahası hem denizde hem karada uzanan ve beş farklı rezervuarı bulunan tek sahadır. Burada petroller viskozite açısından 2cP-10 cP (22 C) arasında.

API (Amerikan Petrol Enstitüsü) yer çekimi kuvvet değerleri 28-40 arasında; n-pentan asfalten % 0.2- %7 arasında değişmektedir. Bu özellikler su-petrol ayrımında ilginç işletimsel problemleri göstermektedir. Problemler genel olarak ayırıcının kısa devre yapması, ekipmanların arıza vermesi ve emülsiyon çözücülerin yüksek miktarda tüketimidir.

4.4. Terimsel İfadeler

Santrifüj: Hızlıca dönen bir konteynırla beraber içeriklere santrifüj kuvveti uygulayan bir makinedir. Bu makine genel olarak farklı yoğunluktaki sıvıları katılardan ayırmak için kullanılır.

Bakır Şerit Korozyonu: Petrol ürünlerinin korozyon seviyesini belirlemek için kullanılan nitelikli bir metodtur.

Emülsiyon veya Emülsiyon Edilebilirlik: Bir sıvının(petrolün) emulsiyondan ayrılabilme oranıdır.

PH Ölçer: Bir akışkanın asitlik ve bazlığını ölçmek için kullanılan bir aygıttır. PH ölçer genel olarak PH elektrotları ve referans elektrotları arasındaki elektriksel gerilim farkını ölçmek için volt ölçer olarak kullanılmaktadır.

Tuz Ölçer: Tuzluluğu ya da çözülmüş bir içeriğin tuz oranını belirlemek için kullanılan bir aygıttır.

5. MATERYAL VE YÖNTEM

5.1. Araştırma Türü

Tuz içeriği ve korozyon mekanizmasını kapsayan bu işlem, deneysel bir çalışma olup çözülen katkı maddelerinin dozunu belirlemek için laboratuar ölçeği üzerinde uygulanmıştır. Bu deneysel çalışmanın parametreleri Arias'ın görüşlerine (2004) dayalıdır.

Bu işlem, herhangi bir objeyi veya obje grubunu belli uyarıcılara (bağımsız değişken) maruz bırakarak oluşan etkileri ve reaksiyonları (bağımlı değişken) inceleme üzerine dayalıdır.

Bu çalışmada incelenen deneysel parametreler korozyon oranı, doz seviyesi ve tuz içeriğidir. Ayrıca tuz giderici bölümde korozyon mekanizmasının fiziksel ve kimyasal değişkenlerle ilişkisi ve uluslararası verilerle tutarlılığı incelenmiştir.

Çalışmanın optimizasyonu ve argümantasyonu faktöriyel dizaynlar kullanılarak farklı deneysel durumlarda yer alacaktır.

Korozyon işlemiyle ilgili metalurjide birçok çalışma olduğu için bu deneysel çalışma daha derin bir betimleme sağlamıştır.

5.2. Araştırma Dizaynı

Bu araştırma, çok az sayıda denemeyle beraber değişkenleri incelemeye olanak tanıdığı için deneysel bir faktöriyel dizayn çalışmasına dayalıdır. Araştırmanın amacı doğru metodları kullanarak korozyon oranını belirlemektir.

