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Corrosive Behaviors of Crude Oils and Their Effects on Ferrous Metals

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ABSTRACT

Crude oil is an essential natural resource regarding the day today industrial applications within adverse experiences on some materials such as the corrosion on metals which is usually known as the formation of metal oxides, sulfides or hydroxides on the metal surface itself. In the current research there were considered the effect of elemental sulfur, mercaptans, organic acids and salts on the corrosion rates of seven different types of ferrous metals. The chemical compositions of ferrous metals were detected by XRF detector. Such corrosive properties of both crude oils were tested by standard methods and adequate instruments. A set of equal sized metal coupons from each metal type were immersed in both crude oils separately and the corrosion rates of each type of metal was determined in order to 15, 30 and 45 days from the immersion by the weight loss method while observing the corroded metal surfaces through an optical microscope. The initial hardness and the hardness after corrosion on each metal coupon were tested by Vicker's hardness tester and the both ferrous and copper concentrations in each crude oil sample were tested by atomic absorption spectroscopy after the interaction with metals. According to the results there were observed strong corrosive tendency from Das Blend crude oil than the Murban crude oil. There were found relatively higher corrosion rates of carbon steels, relatively lower corrosion rates of stainless steels and intermediate corrosion rates form Monel in both crude oils. Most of metals showed some higher corrosion rates in Murban crude oil than the corrosion rates of the same metal in Das Blend crude oil eventually.

Keywords: *Ferrous Metals; Crude Oils; Corrosive Properties; Corrosion Rate; Hardness.*

1.0 Introduction

Corrosion is a severe adverse phenomenon regarding the ferrous metals which is affected for the durability and the deduction of some important properties such as the strength and hardness.

Usually corrosion is known as the formation of such metal oxides, sulfides, hydroxides or any other compound on the metal surface itself [1-5].

The essential factor which is the requirement for the corrosion that the metal should be exposed to either some kind of stronger oxidizing agent than Fe^{2+} or some adequate environment that composed with water and oxygen.

This process will be modified by the salts and organic acids presence in the medium [2-3]. Crude oil is a mixture of hydrocarbon and also composed organic acids, salts and sulfur compounds [4].

Therefore, crude oils can be considered as a corrosive causing compound both directly and indirectly. According to the chemical compositions of crude oils basically elemental sulfur, active sulfur, organic acids and salts have been identified as major corrosive compounds [6-9]. In this research there were investigated the effect of two different types of crude oils which are different in their chemical compositions on the causing of corrosion in seven different types of ferrous metals. In the previous researches there were performed some important investigations about the effect of corrosive properties on the metallic corrosion and the behaviors although in most of experiments unable to find some descriptive comparisons of such corrosive properties on the causing of corrosion in different types of ferrous metals and their important changes of features.

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2.0 Materials and Methodology

2.1 Materials

There were chosen two different types of crude oils that different in their chemical composition. The used metals and their applications in the crude oil refining in industry are given in the Table 1.

Those are Murban and Das Blend which were used in the Sri Lankan crude oil refining industry.

- ✓ Murban
- ✓ Das Blend

Those are slightly different in their chemical compositions. Comparable investigation of the effect of corrosive properties on corrosion rate of such metals was the objective of using two crude oils. Das Blend is considered as a “sour” crude oil the term explained that it is composed relatively high amount of sulfur. Therefore, it will make a good enough experimental background to investigate and distinguish the effect of sulfur on the metallic corrosion.

Table 1: Used Metals and Their Applications

Metal	Typical Applications
Carbon Steel (High)	Heat exchangers
Carbon Steel (Medium)	Storage tanks, transportation tubes
Carbon Steel (Mild Steel)	Storage tanks
410-MN: 1.8 420-MN: 2.8 (Stainless Steel)	Crude distillation unit, pre-heaters
410-MN: 1.7 420-MN: 1.7 (Stainless Steel)	Crude distillation unit, heat exchangers
321-MN:1.4 304-MN:1.9 (Stainless Steel)	Crude distillation units, tube sheets
Monel 400	Heat exchangers, vessels

Table 2: Investigation of the Corrosive Properties in Crude Oils

Property	Method	Readings
Sulfur content	Directly used.	Direct reading
Acidity	Each sample was dissolved in a mixture of toluene and isopropyl and titrated with potassium hydroxide.	End point
Mercaptans content	Each sample was dissolved in sodium acetate and titrated with silver nitrate.	End point
Salt content	Each sample was dissolved in organic solvent and exposed to the cell of analyzer.	Direct reading

2.2 Methodology

In the methodology most of the times there were followed ASTM methods for the testing such corrosive properties of both crude oils. The descriptive summary about the procedures have been given in the Table 2.

The elemental compositions of seven different types of ferrous metals were detected by the XRF detector. According to the working principles of XRF detector it allows to measure the major and trace metallic compositions of some particular bulk of metal and some composed non-metals as well. A set of similar sized metal coupons were prepared by each type of metal and those metal coupons were immersed in both Murban and Das Blend crude oils separately. A batch of metal coupons was taken out after 15 days from the immersion. That batch was consisted with seven types of metals with respect to both types of crude oils. The corrosion rate of each metal coupon was determined by the weight loss method. The same procedure was repeated again twice for another two batches of metal coupons after 30 and 45 days from the immersion and the arithmetic means of such corrosion rates were presented as the average corrosion rate of such metal with respect to such crude oil. The apparatus setup and metal coupons have been shown in the Figure 1.

Fig 1 (a): Metal Coupons and (b) Set Up of Samples

The corrosion rates of metal coupons were determined by the weight loss method and also its mathematical expression has been given in the Equation 1 [10].

$$CR = W * k/(D * A * t) \quad (1)$$

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

Based on the qualitative analysis of corrosive compounds the microscopic analysis experiment was performed regarding the surfaces of corroded metal surface. The surface of each metal coupon was observed through the 400X lens of an optical microscope before the immersion in crude oils and after the formation of corrosive compounds on the metal surface.

The dissolved ferrous concentration in crude oil samples which were exposed to carbon steels and ferrous metals and copper concentrations of crude oil samples which were exposed to Monel metal were tested by the atomic absorption spectroscopy (AAS). According to the methodology of the sample preparation 1 ml of each crude oil sample was diluted with 9 ml of 2-propanol.

The initial hardness and the hardness after formation of the corrosion on each metal coupon were tested by the Vicker's hardness tester. There were measured at least three random points on each metal coupon at once and the arithmetic mean of such values was interpreted as the hardness of that metal coupon at that moment.

3.0 Results and Discussions

According to the readings of XRF detector the elemental compositions of used metals in the experiment are given in the Table 3.

Table 3: Chemical Compositions of Ferrous Metals

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	-
Carbon Steel (Mild Steel)	99.46	0.54	<0.30	-	<0.07	-	-	-	-	-	<0.19	<0.07
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	-	-	-
321-MN:1.4 304-MN:1.9 (Stainless Steel)	72.47	1.44	-	8.65	17.14	-	0.18	-	0.12	-	-	-
Monel 400	1.40	0.84	0.11	64.36	<0.04	33.29	-	-	-	-	-	-

The results of XRF detector show some higher ferrous compositions in carbon steels, intermediate ferrous compositions in stainless steels and the trace amount of ferrous in Monel metal. Also relatively higher trace elemental compositions in stainless steels such as nickel and chromium. Based on the objectives of enhancing the strength, hardness and the corrosive protection the doping of trace elements has been applied for such metals. The Monel metal is an industrial applicable metal which is having trace amount of ferrous while having higher amounts of copper and nickel [1-3]. According to the standard tests of the corrosive properties of crude oils the observed results for the sulfur contents, salt contents, acidities and mercaptans contents of both crude oils have been listed in the Table 4.

Table 4: Corrosive Properties of Both Crude Oils

Property	Murban	Das Blend
Sulfur content (Wt. %)	0.758	1.135
Salt content (ptb)	4.4	3.6
Acidity (mg KOH/g)	0.01	0.02
Mercaptans content (ppm)	25	56

By referring the sulfur contents of both crude oils Das Blend was composed higher amount of elemental sulfur content than the Murban. Usually the elemental sulfur and sulfur compounds take a part of the composition of crude oils in different forms foremost the elemental form, mercaptans, thiophenes, sulfoxides and even hydrogen sulfide also most of them are corrosive compounds. Basically some functional groups attached with sulfur tend to be reacted with metals and to be formed the metallic corrosion [6]. This process is known as the "sufidation" also highly dependable on the temperature typically can be expected properly at about 230^0 as given in the chemical reaction below.

$$8Fe + S8 \rightarrow FeS \quad (2)$$

According to the active sulfur contents of both crude oils Das Blend is much stronger than Murban as twice of the Mercaptans content. Mercaptans are the corrosive sulfur compounds which are having a rode reactive functional group of "RSH" [8]. Das Blend crude oil is much stronger in the content of organic acids than Murban crude oil.

Organic acids are the trace compounds presence in crude oils also considered as corrosive compounds. Organic acids are some kind of trace compounds that presence in the crude oils also called as "naphthenic acids" which are having a formula of "RCOOH". The chemical reactions and the order of those reactions have been given in the below [2] [4] [9].

$$Fe + 2RCOOH \rightarrow Fe(RCOO)2 + H2 \quad (3)$$

$$FeS + 2RCOOH \rightarrow Fe(RCOO)2 + H2S \quad \ldots (4)$$

$$Fe(COOR)2 + H2S \rightarrow FeS + 2\,RCOOH \quad \ldots (5)$$

Murban crude oil is stronger than Murban according to the salt content since weaker in other three corrosive compounds than the Das Blend. According to the natural occurrences of crude oils that those can be composed with different salts such as NaCl, $MgCl_2$ and $CaCl_2$.

According to the heating process of crude oils these salts tend to be broken down into HCl even though HCl is not behaving as a corrosive at the gas phase and high temperatures [7-9].

$$CaCl2 + H2O \rightarrow CaO + 2HCl \quad \ldots (6)$$

However, due to the reduction of the temperature of the system some of HCl molecules react with the moisture and tend to produce hydrochloric acids which are known as corrosive compounds against the metals.

The overall chemical process of the formation of metallic corrosion due to the presence of salts in the crude oils has been given in the chemical reactions below.

$$HCl(g) + H2O \rightarrow HCl(aq) \quad \ldots (7)$$

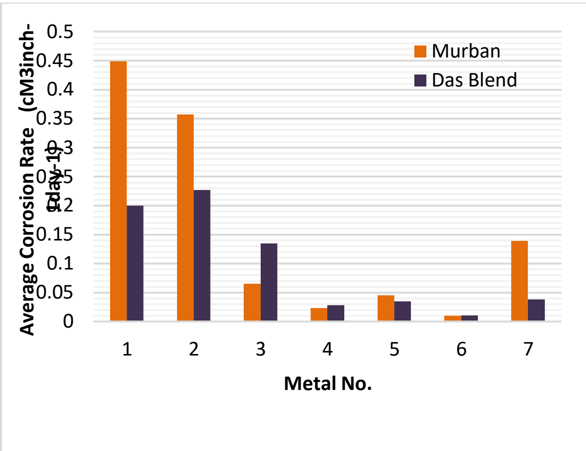
$$HCl + Fe \rightarrow FeCl2 + H2 \quad \ldots (8)$$

$$FeCl2 + H2S\ FeS + 2HCl \quad \ldots (9)$$

FeS is known as the corrosion compound and usually FeS is a black colored compound and also it has some hard powdered properties.

The average corrosion rates of seven types of metals with respect to each crude oil have been given in the Figure 2.

Fig 2: Average Corrosion Rates of Metals



According to the observed results for the average corrosion rates of metal coupons with respect to both Murban and Das Blend crude oils, the least corrosion rates were found from 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) in both crude oils while other two types of stainless steels were also showing lower corrosion rates relative to the all of carbon steels and Monel. Stainless steel is an alloy metal that based on the objectives of having high strength and lower corrosion rate.

Regarding the theoretical explanation about the chemical composition of stainless steel if it is composed some critical amount of nickel and chromium this combination will be able to create a corrosive protection film against the formation of the corrosion.

The typical value for the minimum chromium content for the protection film is 12% with sufficient amount of nickel [1] [4] [5]. By referring the observed results there can be approached easily to the conclusion that the least corroded metal 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) is having ~18% of chromium and ~8% of nickel also recommended as the most stable metal against a corrosive environment.

Furthermore in the current research it was identified the corrosion rates of stainless steels were reduced with the increasing of the chromium contents of stainless steels. Also there were observed a significant impact on the corrosive protection of stainless steels by doping nickel and chromium because when comparing with the corrosion rates of carbon steels these stainless steels showed lower corrosion rates by far.

When considering the effect of crude oils on the rates of corrosion in metal coupons there were obtained four types of metals showed higher corrosion rates in Murban crude oil while three types of metals showed higher corrosion rates in Das Blend crude oils although according to the corrosive strength of both crude oils Das Blend crude oils was stronger than Murban crude oil with respect to the organic acids, elemental sulfur and mercaptans sulfur contents only weaker in the salt content than the Murban crude oil.

The proper progress of the "sulfidation" process can be expected at some of higher temperatures at about 230^{0}C [6] [8]. Therefore, according to the obtained results there can be suggested that it was not happened proper reaction of "sulfidation" and the corrosive causing ability of the salts is higher than the corrosive causing ability of organic acids in the room temperatures. The variations of the corrosion rates of metal coupons with respect to the immersed time period and type of the crude oil have been shown in the Figure 3.

Figure 3 shows the gradual reductions of the corrosion rates of each type of metals with the exposure time to the crude oils. According to the mathematical derivation of the weight loss method interprets a relationship that the corrosion rate of some metal coupon after certain time period is inversely proportional to the exposed time period against the corrosive compound [10]. Therefore, it can be clearly emphasized that inversely proportional relationship according to the obtained results in this experiment.

Fig 3(a): