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Suresh Aluvihara

A Study of the Effects of Crude Oil on the Rate of Corrosion and the Properties of Selected Ferrous Metals

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A STUDY OF THE EFFECT OF CRUDE OIL ON THE RATE OF CORROSION AND THE PROPERTIES OF SELECTED FERROUS METALS

A dissertation submitted to the
Faculty of Science and Technology, Uva Wellassa University in partial fulfilment of the requirements for the award of the Degree of Bachelor of Science in Mineral Resources and Technology

By

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Abstract

In the industry of crude oil refining, can be found wide range of applications of ferrous metals such as in the storage and transportation. The corrosion is a kind of major problem faced in the usage of such ferrous metals. The formation of the oxides, sulfides, hydroxides or the compound related to the carboxylic group on the surface of metal due to the chemical reaction between metals and surrounding are known as the corrosion which is highly depended on the sulfur content, salt content, mercaptans content and the acidity of crude oil as well as the chemical composition of ferrous metals. In the current research it was expected to investigate the effect of Murban and Das blend crude oils on the rate of corrosion of seven different ferrous metals which are used in the crude oil refining industry and also expected to investigate the change in hardness of each metal due to the corrosion. The sulfur content, acidity and salt content of each crude oil were determined. A series of similar pieces of seven different types of ferrous metals were immersed in each crude oil separately for 15, 30 and 45 days. Their rate of corrosion was determined by using their relative weight loss after these time periods. The corroded metal surfaces were observed under the microscope. The hardness of each metal piece was tested before the immersion in crude oil and after the corrosion with the aid of Vicker's hardness tester. It was found that Das blend crude oil contains higher sulfur content and acidity than Murban crude oil. Carbon steel metal pieces show the highest corrosion rates whereas the stainless steel metal pieces show the least corrosion rates in both crude oils. The mild steel piece and the Monel piece show relatively intermediate corrosion rates compared to the other types of ferrous metal pieces in both crude oils. It can be observed that there is a slight decrease in hardness of all the ferrous metal pieces due to corrosion. The corrosion rates of ferrous metals are varied with the properties of crude oils such as sulfur content, acidity and the amount of mercaptans present. Finally the relevant metallic concentration of each crude oil sample was tested using atomic absorption spectroscopy (AAS). According to those results significant Fe and Cu concentrations were observed from some of crude oil samples.

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Chapter 1

Introduction

1.1. Literature Survey

In the industry of crude oil refining, it can be found wide range of applications in ferrous metals along various processes such as transportation, storage and heating. The corrosion is a major problem regarding the usage of ferrous metals in the industry of crude oil refining [1]. The corrosion can be affected adversely for the industry of crude oil refining based on the economy. In briefly the word "corrosion" is expressed an idea about the deterioration of material as a result of interaction between the material and the surrounded environment. As an essential components for the corrosion, the ferrous metal need to exposure either some kind of stronger oxidizing agent than Fe^{2+}or an environment consist with water and oxygen. That process is modified with the effects of acids and salt presence in the medium. Basically regarding the corrosion of ferrous metals the formation of oxide, sulfide or hydroxide on the surface of metal itself. Usually this problem is found in crude distillation column head, heat exchangers transportation tubes and storage tanks. Crude oil is a mixture of hydrocarbon which is not behave as a corrosive compound, however due to the presence of some specific compounds cause the corrosion of metals in different ways. In the crude oil the corrosion of ferrous metal can be explained under different chemical concepts as given in the below.

1.1.1. Corrosion due to the salt

The raw crude oil may consist with different types of salts which are related to the occurrences of crude oil such as NaCl, $CaCl_2$ and $MgCl_2$. During the heating processes of crude oil the temperature raised into higher temperatures of more than 100^0C. At that much of temperatures such salts are broken down into HCl.

$$CaCl_2 + H_2O \longrightarrow CaO + 2HCl \text{………………..} \quad (1.1)$$

HCl is not behave as corrosive compound in the state of gas and with the reduction of the temperature some of HCl molecules tend to be reacted with the moisture and produced hydrochloric acids and also tend to be formed H_2S, which is likely to cause the metallic corrosion.

$$HCl + Fe \longrightarrow FeCl_2 + H_2 \text{ .... } (1.2)$$

$$FeCl_2 + H_2S \longrightarrow FeS + 2HCl \text{ .... } (1.3)$$

The reproducing mechanism of HCl is highly influenced in the continuous process of corrosion of metals. FeS is known as the corrosion compound and it has unique and distinguish properties used to be identified among other compounds.

1.1.2. Corrosion due to the acids

According to the geological formation of crude oil can be consisted with significant amount of naphthenic acids which is having a general formula of RCOOH. In the crude oil chemistry, organic acids are known as "naphthenic acids". Results of the previous researches interpreted some kind of relationships in between the corrosiveness and the amount of acid presence in such crude oil [2]. Even though regarding the past results there cannot be correlated a general relationship in between these two properties. The general chemical reaction happened in the acidic corrosion is given in the below [4].

$$Fe + 2\ RCOOH \longrightarrow Fe(RCOO)_2 + H_2 \text{ .... } (1.4)$$

$$FeS + 2\ RCOOH \longrightarrow Fe\ (COOR)_2 + H_2S \text{ .... } (1.5)$$

$$Fe(COOR)_2 + H_2S \longrightarrow FeS + 2\ RCOOH \text{ .... } (1.6)$$

1.1.3. Corrosion due to the elemental sulfur and organic molecules

Crude oil usually contain sulfur in different forms such as mercaptans, thiophenes, sulfoxides, elemental sulfur and hydrogen sulfide. Most of them are corrosive compounds except a few of them. Sulfur compounds which are having a fraction or functional group can be reacted with metallic compounds tends to be created the corrosion generally called the "sulfidation" [2]. That type of compounds are known as "active sulfur" compounds including elemental sulfur, hydrogen sulfide and mercapatans and also the sulfidation process is depended on the conditions of the temperature. Usually it happens at about 230^0C in properly.

1.1.4. Corrosion due to the effect of bacteria

The effect of microbiology also considered as a prior corrosive factor regarding the crude oil. Under the major processes of reduction of the sulfate the corrosive property mainly the temperature above 40^0C is further described as given in the chemical reaction below [4].

$$SO_4^{2-} + H_2 \longrightarrow H_2S + H_2O \ldots\ldots\ldots\ldots\ldots\ldots (1.7)$$

However in the current research, it was not expected to investigate the effect of the bacteria on the meal corrosion.

1.1.5. Types of corrosion in ferrous metals

In the metallic corrosion, there can be defined various processes with distinguish properties under various conditions such as the composition of such metals, temperature condition and the conditions of surrounding environment [3]. A brief discussion on the types of corrosion and behaviors of them has been given in the Table 1.1.

Table 1.1: Types of corrosion

Corrosion Type	Behaviors
General Corrosion	Associated with atmospheric corrosion. Oxidation and sulfidation in high temperature are the major processes in this type of corrosion.
Pitting Corrosion	Creation of pits on the surface of metal. Pits can be formed within less or lack of general corrosion.
Crevice Corrosion	Similar to pitting corrosion. Associated with crevices. In stainless steel, there can be seen this type of corrosion abundantly.
Intergranular Corrosion	Corrosion reaction is happened in grain boundaries of the metal. Corrosion is happened due to the thermal treatments.
Dealloying	Removal of one element from and alloy into the environment of corrosive.
Corrosion Fatigue	Formation and extension of the cracks due to the overall effect of the stress and corrosive reactions.
Galvanic Corrosion	Acceleration of the corrosion due to the coupling of the noble trace metal with another metal.

Erosion- Corrosion	Acceleration of corrosion due to the flowing fluids, solids or gases while the formation of cavities and eroding the surface of the metal.
Stress Corrosion Cracking	Generation and propagation of cracks due to the overall effect of the corrosive environment and the tensile stress. The process of cracking tend to be increased with the temperature.
Hydrogen Damage	Hydrogen induced cracking with the contribution of tensile stress and hydrogen atoms.

According to the above conditions of the corrosion in the current research, it was expected to describe the general corrosion under the process of sulfidation, pitting corrosion and the partial formation of other types of corrosions regarding the chemical composition of such ferrous metals and crude oils. However the effect of temperature mightn't be investigated in the experiment.

1.1.6. Hardness of metals

The resistance to scratching and to wear of material also generally defined as the resistant to the permanent indentation. According to the values of hardness there can be predicted about the strength of material. However the property of hardness is depended on the structure of the material [3]. And also the hardness of any bulk of material can be varied with the position on the metal surface, which may be affected with the deterioration of the material from the surface of metal. Therefore the investigation of the effect of corrosion on the stability of the hardness is quite important in the science of material and chemical.

1.2. Aims and Objectives

In the current research every kind of tasks were based on the interaction between ferrous metals and crude oil cause the incident of corrosion and the effects of the corrosion on the important properties of ferrous metals such as the hardness as listed in the below.

- ✓ Identification of different types of ferrous metals which are more prone to corrosion when they are exposed to crude oil.
- ✓ Study the rate of corrosion in such ferrous metals.
- ✓ Investigate the mutation of properties due to corrosion in those ferrous metals such as the hardness.
- ✓ Identify the most suitable ferrous metal to be used in crude oil refining industry.

1.3. Achievements

Basically in the current research it was expected to study about the effect of Murban and Das Blend crude oil on rate of corrosion in seven different types of ferrous metals including carbon steel, stainless steel and Monel which are used in the industry of crude oil refining and also the variation of some important properties of such metals due to the corrosion.

As a results of the current research there were obtained the variety of corrosion rate regarding the type of metal and also the composition of such ferrous metals, some sequence of the rate of corrosion with the exposure time in same metal, variation of the hardness due to the corrosion and the invisible weight loss of some metal pieces after exposed to the crude oil as a special incident during the current research.

Chapter 2

Problem Statement

2.1. Preliminaries

In the industry of crude oil there are some different usages of ferrous metals such as storage, transportation and usage for equipment. When concerning about the interaction between metals and crude oil or their end products different types of transactions can be identified with different types of observations and experimental results. Among those interactions some beneficial and adverse effects for the industry also can be categorized. Corrosion is a type of major adverse effect on the metal as well as the industry of crude oil in the economy as well as in the technology such as mutation of original properties of metals and higher maintains cost for equipment after the corrosion. The corrosion is directly effected on the properties of metals such as hardness, tensile strength and toughness. In the industry of crude oil under different stages of refining such as distillation, storage and transportation above properties are much important because of the processes are occurring under high temperature and pressure. Basically in the industry of crude oil formation of the metal sulfide is considered as the corrosion due to the chemical composition of crude oil and also the chemical composition of ferrous metals. Apart from that due to the corrosion, some corrosion compounds might be added into the crude oil and that would be directly affected in the standard chemical composition of the crude oil.

2.2. Problem Statement

When concerning about the corrosion of ferrous metals related to the industry of crude oil the rates of corrosion and the decaying amount of material are highly varied with the chemical compositions of crude oil and metals and also some important components such as carbon composition and chromium composition of metal and the content of sulfur mercaptans in the crude oil. The rate of mutations of some properties also can be explained with the chemical composition of metals and crude oil and the presence of some additives such as alloys. Some of metals show various types of decays such as dissolving, corroding etc. This transaction is an important observation to be theoretically explained with the analysis of experimental results.

Chapter 3

System Modeling

3.1. Selection of samples

In the industry of crude oil ferrous metals are widely used materials which are important in transportation and storage. Due to the interaction between crude oil and metals the decay of metals happened in various amounts based their chemical composition and the conditions of crude oil. The brief introduction about the testing samples is given below.

3.1.1. Ferrous metals

3.1.1.1. Carbon Steel

This is an alloy of iron and carbon containing trace elements such as Chromium, Nickel, Molybdenum, Cobalt, Vanadium and Copper as well as other non-metals such as Phosphorous and Silicon [3]. The percentage of carbon is vary in between 0.06% - 1.5%. According to the composed amount of carbon, steels categorized as give in the Table 3.1.

Table 3.1: Classification of Carbon Steel

Category	Carbon Content (%)
Low Carbon(Mild) Steel	0.15- 0.45
Medium Carbon Steel	0.45-0.80
High Carbon Steel	0.80-1.50

3.1.1.2. Stainless Steel

Stainless steel is a metal which is having good corrosive resistance in each type of environment. It is composed with chromium which is highly corrosive resistant in high sulfur environment and high temperature operations [3]. In the process of petroleum refining the stainless steel play a major role in different processing units. Such as,

- ✓ Crude Distillation
- ✓ UnitTransfer Lines for Preheat Furnaces

- ✓ Hydro- treating unit(Desulfurization)
- ✓ Tube Sheets of Heat Exchangers

The chemical compositions of stainless steel are given in the Table 3.2.

Table 3.2: Chemical composition of Stainless Steel

Element	Wt.%
Cr	12- 18
Ni	0- 8.65
C	0.08- 0.40
Mn	0.28-1.44
P	0.18
Si	0.12
Fe	72.47-88.25

3.1.1.3. Monel

Monel 400 is an alloy of Nickel and Copper it has high strength and toughness with an ability of resistance against the environment of the corrosive. In the industry of crude oil mainly used this metal in the components of heat exchangers of crude oil, transportation pipes, vessels etc. The typical chemical composition of the Monel is given in the Table 3.3.

Table 3.3: Chemical composition of Monel

Element	Wt.%
Ni	63.0
Cu	28.0
Fe	2.5
Mn	2.0
Si	0.5
S	0.02
C	0.3

Due to some enhanced properties of Monel 400 more than carbon steel, it is gained wide range of applications in some chemical and mechanical industries. Such as,

- ✓ Tensile Strength
- ✓ Hardness
- ✓ Compressive Strength
- ✓ Higher Corrosive Resistance

3.1.2. Crude Oil

Crude oil is a naturally occurring liquid which is mixture of hydrocarbon. Crude Oil are mostly consist with elements of Carbon and Hydrogen any also contained with small amounts of Sulfur, Nitrogen and Oxygen. Crude Oil are containing three basic chemical series.

- ✓ Paraffin
- ✓ Naphthene
- ✓ Aromatics

3.1.2.1. Murban

Murban is a type of crude oil which is imported to Sri Lankan refineries from Abu Dhabi. According to the type of formation of the crude oil the chemical and physical properties might be varied. Some important physical and chemical properties of Murban crude oil are given in the Table 3.4.

Table 3.4: Properties of Murban crude oil

Property	**Value**
API Gravity	40.5
Total Sulfur (wt %)	0.78
Mercaptan Sulfur(ppm)	25
Acidity (mg KOH/g)	0.01
Salt Content	Trace

3.1.2.2. Das Blend

Das Blend is a type of crude oil imported from Abu Dhabi which has some of relatively high percentage of total sulfur amount. Some of physical and chemical properties of Das Blend crude oil are given in the Table 3.5.

Table 3.5: Properties of Das Blend crude oil

Property	Value
API Gravity	39.2
Total Sulfur (wt %)	1.12
Mercaptan Sulfur	56
Acidity (mg KOH/g)	0.02
Salt Content	Trace

3.2. Methods and Techniques

3.2.1. Weight loss method

The rate of corrosion of each metal can be determined in the method of weight loss. This is the simplest method in corrosion rate analyzing and can be expressed an important parameter about the corrosion of metal. The most important readings under this analysis are the initial weight of metal piece before expose to the corrosive environment and the final weight of the cleaned metal piece after the corrosion. In this method the rate of corrosion can be determined without following complex procedure and using complex equipment. In here the most important thing is requirement of metal piece with the appropriate shape because of the surface area of metal piece also need to be calculated as a factor of the formula. Some special advantages in usage of this method are given in the below.

- ✓ No need any sophisticated instrument.
- ✓ Direct readings can be obtained.
- ✓ Applicable in every type of corrosive environments.

The equation 3.1 expressed the terms of corrosion rate due to the method of weight loss and the terms are defined below.

$$CR = \frac{W}{(D \times A \times t)} \times k \qquad \text{............ (3.1)}$$

Where;

W = weight loss in grams

k = constant (22,300)

D = metal density in g/cm^3

A = area of metal piece ($inch^2$)

t = time (days)

CR= Corrosion rate of metal piece

3.2.2. Microscopic Analysis

The qualitative analysis of metal corrosion on the surface of the metal piece was the major purpose regarding the analysis of microscope. An optical microscope was used in the experiment and the metal surface was observed under 400X lens before the immersion in the crude oil and after the corrosion. In the classification of corroded particles on the metal surface, some important physical properties were used as indicators and also some specific colors have been used in the identification of corrosive compounds such as metal oxides and metal sulfides.

3.2.3. Hardness Test

The hardness test was performed to test the mutation of the hardness of metal piece due to the corrosion. The instrument was the Vicker's hardness tester. According to the hardness scale of Vicker's usually the hardness value interprets as a numerical value relevant to the tested position on the metal surface. In the further explanation of the theory behind the test method of hardness, can be explained under the expression given in the below.

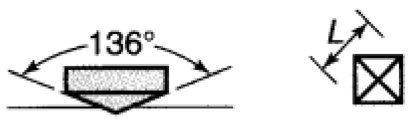

Figure 3.1: The indenter of Vicker's hardness tester

$$HV = \frac{1.854\ P^2}{L^2} \quad \text{.........................} \quad (3.2)$$

Where;

HV= Hardness

P= Applied Load on the surface of metal

L= Diagonal length of square

In the testing method of hardness a load is applied via a pyramid shape diamond indenter and the diagonal length on the metal surface which is created by the tip of the indenter of the hardness tester is the reading of the machine. Using equation 3.2 the Vicker's hardness number is calculated although the determined Vicker's hardness number is given as the reading in digital Vicker's hardness tester.

3.2.4. Analysis of dissolved metal concentration in crude oil

Due to the chemical interaction in between the metal and the crude oil, some amount of metal tend to be dissolved in crude oil and the analysis and interpretation of the metal concentration in crude oil are the purposes of the analysis of metal concentration in each crude oil sample using atomic absorption spectroscopy (AAS). Regarding crude oil samples interacted with Monel metal which is composed high percentage of Cu were tested for the concentration of Cu and other samples of crude oil were tested for the concentration of Fe respect to the interacted metals such as carbon steel and stainless steel. In the sample preparation 1ml of each crude oil sample was diluted with 9ml of 2-propanol and filtered out some precipitates.

3.2.5. Test of some important properties of crude oil

In this experiment some of important corrosive properties were tested regarding both crude oil by following standard methods and instruments. A descriptive summary of those experiments have been given in the Table 3.6.

Table 3.6: Important properties of crude oil

Property	Chemicals	Procedure	Instrumentation	Data Recording
Sulfur Content	-	Directly used the sample	XRF Analyzer	Direct Reading
Salt Content	Organic Solvents	Sample is dissolved in a solvent and exposed to the test cell.	Analyzer of salt in crude oil	Direct Reading
Acidity	Toluene, Isopropyl and Potassium Hydroxide	Crude oil sample is dissolved in a mixture of toluene and isopropyl. The mixture was	-	End point of the titration

		titrated with potassium hydroxide		
Mercaptans Content	Sodium Acetate, Silver Nitrate	Crude oil sample is dissolved in Sodium Acetate and titrated potentiometrically with Silver Nitrate Solution	Glass reference electrode and Silver Sulfide indicating electrode	End point of the titration

Chapter 4

Theoretical Development

4.1. Analysis of the corrosion

The corrosion of ferrous metal can be analyzed in several ways which can be classified as qualitatively and quantitatively. In the current research there were used some analytical method to represent both qualitative and quantitative analysis of the corrosion of metal on the surface of each metal. Under the scope of the research it was tested the hardness of each metal piece before and after the immersion of crude oil and using the hardness difference the variation of the hardness was calculated.

4.2. Sequence of the corrosion rate

According to the equation of the corrosion rate calculation, the corrosion rate is inversely proportional with the exposure time of some particular metal. At the beginning it was expected to interpret some specific sequence in the rate of corrosion with the exposure time and also it was expected to derive suitable mathematical formula regarding the variation of corrosion rate with the exposure time. The results of the current research proved that conditions. Because the rate of corrosion in same metal piece was reduced when increase the exposed time.

4.3. Relationship between the corrosion rate and hardness

At the beginning, it was expected to test whether there can be built any relationship between the rate of corrosion and the mutation of the hardness. But anyway according to the variation of hardness unable to keep in order as a symmetric distribution of that property while the rate of corrosion shows symmetric distribution in each type of metal.

4.4. Decay of metal into the crude oil

According to the obtained results due to the current research it was observed some invisible weight loss of metal pieces apart from the corrosion. Under that phenomenon it was expected to build some satisfaction with the total weight loss and metal decay. But anyway the decay of metal also was not happened in symmetric way.

Chapter 5

Methodology

5.1. Methodology of composition test of metals

The compositions of each type of metal were detected by using the XRF detector. According to the conditions of the XRF detector, allowed to detect the concentration of each metallic element and some of non-metallic elements except carbon presence in the ferrous metals as a percentage of the weight.

5.2. Methodology of corrosion test

In the current research, there were used seven different types of ferrous metals as same dimension in each metal piece and six metal pieces were prepared from each metal type. Each metal surface was entirely cleaned to remove impurities and corroded particles. The dimensions and the initial weight of each metal piece was measured by using vernier caliper, meter ruler and the analytical balance. Each metal piece was completely immersed in the relevant crude oil separately for certain period of exposure time. As a first stage, after 15 days one metal piece was taken out from every types of ferrous metals and also relevant to both crude oil. As further stages after 30 days and after 45 days the same procedure was repeated. The surfaces of the immersed metal pieces were observed under the 400X lens in optical microscope as a qualitative analysis of the corrosion on the metal surface itself. The corroded particles were removed from the surface of each metal piece using a mechanical method with the aid of sand papers and isooctane as a corrosive protection compound. At the end of the cleaning the weight of each metal piece was measured by using analytical balance and with the difference in between the initial weight and the final weight the weight loss was determined. Apart from that the total surface areas and the densities were calculated regarding each metal piece. Finally the corrosion rate of each metal piece was calculated by using the equation given in the below.

$$CR = \frac{W}{(D \times A \times t)} \times k \qquad \text{……………………. (5.1)}$$

Where;

W = weight loss in grams

k = constant (22,300)

D = metal density in g/cm^2

A = area of metal piece (inch^2)

t = time (days)

CR= Corrosion rate of metal piece

5.3. Methodology of microscopic analysis

As a part of qualitative analysis of the corrosion on the surface of metal the microscopic analysis was used under the 400X lens in optical microscope. Before the immersion and after the immersion the microscopic analysis was performed to identify the formation of the corrosion on the surface of metal. Finally the microscopic observation of cleaned metal surface was investigated the degree of removing the corrosion from the surface of the metal. In the analysis of corrosion on the surface of the metal, it was based on the physical appearances of those compounds foremost the color and also the distribution of the corrosion on the surface of metal.

5.4. Methodology of hardness test

Based on the investigation of the variation of hardness on the corroded metal surface the hardness test was performed. The initial hardness of each metal piece was tested before the immersion in the crude oil and the same test was done after immersion of the metal piece in crude oil by using the Vickers hardness tester which gives direct reading for hardness with respect to the corresponding position on the metal surface as a numerical reading. According to the procedure of the hardness testing, there were tested at least three positions on the metal surface and the average value of those readings were interpreted as the overall hardness of the metal piece.

5.5. Methodology of the test of properties in crude oil

When testing the corrosive properties of crude oil the sulfur content of both crude oil was tested by XRF analyzer. Salt content in both crude oil was tested using analyzer of the salt in crude oil digital instrument. The samples of both crude oil were diluted with organic solvent by mixing 5ml of each crude oil sample with 5 ml of organic solvent. The acidity and the amount of mercaptans sulfur in both crude oil were determined by using ASTM potentiometric titration methods.

5.6. Methodology of the test of the metal concentration in crude oil

In the analysis of the metal concentration in crude oil samples with respect to each type of metal the atomic absorption spectroscopy (AAS) was used as the instrument. According to the procedure of sample preparation 1ml of each crude oil sample was diluted with 9ml of 2-propanol separately and each sample was filtered out altogether as 14 samples. The Fe concentrations were tested in 12 crude oil samples which were respected to the carbon steel and stainless steel while Cu concentrations were tested in 2 crude oil samples which were respected to the Monel metal. As the blank solution for the instrument the 2-propanol solution was used. Finally the readings were recalculated by multiplying the factor of dilution respect to the Fe and Cu elements.

Chapter 6

Results, Analysis and Discussion

According to the observations and readings of the experiment the results and the analysis of those results have been discussed in this chapter.

6.1. Chemical composition of metals

The chemical compositions of used metals in the experiments according to the XRF analysis are given in the Table 6.1.

Table 6.1: Chemical composition of metals used in the experiment

Metal	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cr (%)	Cu (%)	P (%)	Mo (%)	Si (%)	S (%)	Ti (%)	V (%)
Carbon Steel (High)	98.60	0.43	-	0.17	0.14	0.37	0.12	0.086	0.09	-	-	-
Carbon Steel (Medium)	99.36	0.39	-	-	-	-	0.109	-	0.14	<0.02	<0.04	-
410-MN: 1.8 420- MN: 2.8 (Stainless Steel)	88.25	0.28	-	0.18	10.92	0.10	0.16	-	0.11	-	-	-
410-MN: 1.7 420- MN: 1.7 (Stainless Steel)	87.44	0.30	-	-	11.99	-	0.18	-	0.09	-	-	-
Monel 400	1.40	0.84	0.11	64.36	<0.04	33.29	-	-	-	-	-	-

321-MN:1.4 304- MN:1.9 (Stainless Steel)	72.47	1.44	-	8.65	17.14	-	0.18	-	0.12	-	-	-
Carbon Steel (Mild Steel)	99.46	0.54	<0.30	-	<0.07	-	-	-	-	-	<0.19	<0.07

According to the chemical composition of ferrous metals the variations in the elements can be identified. Basically in carbon steel, the ferrous content is approximately near 99% and it is also composed with some trace elements such as Ni, Cr and Cu. Apart from that some of them are composed of non-metals such as S and Si due to the purposes of enhancements of the properties of those metals such as hardness and strength [1] [3].

Regarding the composition of stainless steel, those metals are also highly composed with the element of ferrous. According to these results the Fe composition of stainless steel is less than that of carbon steel and also the stainless steels are highly composed with Cr in between the range of 11-18%. Based on the purpose of prevention of the corrosion, the Cr composition has been increased while doping some amount of Ni. In a certain ratio between Ni and Cr the surface of metal tend to be created some corrosive protection film [1] [3]. The minimum requirement of the Cr amount for that protection film is approximately 12%. In the composition of trace element in stainless steel, the percentage of Cr was represented significant amount. As same as in the carbon steel, stainless steel also composed with some non-metals such as S and Si for the same purposes as mentioned about carbon steel.

According to the chemical composition of Monel metal, the major element present is Ni. And also it is composed of Cu. Unlike in the other metal used, Fe plays a role of a trace element which appears as 1.4%. Beside of the corrosion due to the iron, Cu and Ni also tend to be created some corrosive compounds such as oxides and sulfides [5].

6.2. Tested corrosive properties of crude oil

6.2.1. Sulfur content in both crude oil

The contents of sulfur as an element in both crude oil according to the readings of XRF analyzer are given in the Table 6.2.

Table 6.2: Sulfur content of crude oils used

Crude oil	Sulfur Percentage (wt. %)
Murban	0.758
Das Blend	1.135

According to the results of sulfur percentages of crude oils, the highest sulfur percentage was observed with Das Blend crude oil. The reaction of elemental sulfur and sulfur compounds with the water presence in crude oils at some high temperatures, tend to be caused the metallic corrosion which is called as the localized corrosion[6]. And also the elemental sulfur tend to be formed the iron sulfide on the surface of the metal as given in the reaction below.

$$8\ Fe + S_8 \longrightarrow 8\ FeS \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

Therefore, according to the results of the sulfur content in both crude oils, Das Blend crude oil has the higher tendency of corrosion than the Murban crude oil with the collaboration of environmental conditions such as the temperature.

6.2.2. Salt content in both crude oils

The content of salt in both crude oil according to the digital analyzer are given in the Table 6.3.The values are given in the unit of pounds per thousand barrels (ptb).

Table 6.3: Salt content in both crude oils

Crude oil	Salt content/ ptb
Murban	4.4
Das Blend	3.6

When comparing the results of the salt content in both crude oils, it was shown higher amount of salt in Murban crude oil than the salt content in Das Blend crude oil. Due to the chemical reaction between those salts and water at some higher temperatures, salts can be broken into HCl. When the system is approaching to the low temperatures, those HCl can be behaved as a highly corrosive compounds and finally, it can be formed the metal sulfide on the surface of metal as explained in the equations below [7].

$$CaCl_2 + H_2O \longrightarrow CaO + 2HCl \quad \text{.................. (6.2)}$$

$$HCl + Fe \longrightarrow FeCl_2 + H_2 \quad \text{..................... (6.3)}$$

$$FeCl_2 + H_2S \longrightarrow FeS + 2HCl \quad \text{.................. (6.4)}$$

In this experiment, the salt content as a mixture of NaCl, $MgCl_2$ and $CaCl_2$ in each crude oil was tested. So the above chemical reaction can happen with each of chloride. Under that condition the corrosive tendency of Murban crude oil is higher than the corrosive tendency of Das Blend crude oil.

6.3. Corrosion rate of metals

6.3.1. Corrosion rate of metals after 15 days in Murban crude oil

The rates of corrosion of metals exposed to the Murban crude oil with in the period of 15 days are given in the Table 6.4.

Table 6.4: Corrosion rate of metalafter 15 days in Murban crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)**
1	Carbon Steel(High)	0.811971
2	Carbon Steel(Medium)	0.817791
3	410-MN: 1.8 420- MN: 2.8 (Stainless Steel)	0.041784
4	410-MN: 1.7 420- MN: 1.7 (Stainless Steel)	0.11626
5	Monel 400	0.356263
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.016612
7	Carbon Steel (Mild Steel)	0.10973

According to the above results the highest corrosion rate was observed with carbon steel (medium) while the least corrosion rate was shown by 321-MN: 1.4 304- MN: 1.9 (Stainless Steel). As overall results a series of carbon steel showed the highest corrosion rate in Murban crude oil.

6.3.2. Corrosion rate of metals after 15 days in Das Blend crude oil

The rates of corrosion of metals exposed to the Das Blend crude oil with in the period of 15 days are given in the Table 6.5.

Table 6.5: Corrosion rate of metals after 15 days in Das Blend crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}days^{-1}$)**
1	Carbon Steel(High)	0.350249
2	Carbon Steel(Medium)	0.481055
3	410-MN: 1.8 420- MN: 2.8 (Stainless Steel)	0.044146
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	0.053701
5	Monel 400	0.061554
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.022894
7	Carbon Steel (Mild Steel)	0.162883

According to the above results the highest corrosion rate was observed with carbon steel (medium) while least corrosion rate was observed with 321-MN: 1.4 304- MN: 1.9 (Stainless Steel) in Das Blend crude oil. In both crude oil the Monel metal showed an intermediate corrosion rate which is frequent with mild steel.

6.3.3. Corrosion rate of metals after 30 days in Murban crude oil

The rates of corrosion of metals exposed to the Murban crude oil with in the period of 30 days are given in the Table 6.6.

Table 6.6: Corrosion rate of metals after 30 days in Murban crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}days^{-1}$)**
1	Carbon Steel(High)	0.466425
2	Carbon Steel(Medium)	0.180339
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	0.016075
4	410-MN: 1.7 420- MN:1.7	0.011968

	(Stainless Steel)	
5	Monel 400	0.034877
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.007453
7	Carbon Steel (Mild Steel)	0.048244

According to the above results, there were shown the highest rate of corrosion in carbon steel (high) while the least corrosion rate was observed with 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) also the high corrosion rates were observed with carbon steel. The rate of corrosion in carbon steel (high) was raised up according to these observations.

6.3.4. Corrosion rate of metals after 30 days in Das Blend crude oil

The rates of corrosion of metals exposed to the Das Blend crude oil with in the period of 30 days are given in the Table 6.7.

Table 6.7: Corrosion rate of metals after 30 days in Das Blend crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)**
1	Carbon Steel(High)	0.224901
2	Carbon Steel(Medium)	0.140654
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	0.034035
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	0.034841
5	Monel 400	0.037655
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.006503
7	Carbon Steel (Mild Steel)	0.141093

According to the above results, there were shown the highest corrosion rate in carbon steel (high) while the least corrosion rate was observed with 321-MN: 1.4 304- MN: 1.9 (Stainless Steel) as usual also in here some significant difference can be identified between the rate of corrosions in carbon steel (high) and carbon steel (medium). In both crude oil, mild steel and Monel metal showed intermediate corrosion rate again.

6.3.5. Corrosion rate of metals after 45 days in Murban crude oil

The rates of corrosion of metals exposed to the Murban crude oil with in the period of 45 days are given in the Table 6.8.

Table 6.8: Corrosion rate of metals after 45 days in Murban crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)**
1	Carbon Steel(High)	0.068794
2	Carbon Steel(Medium)	0.073358
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	0.011801
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	0.007574
5	Monel 400	0.026729
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.005599
7	Carbon Steel (Mild Steel)	0.038592

6.3.6. Corrosion rates of metals after 45 days in Das Blend crude oil

The rates of corrosion of metals exposed to the Das Blend crude oil with in the period of 45 days are given in the Table 6.9.

Table 6.9: Corrosion rate of metals after 45 days in Das Blend crude oil

Metal Number	**Metal**	**Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)**
1	Carbon Steel(High)	0.024738
2	Carbon Steel(Medium)	0.05911
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	0.006149
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	0.016363
5	Monel 400	0.016067

6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.002825
7	Carbon Steel (Mild Steel)	0.100635

6.3.7. Average corrosion rate of metal pieces

The average corrosion rate with respect to the each type of metal regarding each crude oil are given in the Table 6.10 and Table 6.11 which are representations of the behavior of corrosion of each type of metal relevant to the each type of crude oil.

Table 6.10: Average corrosion rate of metals in Murban crude oil

Metal Number	Metal	Average Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)
1	Carbon Steel(High)	0.449063
2	Carbon Steel(Medium)	0.357162
3	410-MN: 1.8 420- MN: 2.8 (Stainless Steel)	0.02322
4	410-MN: 1.7 420- MN: 1.7 (Stainless Steel)	0.045268
5	Monel 400	0.13929
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.009888
7	Carbon Steel (Mild Steel)	0.065522

Table 6.11: Average corrosion rate of metals in Das Blend crude oil

Metal Number	Metal	Average Corrosion Rate /(cm^3 $inch^{-2}$$days^{-1}$)
1	Carbon Steel(High)	0.199963
2	Carbon Steel(Medium)	0.22694
3	410-MN: 1.8 420- MN: 2.8 (Stainless Steel)	0.02811
4	410-MN: 1.7 420- MN: 1.7 (Stainless Steel)	0.034968
5	Monel 400	0.038425

6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	0.01074
7	Carbon Steel (Mild Steel)	0.13487

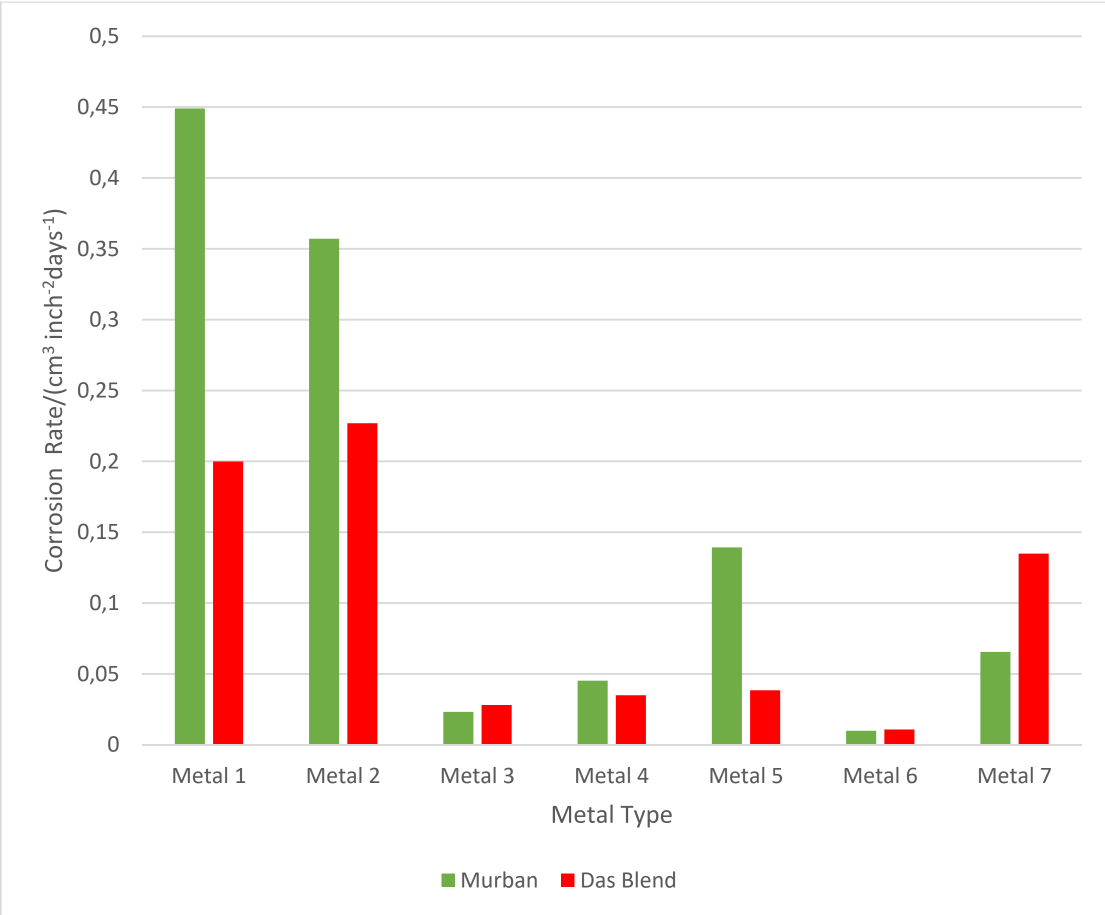

Figure 6.1: Average corrosion rate of metals in both crude oil

Above results showed the different rates of ferrous metal corrosion in both crude oiland also the least corrosion rate was observed from the stainless steel as assumed at the beginning of the implementation of the current research. According to the theoretical concept about the stainless steel, it is composed with amount of Cr mixed with Ni which can be attacked against corrosive media with the effect of Ni and Cr protection film for the corrosive conditions. The minimum Cr content for above protective film is 12% and also 18% of Cr is most stable [1] [4] [5]. The least corrosion rate was observed from stainless steel which is composed 18% of Cr and also relatively lower corrosion rates were observed form stainless steel which are composed 12% and 13% of Cr. According to the variety of corrosion rate of carbon steel there were observed the reduction of the rate of corrosion with the content of carbon in order to highest corrosion rate from high carbon steel and lowest corrosion rate from mild steel among carbon steels.

When considering the influence of the salt content and sulfur percentage of both crude oil, there were observe higher salt content from Murban and higher sulfur percentage from Das Blend crude oil. According to the analyzed results, most of metals showed higher corrosion rate in Murban than the corrosion rate in Das Blend crude oil. In the consideration of those properties and corrosion rate of metals in both crude oil, it can be concluded that the corrosive tendency of Murban is higher than the corrosive tendency of Das Blend crude oil. In the explanation, it was suggested that the corrosion of metal due to the influence of salts is happened stronger than the process of "Sulfidation" which happened due to the presence of sulfur in crude oil. Further the conditions of temperature can be expressed as the reason for the variations of those processes. Usually the process of breaking sulfide is occurred at high temperatures and formed HCl can be remained in the crude oil and under the low temperature conditions it tends to react with moist and to form FeS. But the "Sulfidation" process is properly occurred at high temperatures the range in between 230-460^0 C while presence of elemental sulfur or sulfur compounds in the crude oil [8]. Even in the performance of experiment under the room temperature, it can be concluded the corrosion occurred due to the presence of salt in crude oil in most of cases.

Apart from that some of metals showed higher corrosion rate in Das Blend crude oil than the Murban crude oil. In the consideration of other corrosive properties of crude oil the acidity plays a major role [9] which the presence of naphthenic acid and organic acids in crude oil. The influence of the acids in the corrosion of metal is explained in the chemical reactions below.

$$Fe + 2\ RCOOH \longrightarrow Fe(RCOO)_2 + H_2 \text{.........} \ (6.5)$$

$$FeS + 2\ RCOOH \longrightarrow Fe\ (COOR)_2 + H_2S \text{........} \ (6.6)$$

$$Fe(COOR)_2 + H_2S \longrightarrow FeS + 2\ RCOOH \text{.........} \ (6.7)$$

According to the acidity of both crude oil, the acidity of Das Blend crude oil is relatively higher than the acidity of Murban crude oil. This reason can be suggested as the reason for the observations of high corrosion rate of some metals in Das Blend crude oil.

6.3.8. Variation of the corrosion rate of metal pieces with the exposure time.

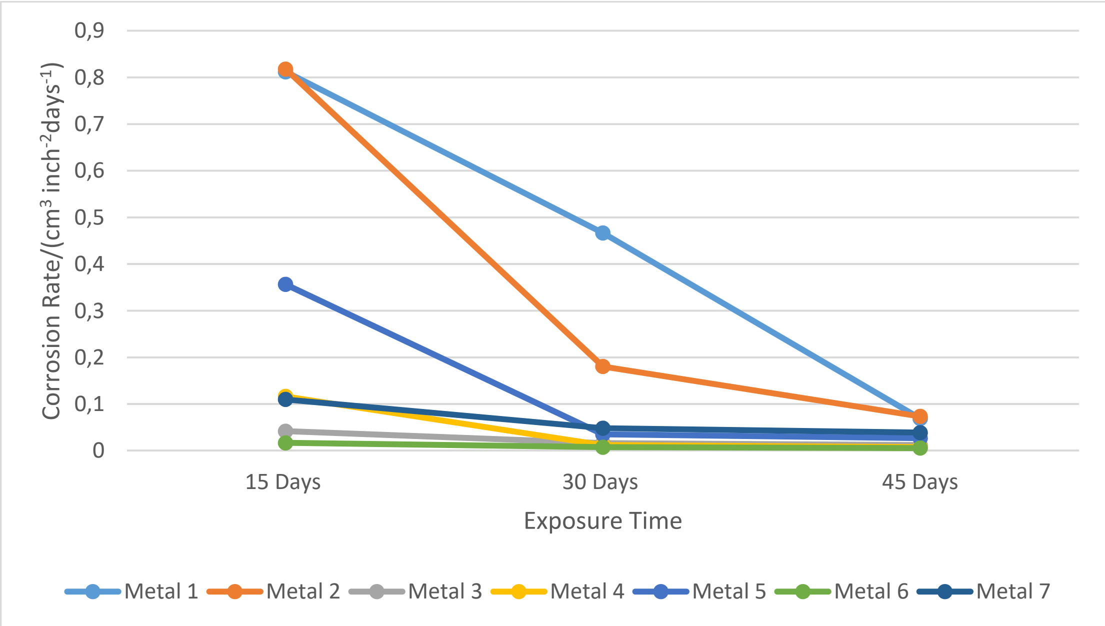

Figure 6.2: Variation of the rate of corrosion in Murban with exposed time

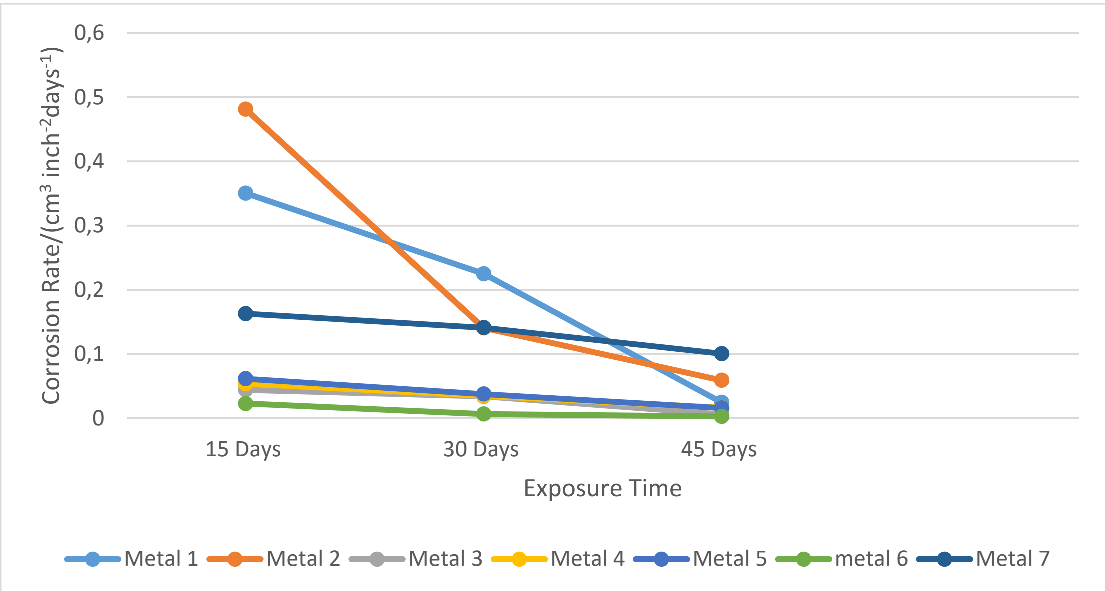

Figure 6.3: Variation of the rate of corrosion in Das Blend with exposed time

Above results showed the reduction of the rate of corrosion in same metal type regarding the same crude oil. According to the variation of the rate of corrosion in same metal piece with the immersed time period, the rate of corrosion was decreased when the immersion time period was increased can be proved the relationship of the equation in weight loss method [10].

6.4. Hardness of metal pieces

6.4.1. Initial hardness of metal pieces

The average initial hardness of each metal type according to the Vickers hardness tester is given in the Table 6.12.

Table 6.12: Initial hardness of metal pieces according to the Vicker's hardness tester

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	267.63
2	Carbon Steel(Medium)	215.2
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	207.43
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	184.5
5	Monel 400	269.3
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	225.13
7	Carbon Steel (Mild Steel)	265.85

According to the initial hardness of metals the highest initial harness was observed from Monel. Also relatively higher hardness was observed from carbon steel than stainless steel. By considering the iron percentage and carbon percentage it can be concluded the hardness of metals is increasing with the amount of carbon present in the metal [1].

6.4.2. Hardness of metal pieces after the corrosion of 15 days in Murban crude oil

The average hardness of each metal piece after the corrosion in Murban crude oil within 15 days is given in the Table 6.13.

Table 6.13: Hardness of metal pieces after the corrosion of 15 days in Murban crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	258.38
2	Carbon Steel(Medium)	203.75
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	185.28
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	182.68
5	Monel 400	251.9
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	212.23
7	Carbon Steel (Mild Steel)	263.68

According to the results in Table 6.12 and 6.13, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Murban crude oil in the period of 15 days.

6.4.3. Hardness of metal pieces after the corrosion of 15 days in Das Blend crude oil

The average hardness of each metal piece after the corrosion in Das Blend crude oil within 15 days is given in the Table 6.14.

Table 6.14: Hardness of metal pieces after the corrosion of 15 days in Das Blend crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	258.85
2	Carbon Steel(Medium)	204.33
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	179.75
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	173.55
5	Monel 400	262.45
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	224.68

7	Carbon Steel (Mild Steel)	261.43

According to the results in Table 6.12 and 6.14, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Das Blend crude oil in the period of 15 days. In the comparison of the reduction of the value of hardness in both crude oil unable to distinguish the variation of hardness.

6.4.4. Hardness of metal pieces after the corrosion of 30 days in Murban crude oil

The average hardness of each metal piece after the corrosion in Murban crude oil within 30 days is given in the Table 6.15.

Table 6.15: Hardness of metal pieces after the corrosion of 30 days in Murban crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	260.9
2	Carbon Steel(Medium)	207.85
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	150.075
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	167
5	Monel 400	250.625
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	219.275
7	Carbon Steel (Mild Steel)	243.35

According to the results in Table 6.12 and 6.15, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Murban crude oil in the period of 30 days.

6.4.5. Hardness of metal pieces after the corrosion of 30 days in Das Blend crude oil

The average hardness of each metal piece after the corrosion in Das Blend crude oil within 30 days is given in the Table 6.16.

Table 6.16: Hardness of metal pieces after the corrosion in 30 days in Das Blend crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	260.2
2	Carbon Steel(Medium)	210.975
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	188.2
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	166.175
5	Monel 400	252.775
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	201.725
7	Carbon Steel (Mild Steel)	247.375

According to the results in Table 6.12 and 6.16, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Das Blend crude oil in the period of 30 days.

6.4.6. Hardness of metal pieces after the corrosion of 45 days in Murban crude oil

The average hardness of each metal piece after the corrosion in Murban crude oil within 45 days is given in the Table 6.17.

Table 6.17: Hardness of metal pieces after the corrosion of 45 days in Murban crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	254.925
2	Carbon Steel(Medium)	200.35
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	194.775
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	190.2
5	Monel 400	248.375
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	213.625

7	Carbon Steel (Mild Steel)	244.225

According to the results in Table 6.12 and 6.17, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Murban crude oil in the period of 45 days.

6.4.7. Hardness of metal pieces after the corrosion of 45 days in Das Blend crude oil

The average hardness of each metal piece after the corrosion in Das Blend crude oil within 45 days is given in the Table 6.18.

Table 6.18: Hardness of metal pieces after the corrosion of 45 days in Das Blend crude oil

Metal Number	Metal	Hardness(HV)
1	Carbon Steel(High)	254.2
2	Carbon Steel(Medium)	194.75
3	410-MN: 1.8 420- MN:2.8 (Stainless Steel)	188.575
4	410-MN: 1.7 420- MN:1.7 (Stainless Steel)	171.225
5	Monel 400	255.475
6	321-MN:1.4 304- MN:1.9 (Stainless Steel)	201.1
7	Carbon Steel (Mild Steel)	226.1

According to the results in Table 6.12 and 6.18, there can be identified slight reductions of the value of hardness from the initial hardness of each metal after the corrosion in Das Blend crude oil in the period of 45 days.

6.4.8. Variations of the hardness of metal after corrosion of 15 days period in both Murban and Das Blend crude oil

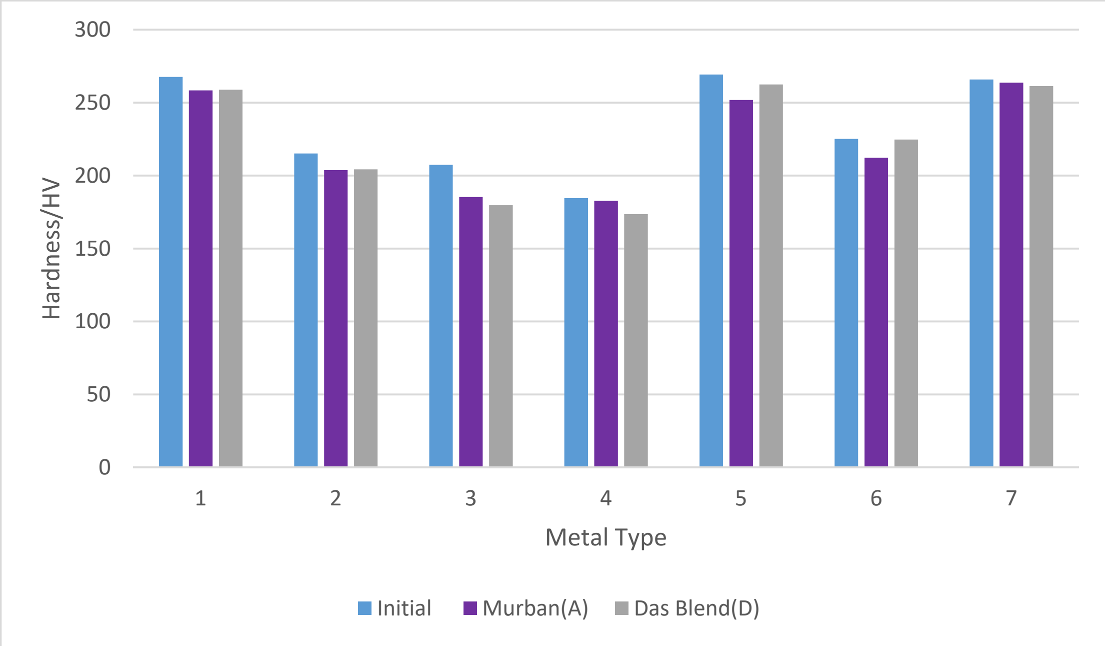

Figure 6.4: Variations of hardness of metal pieces after 15 days exposure time in both crude oil

After the immersion time period of 15 days in crude oil, there were identified the reduction of hardness simultaneously with the corrosion. When comparing types of metals, in carbon steels the reduction of hardness has not occurred in significant way and even in stainless steels the reduction of hardness has not occurred in considerable amount

6.4.9. Variation of the hardness of metals after corrosion of 30 days period in both Murban and Das Blend crude oil

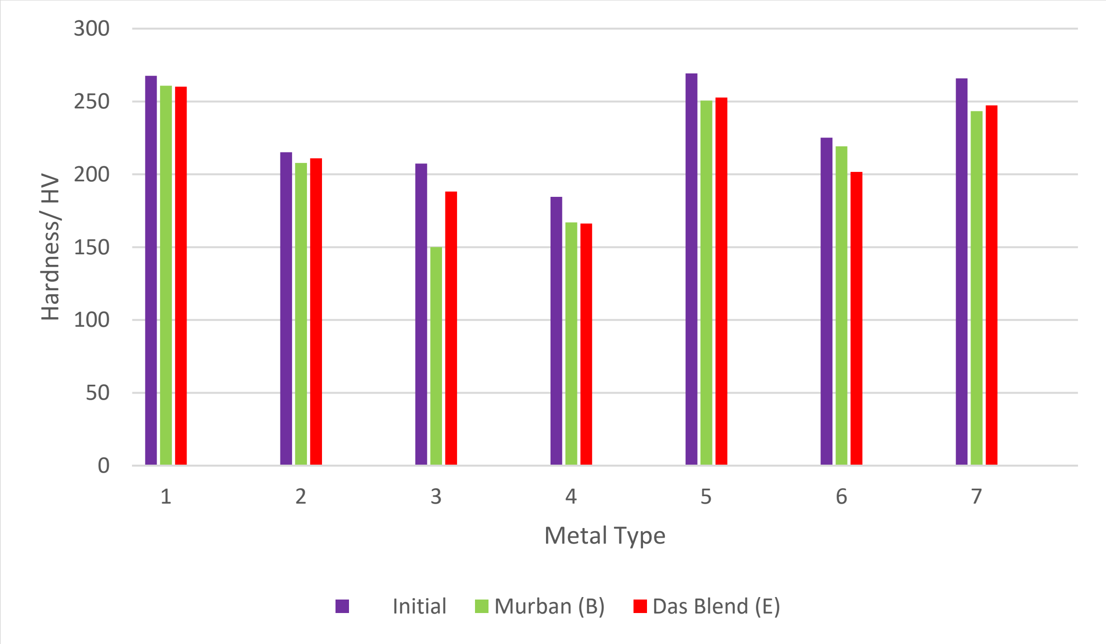

Figure 6.5: Variations of hardness of metal pieces after 30 days exposure time in both crude oil

After the time period of 30 days there were identified the reduction of hardness after the corrosion. When comparing types of metals in here also carbon steels showed slight reduction of hardness weren't happened in significant way and also in stainless steels the reduction of hardness were happened in some considerable amount same as the previous distribution of hardness in Figure 6.4.

6.4.10. Variation of the hardness of metals after corrosion of 45 days period in both Murban and Das Blend crude oil

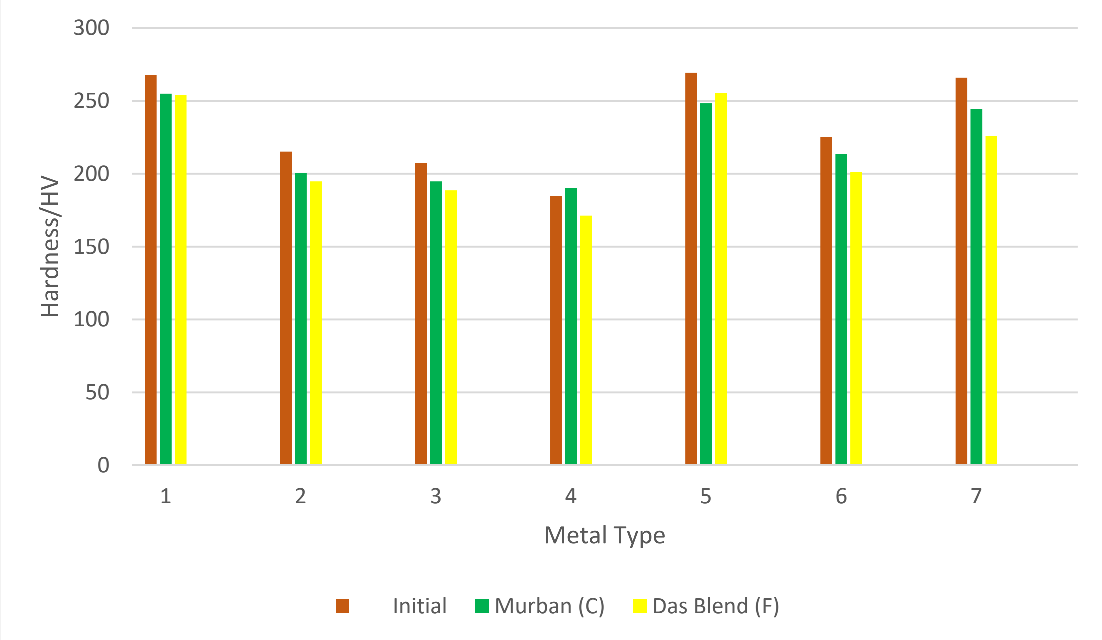

Figure 6.6: Variations of hardness of metal pieces after 45 days exposure time in both crude oil

After the time period of 45 days there were identified the reduction of hardness after the corrosion. When comparing types of metals in here also carbon steels showed slight reduction of hardness weren't happened in significant way and also in stainless steels the reduction of hardness were happened in some considerable amount same as the previous distributions. According to the variation of the hardness of metal pieces slight reduction in each metal piece was observed as results. By referring the distribution of the variation of the hardness unable to express any sequence or a relationship with the corrosion rate of relevant metal, crude oil or the exposed time period to the crude oil. In the description of furthermore analysis, there can be concluded the asymmetric distribution of hardness and also the less amount of hardness reduction was happened in every type of carbon steel showed slight reduction of the hardness.

In the analysis of the reduction of the hardness with the exposed time period in the crude oil, exactly there cannot be identified any sequence or order. Although there can be identified some unexpected situation because of the observation of the increment of the hardness at once. The hardness of metals may be varied with the position of test and due to that reason, some of result was observed in the experiment [1]. After the formation of corrosive compound on the metallic surface the stability of the metallic surface will be reduced due the tendency of removing those compounds [1] [2]. The reduction of hardness also happened with under those conditions. Finally the asymmetric variation of the reduction of the hardness also can be concluded as some variations of values due to the position on the metal surface and due to the asymmetric corrosion distribution on the metallic surface as shown under the microscopic analysis.

6.5. Microscopic Analysis

6.5.1. Carbon Steel (High)

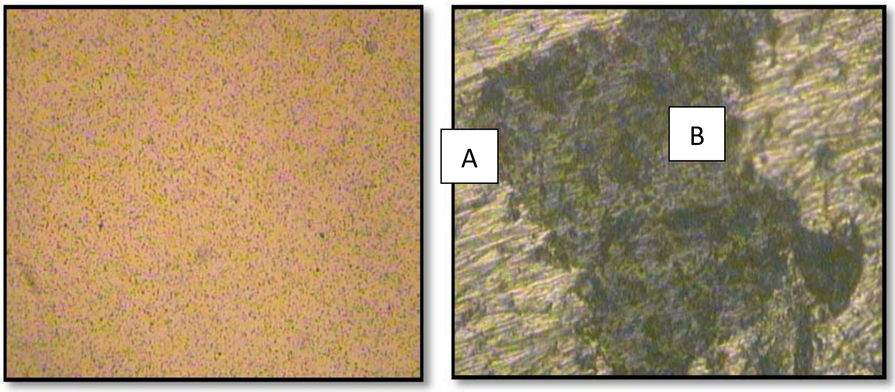

Figure 6.7: Corroded surface of Carbon Steel (high) in Murban

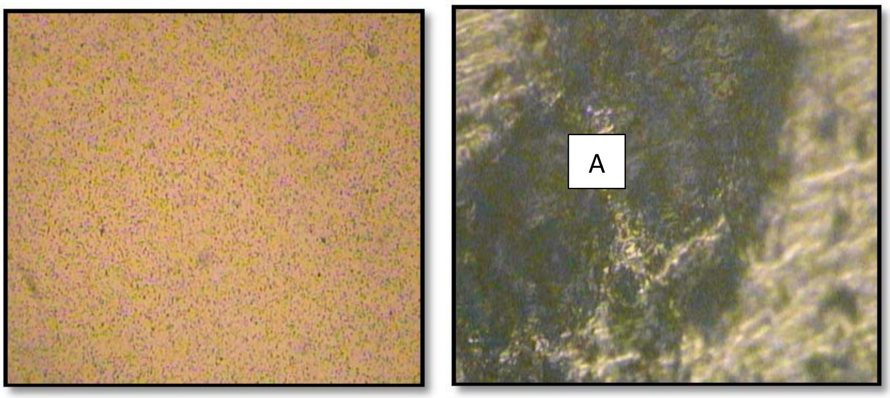

Figure 6.8: Corroded surface of Carbon Steel (high) in Das Blend

6.5.2. Carbon Steel (Medium)

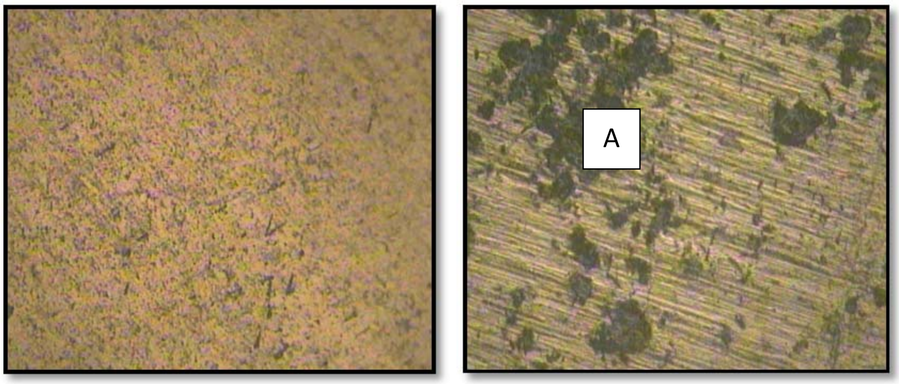

Figure 6.9: Corroded surface of Carbon Steel (medium) in Murban

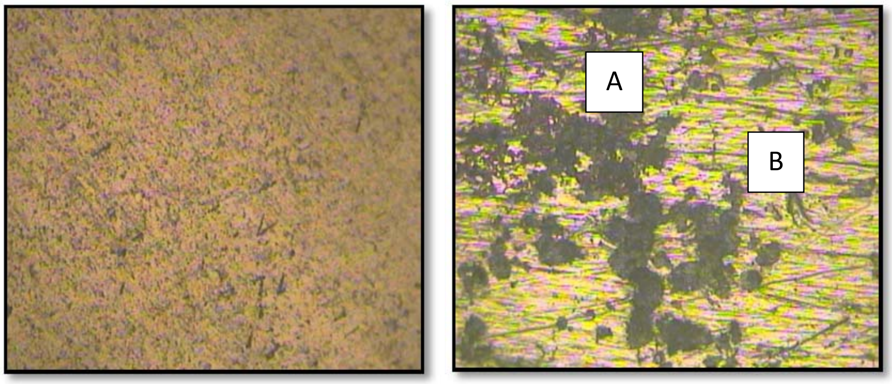

Figure 6.10: Corroded surface of Carbon Steel (medium) in Das Blend

6.5.3. 410-MN: 1.8 420-MN: 2.8 (Stainless Steel)

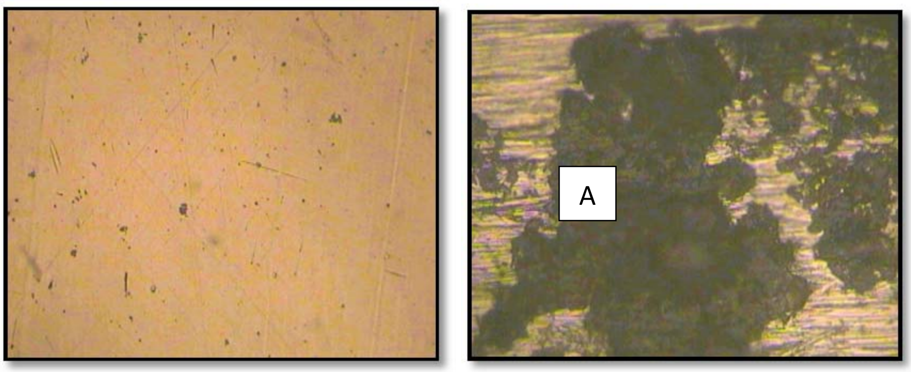

Figure 6.11: Corroded surface of 410-MN: 1.8 420- MN: 2.8 (Stainless Steel) in Murban

Figure 6.12: Corroded surface of 410-MN: 1.8 420- MN: 2.8 (Stainless Steel) in Das Blend

6.5.4. 410- MN: 1.7 420 – MN: 1.7 (Stainless Steel)

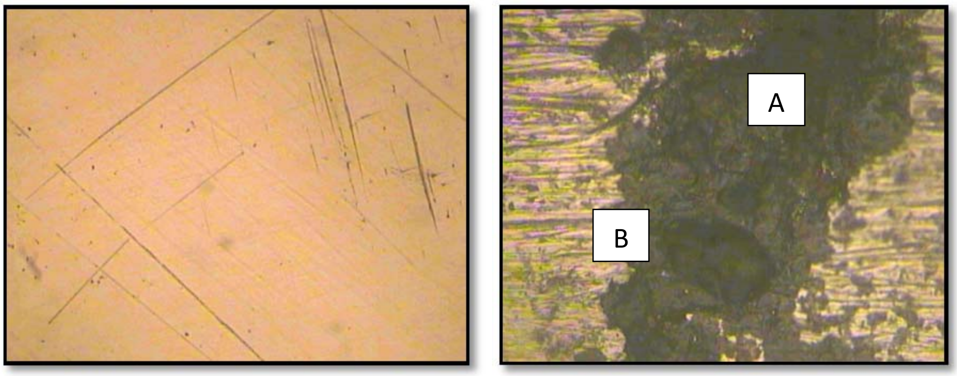

Figure 6.13: Corroded surface of 410-MN: 1.7 420- MN: 1.7 (Stainless Steel) in Murban

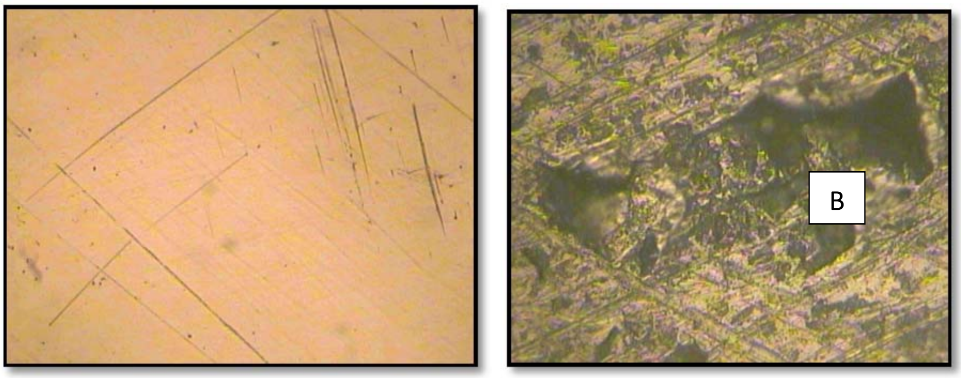

Figure 6.14: Corroded surface of 410-MN: 1.7 420- MN: 1.7 (Stainless Steel) in Das Blend

6.5.5. Monel 400

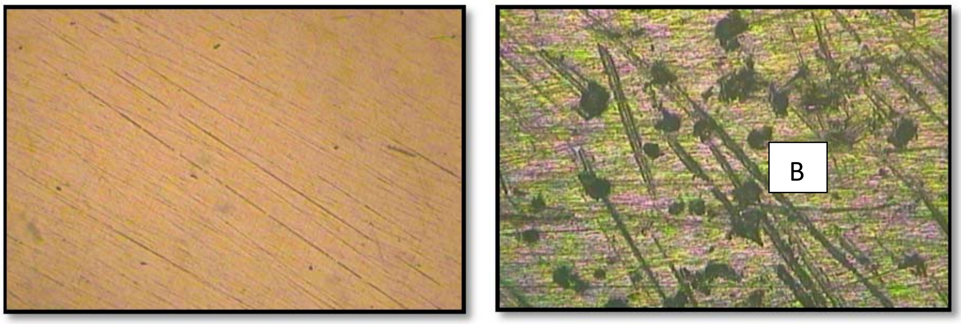

Figure 6.15: Corroded surface of Monel 400 in Murban

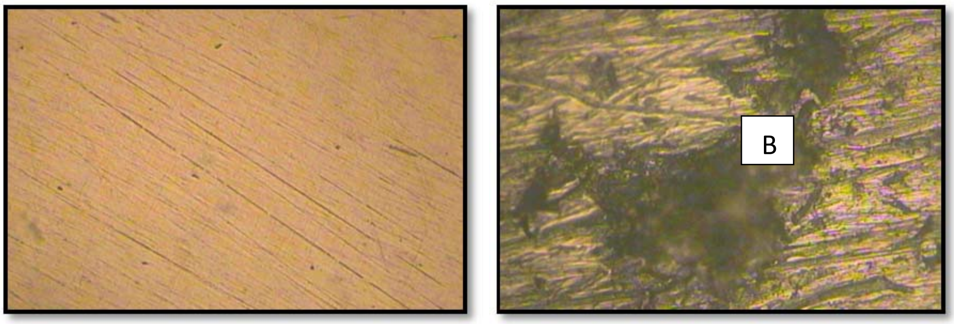

Figure 6.16: Corroded surface of Monel 400 in Das Blend

6.5.6. 321- MN: 1.4 304- MN: 1.9 (Stainless Steel)

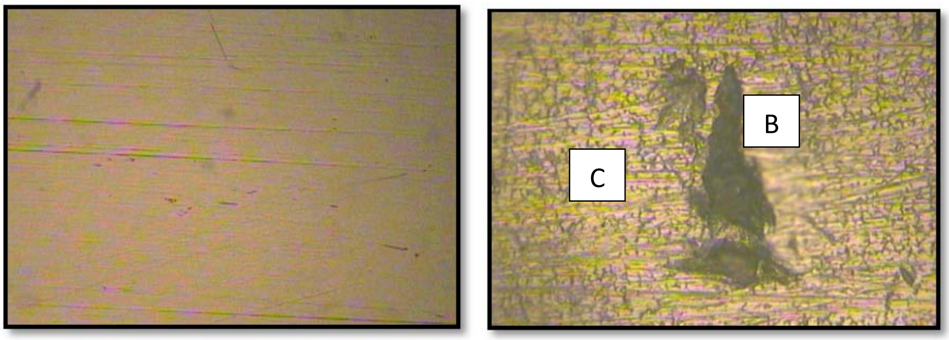

Figure 6.17: Corroded surface of 321- MN: 1.4 304- MN: 1.9 in Murban

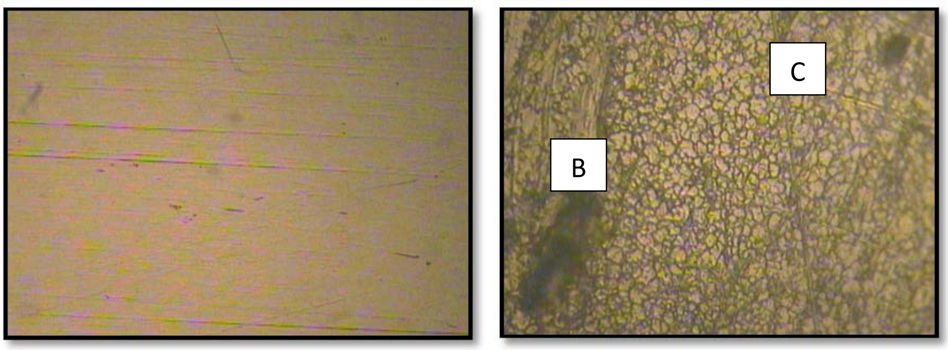

Figure 6.18: Corroded surface of 321- MN: 1.4 304- MN: 1.9 in Das Blend

6.5.7. Carbon Steel (Mild Steel)

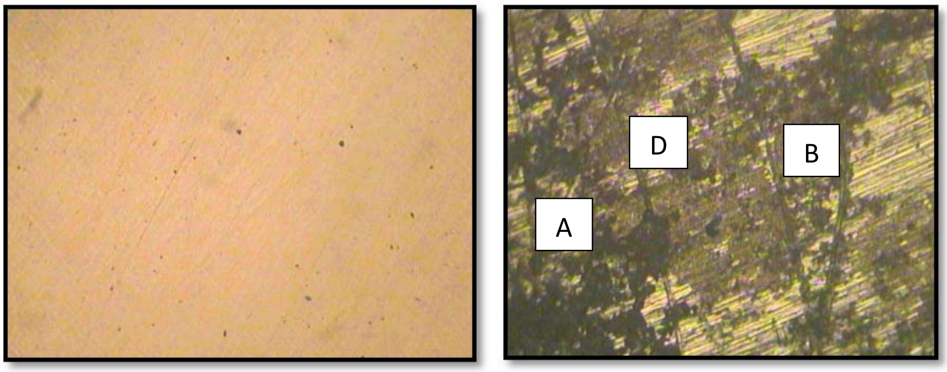

Figure 6.19: Corroded surface of Carbon Steel (Mild Steel) in Murban

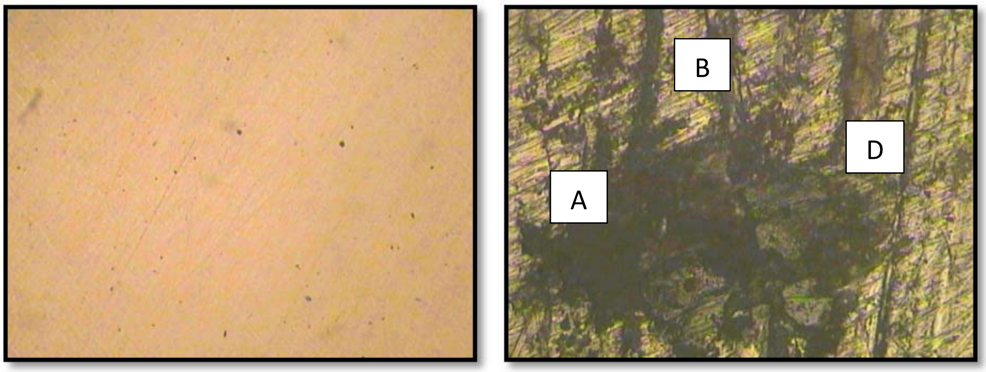

Figure 6.20: Corroded surface of Carbon Steel (Mild Steel) in Das Blend

By considering the features and properties of corrosion compounds some of important features were identified and those properties have been discussed with the corresponding sign. The description about the above feature have been given in the below.

A- Ferrous Sulfide and Trace Compounds
B- Pitting Corrosion
C- Corrosion Cracks
D- Ferrous Oxides and Trace Compounds

According to the qualitative analysis of corrosion on the microscopic analysis interpreted some important information to confirm the formation of corrosion compounds on the surface of the metal. The identifications were based on the physical appearance of those compounds foremost the color [3]. A descriptive summary about those corrosive compounds have been explained in the Table 6.19.

Table 6.19: Descriptive summary about the corrosion compounds

Compound	Appearances	Relationship with Current Observations
FeS	Black, Brownish Black, Property of Powder, Pitting, Cracking	Observed several features on the surface of each metal
Fe_2O_3	Rusty Color	Identified Rarely
CuS	Dark Indigo/ Dark Blue	Unable to Specify

Regarding the analysis of the corroded surface of the metal, there can be concluded some kind of pitting corrosion was happened in most of times. In the microscopic analysis, there were identified most of features that relevant to the above compound and also there could be identified some cavities on the corroded metal surface. Under every kind of corrosion some corrosion cracks were observed on corroded metal surfaces foremost on the surface of stainless steel.

6.6. Concentration of decayed metals in crude oil

Concentrations of decayed metal in crude oils obtained by Atomic Absorption Spectroscopy (AAS) analysis are given in the Table 6.20.

Table 6.20: Dissolved metal concentration in crude oils

Metal	Crude Oil	Fe Concentration /ppm	Cu Concentration /ppm
Carbon Steel (High)	Murban	0.47	-
	Das Blend	1.10	-
Carbon Steel (Medium)	Murban	0.54	-
	Das Blend	0.02	-
410-MN: 1.8 420-MN: 2.8 (Stainless Steel)	Murban	-0.65	-
	Das Blend	-0.78	-
410-MN: 1.7 420-MN: 1.7	Murban	-0.71	-
	Das Blend	-0.79	-

(Stainless Steel)			
Monel 400	Murban	-	10.47
	Das Blend	-	9.49
321-MN:1.4 304-MN:1.9 (Stainless Steel)	Murban	-0.44	-
	Das Blend	-0.17	-
Carbon Steel (Mild Steel)	Murban	-0.08	-
	Das Blend	-0.48	-

6.6.1. Comparison of the decay of Fe in both crude oil

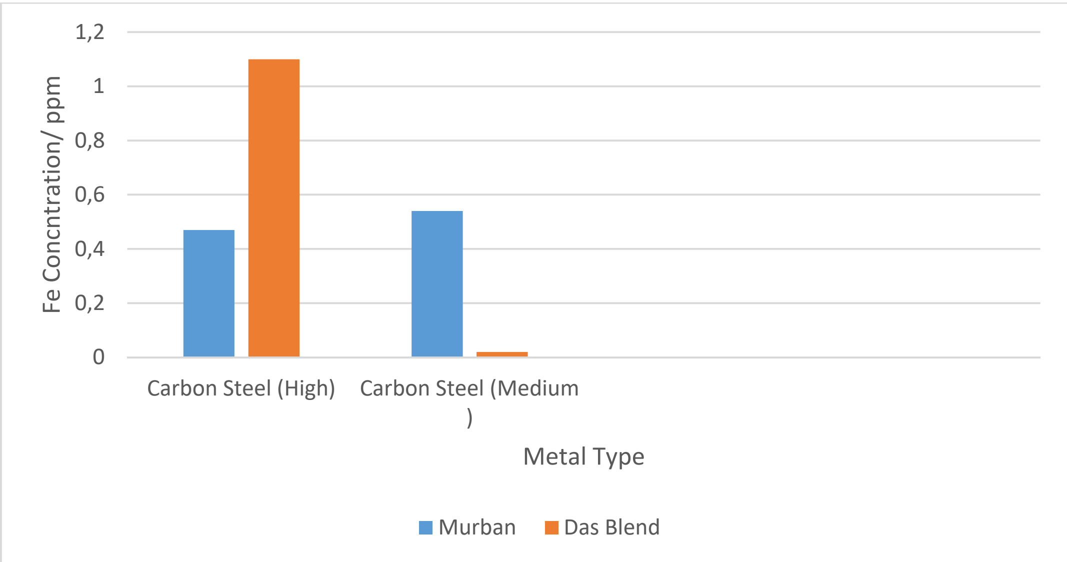

Figure 6.21: Comparison of the decay of Fe in both crude oil

6.6.2. Comparison of the decay of Cu in both crude oil

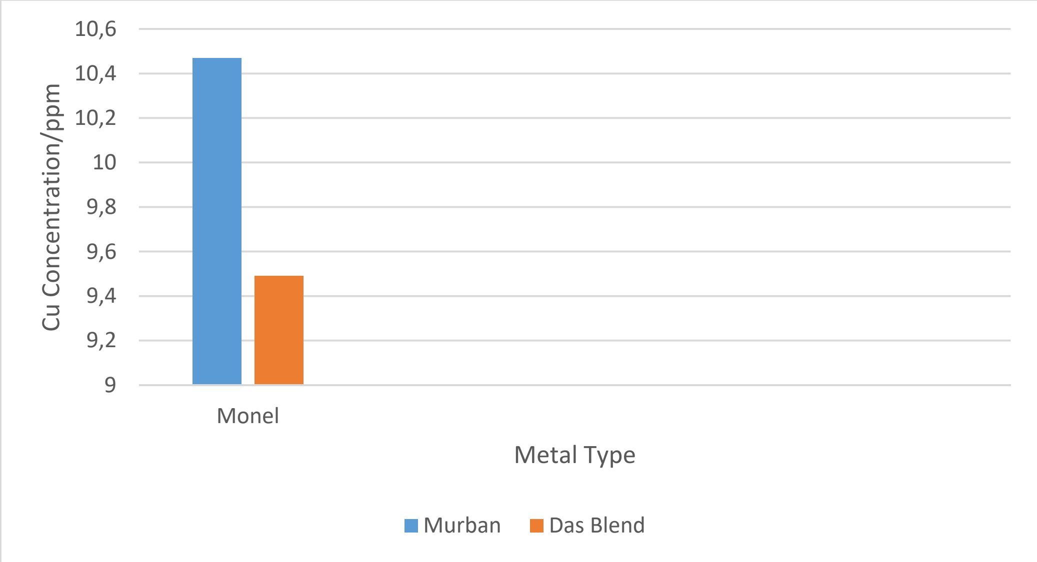

Figure 6.22: Comparison of the decay of Cu in both crude oil

Under the observations during the weighing of metal pieces after removing corroded particles, there were observed an invisible weight loss. Based on the assumption of the decay of corroded particles into crude oils, it was investigated under the metal concentration analysis in crude oil by absorption the atomic spectroscopy (AAS).This can be explained under the mechanism of corrosion because of the occurrence of the corrosion usually formed the metallic oxide, sulfide, hydroxide or a certain metallic compound. After the formation of the corrosion the relevant compounds tend to be removed from the metal surface due to the repulsive and attractive forces in between successive electrons and protons [3]. That incident can be concluded as a reason for the invisible weight loss of the metal pieces and in furthermore discussion there can be concluded some kind of distinguish relationship in between the corrosion rate and the amount of relevant metal concentration in the crude oil.

According to the obtained results highest corrosion rates were observed from the types of carbon steel also observed relatively high amount of Fe concentration in both crude oil and the least corrosion rates were observed from the types of stainless steel also any crude oil wasn't composed with Fe regarding every kind of stainless steel. According to the results of Monel metal an intermediate corrosion rate was observed from the Monel. But relatively high amount of Cu concentration was observed in both crude oil regarding the Monel metal. When comparing both crude oil most of metals showed the higher corrosion rate in Murban crude oil than in Das Blend crude oil and also the higher metallic concentration regarding carbon steel and Monel in Murban crude oil than Das Blend crude oil. Among those observations an intermediate corrosion rate was observed from Mild Steel in both crude oil with lack of Fe concentration in both crude oil.

Chapter 7

Conclusion

7.1. Conclusion

According to the obtained results the least corrosion rate was observed from the 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) in both crude oil while the highest corrosion rate was observed from the high carbon steel. The intermediate corrosion rate was observed from the Monel in both crude oil which is contained significant amount of Ni and Cu including trace amount of Fe. When considering about the crude oil the most of metals were shown higher corrosion rate in Murban crude oil than the Das Blend crude oil. According to the overall distribution of corrosion rate of seven types of ferrous metals in both crude oil asymmetric sequences were observed. As a conclusion every types of stainless steel were shown relatively lower corrosion rate than the types of carbon steel including mild steel and Monel. Regarding the correlation of the corrosion rate with the carbon content of the metal, there were observed higher rate of corrosion in metals which are having high percent of carbon. In detailed results related to carbon steel and stainless steel showed an identical variation of the corrosion rate in high carbon steel, medium carbon steel and mild steel among carbon steels. Also in the stainless steel the same results were observed. According to the microscopic analysis on the corroded metal surface, there could be identified different kind of compounds with the aid of the external features of those compounds. There can be concluded the black color compounds as Iron Sulfide or Copper Sulfide and also the trace amount of rusty color compounds as Iron Oxides according to the physical properties of such compounds. Under the optical microscope (400X) there could be identified asymmetric distribution of corrosion on the surface of each metal piece. Based on the features, there were identified some corrosion cracks and cavities on the corroded metal surfaces. Especially on the corroded surface of stainless steel, most of small cracks were observed. Regarding every types metals the cavitation phenomena was identified in various sizes.

In the variation of hardness, each metal piece was shown the slight reduction from the initial hardness. After referring the values of relevant hardness and the mutation of the hardness unable to create a certain sequence or comparison related to the metals or crude oils.

Apart from that based on the observation some kind of invisible weight loss of metal pieces were observed. So the atomic absorption spectroscopic (AAS) analysis was interpreted the real incident which is happened in the crude oil and metal chemical interaction. According to the results of atomic absorption spectroscopic (AAS), significant Fe concentration was observed from both crude oil samples which were exposed to the high carbon steel and medium carbon steel metal pieces. Monel is a metal which is consist relatively high amount of Nickel and Copper. According to the analysis of atomic absorption spectroscopy, significant concentration of Cu was observed in both crude oil exposed to the Monel pieces. When comparing the Cu concentration in both crude oil regarding the Monel, higher Cu concentration was observed from Murban crude oil than the Das Blend crude oil. The special observation was the lack of Fe concentration in both crude oils which were exposed to the any type of Stainless Steel and also the Mild Steel metal pieces.

7.2. Recommendation for Future Research

Ferrous metals are composed with several elements such as Fe, Mn, Cr etc. So the relevant metals could be chemically reacted with surroundings such as crude oil and tend to be dissolved in such medium. In the current research it was tested only the concentration of one metal in order to Fe for carbon steel and stainless steel and Cu for Monel. According to the observed results there were significant amount of such metal have been dissolved in the crude oil samples. Then the analysis of the metal dissolving with respect to the each type of element presence in relevant ferrous metal would be expressed a classified interpretation about the interaction between the metal and the surroundings. It can be recommended the analysis of elemental concentration with respect to each type of element presence in such ferrous metals with the aid of atomic absorption spectroscopy (AAS) and also according to the qualitative analysis of corrosion on the surface of metal, several features of corroded particles were identified and discussed. As a further improvement of the research and the analysis of the metal corrosion the compositional analysis of corroded particles with the aid of X-Ray diffraction (XRD) can be recommended to enhance the accuracy of the research.

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Appendices

Appendix A- Important types of corrosion and relevant features

Types of Corrosion happened in Ferrous Metals and the Chemical Theory behind the Metallic Corrosion.

- ✓ Pitting Corrosion.

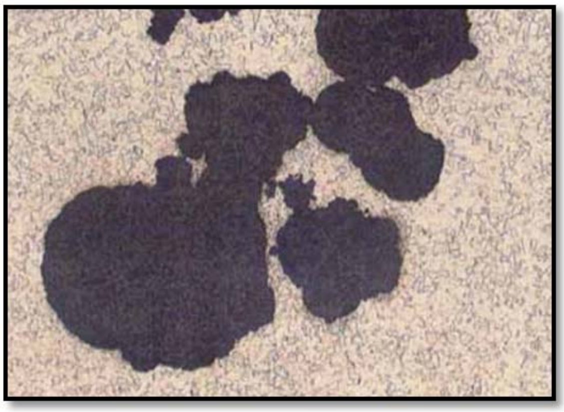

Figure 01: Pitting Corrosion

Pitting corrosion is a form of corrosion can be identified with the aid of the properties, based on the formation of pits on the surface of the metal and the size of pits may be varied [3] [4].

- ✓ Corrosion Cracks

Figure 02: Corrosion Cracks

This type of corrosion is happened due to the effect of tensile strength and corrosive environment. In the industry of crude oil refining, there can be happened some forces due to the high pressure at high temperatures and also the presence of corrosive compound in crude oil. Altogether the thermal corrosion cracking can be easily happened in the devices of crude oil refining. The propagation of crack will be accelerated at high temperature.