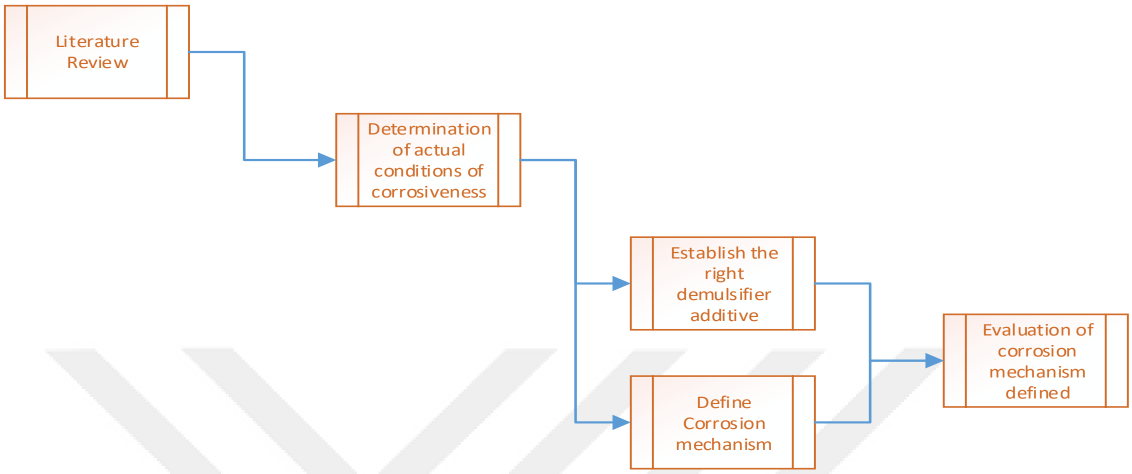
Çizelge 5.1 KAR içinde koroziflik Şartname Denetimi / CPS kompleksi.

Parametre	Resmi Mera
Corrosion rate, max	2 mpy
Water content, Max	2 %
Salt content in crude, max	20 PTB
pH	< 10,5

Source: (KAR Process Handbook, 2010)

Deneysel çalışmanın uygulanması ilk olarak optimize edilmiş düzeyde emülsiyon çözücü dozunu gerektirmektedir.

Belirtilen aşamalar planlanan deneysel dizaynı belirtmektedir.



Şekil 5.1 deneysel dizaynı .

5.2.1. Döküman İncelemesi

1. Bu aşama belirilen faaliyetleri içermektedir:
2. Araştırma merkezleri, kütüphaneler, internet sitelerini yoklamak.
3. İlgili olan bilgi kaynaklarının seçimi.
4. Seçilen kaynakların içerik analizi.
5. Tuz gidericilerde geliştirilen korozyon mekanizmalarıyla ilgili bilimsel, makale ve kaynak kitaplarının kullanımı .
6. Emülsiyon çözücülerinin etkililiğini değerlendirmek için metod incelemesi.

5.2.2. Korozyon İşleminin Mevcut Durumu Belirleyip Yeterli Bilgi Edinmek Amacıyla Bir Strateji Geliştirmek

Bu adım Kurulmuş edilecek testlerin protokol arada gerçek koşullarda, müdahale olmaksızın gerçek bir mekanizma ayrıntıları bilmek için kullanılacaktır.

Çizelge 5.2 Protokol gerçek koşulları elde etmek.

Parameter	Official Method and Procedure
Iron	ASTM D 1193
Water content, Max	NACE/ASTM D1796
Demulsibility	ASTM D2711
pH	ASTM G51/SP0285
Salt content	ASTM/NACE D 3230
Magnesium, Calcium and Total Hardness	ASTM D 2340
Alkalinity in wáter	ASTM D1067-02
Total disolved solids	SM-2540
Disolved Oxygen	ASTM D 888-87
Total Disolved Salts (TDS)	SM-2540
Conductivity	BC 3020
Chloride	ASTM D 4458-05
Density and API	ASTM D 1298
Bottle test	ASTM D 4007

Bu aşamada ele alınacak faaliyetler şunlardır:

1. Kullanıma koymadan önce doğru sonuçlar vermesini sağlamak amacıyla metodların düzenlenmesi ve test edilmesi.
2. Temsili örnekleri yapma ve tuz giderici bölümde korozyon işleminin mevcut durumunu belirleme.

Table 5.3 Örnekleme tarih ve saat.

Date and time of sampling		Types of samples
25/11/2015	8:00 AM	Crude oil before entering into desalter
8/2/2016	1:00 PM	Water from outlet of desalter/first time
10/2/2016	1:00 PM	Water from outlet of desalter/second time
2/12/2015	8:00 AM	Demulsifier/BAKER HUGHES
18/12/2015	8:00 AM	Demulsifier/CHEMIC
5/1/2016	8:00 AM	Demulsifier/TEKKON
15/1/2016	8:00 AM	Demulsifier/PETROFANN

3. Emülsiyon çözücülerin dozunun ve korozyon mekanizmasının belirlenmesi için sonuçların analiz edilmesi.

5.2.3. Petroldeki Tuz İçeriğini Azaltmak Amacıyla Emülsiyon Çözücünün Optimal Dozunu Belirlemek ve Böylece Uluslararası Standart ve Referansların Belirttiği Şekilde Korozyonu Azaltmak

Optimal düzeyde emülsiyon çözücüyü belirlemek için kullanılan sayaç şunları göstermelidir:

1. Düşük tuz içeriği
2. Düşük korozyon oranı
3. Boşaltılmış su oranı

Bu deneyde %10- %150 oranı arasında tuz içeriği tespit edilmiş ve korozyon oranı ölçülmüştür. Bu oranlar ölçüldükten sonra daha uygun korozyon mekanizmaları ve kimyasal- matematiksel simülasyonla tutarlılığı belirlenmiştir. Bu çalışmada NACE ve ASTM metodları kullanılmıştır.

5.2.4. Tuz Gidericide Emülsiyon Çözücünün Yeni Dozunu Uygulamak Amacıyla Korozyon Mekanizmasının Etkisini Değerlendirme

Bu aşamada elde edilen sonuçlar ve uygulanan mekanizma değerlendirilmiştir. Değerlendirme korozyon bölümündeki profesyonel personel tarafından yapılmış ve uygulanan korozyon mekanizması daha öncekilerle karşılaştırılmıştır.

5.3. Yöntem ve Ekipmanları

Bu araştırmada kullanılacak yöntem ve ekipmanları listesi vardır:

Çizelge 5.3 Bu araştırmada kullanılacak KAR'ın yöntem ve teçhizatlarının bir listesi bulunmaktadır.

Parameter	**Equipments**
Water content, Max	Centrifugal Model koehler Instrument company.inc.
Demulsibility	Water bath PMT est.1878 Instrument. HOLLAND
pH	HANNA HI 2211 Ph/ORP meter
Salt content	SALTMETER, STANHOPE-SETA Salt-in-crude analyzer
Iron	Spectrophotometer ECLAB
Magnesium, Calcium and Total Hardness	Volumetric glassware
Alkalinity in water	Volumetric glassware
Total disolved solids	Oven GX-45BE
Disolved Oxygen	Dissolved oxygen test kit, visual colorometric analysis, 1-12 ppm
Total Disolved Salts (TDS)	Volumetric glassware
Conductivity	conductivity meter TRANS BC3020
Chloride	Volumetric glassware
Density and API	Hydrometer and sensitive balance
Bottle test	Water bath PMT est.1878 Instrument. HOLLAND

6. BULGULAR VE TARTIŞMA

Çalışmanın bu bölümünde tuz gidericide korozyon mekanizmalarının nasıl bulunduğu ile ilgili sonuçlar ve açıklamalarda bulunulmuştur.

6.1. Emülsiyon Çözücünün Makul Dozunu Belirlemekle İlgili Sonuçlar

Makul dozdaki emülsiyon çözücü ürünlerden birisidir ki çok az ya da hiç emülsiyon ayrıca tuz gidericide ham petrolden sulu faza geçmiş çözünmüş tuz ile beraber suyun ayrımı için özel bir zamana ihtiyaç duymaktadır.

Koşulların uygulanması ve işleminden sonra her iki faz da (ham petrol ve su) ayrılmıştır. Bu durum, korozyon mekanizmasının tanımlanması üzerinde oldukça etkilidir. Aşağıdaki tablo ve grafiklerde her bir emülsiyon için sonuçlar değerlendirilmiştir.

Uygun emülsiyon çözücüyü seçmek için kullanılan kriterler:

a) Alınan en yüksek su miktarı.
b) Organik fazdan sulu faza doğru alınan en yüksek tuz yüzdesi.
c) Daha düşük ve daha stabil emülsiyon değeri.

6.2. Tuz Giderme Süreci Sırasında Oluşan Korozyon Türlerinin Hesaplanması

6.2.1. Tuz Giderme Süreci Öncesindeki Durumlar

Bir korozyon mekanizmasının var olup olmadığını belirlemek korozyonun yan etkilerini saptamak ve tanımlamak için gereklidir.

Bu koşullara bağlı olarak, belli korozyon mekanizmalarının var olup olmadığını belirlemek için bir dizi hesaplama yapılmıştır. Bu amaçla, ayırma işleminden sonra sıvı örnekler alınmış ve kimyasal karektarizasyona devam edilmiştir. Fazlardan oluşturulmuş ürünlerin karakterizasyon sonuçları şu şekildedir:

6.2.2. Çalışma Sürecinde Korozyon Türlerinin Saptanması ve Tanımlanması

Kimyasal oksijenik korozyon türlerinin tanımlanması kimyasal oksijen yoluyla olmaktadır ve elektro kimyasal oksijenik denge kimyasal oksijenik tuz gidericide oluşmaktadır. Bu açıdan uygulanacak olan yöntemler şunlardır:

1. Heterojen denge (Sürekli çözünürlük ürünü Ksp).
2. Elektro Kimyasal Denge ve Korozyon hücrelerinin varlığı

Uygulanan Kriterler ise şunlardır:

1. Heterojen Denge: Bir kimyasal oksijen bir fazda mevcut olduğunda ve karışma yoluyla korozyona sebep olduğunda daha yüksek bir çözünürlük faktörüne ya da gerekli bir çözünürlük dengesine ihtiyaç vardır. Bu amaçla deneysel Ksp'nin teorik Ksp ile karşılaştırılması kimyasal oksijenik korozyon türlerinin var olup olmadığı ile ilgili ipucu verir.
2. Elektro Kimyasal Denge: Eğer bir korozyon hücre potansiyeli pozitif ise, korozyon da pozitiftir. Bu nedenle, hess operasyonu uygulanmalıdır.

7. SONUÇ

Baskın korozyon mekanizmasını belirlemek amacıyla uygulanan korozyon çalışması, çöküntüleri oluşturmakla kombine edilmiş elektro kimyasal mekanizmadır. Bu çalışma, işlemsel durumları geliştirerek ya da katot (eksi uç) koruması sağlayarak (elektro kimyasal mekanizmasının korunması için en iyi seçenek) hemen bakılması gereken spontane korozyon fenomenini sergilemektedir. Khormala CPS durumu 0.018 V (pozitif) olup korozyon sürecini desteklemiştir.

Çöküntü oluşumundan üretilen korozyon şunların varlığından dolayıdır: ($FeCO_3$, $FePO_4$, $Fe(OH)_3$, $Fe(OH)_2$, FeS, $Mg(OH)_2$, $CaCO_3$, $MgCO_3$).

Desalinasyon sürecinden sonra sudan ayrılan bu bileşikler, korozyon oranını arttıracak bu yüzden en iyi seçenek nötr bir emülsiyon çözücü ve tuz giderici bölümleri koruyan kalite kontrol aracıdır. Diğer bir yandan tuz gidericinin katı bir şekilde tuz üretiminden kaçınmak ve daha iyi çözülmüş tuz üretimi için en iyi seçenek stabil bir araç olacaktır.

Elde edilen sonuçlara göre en iyi emülsiyon çözücü 42 ppm optimal dozuyla Baker emülsiyon çözücüsü olup 1.8 PTB'den daha az tuz vermektedir.

Bu emülsiyon çözücüyle beraber petroldeki tuz içeriği azaltılmaya çalışılacak ve böylece uluslararası standartlar ve kaynakların direkte ettiği şekilde korozyon oranı azaltılacaktır.

CURRICULUM VITAE

He was born in Nawdasht, Sulaimania in Iraq, 1986. He has completed his primary and secondary education in Sulaimania. During the period of 2008-2011 He had studied in University of Sulaimania, the college of Science, Department of Chemistry. After graduating in 2011 He got his first job as chemical treatment in Khurmala Oil Company. At the September of 2014 He started his master study in Yuzuncu Yil university.

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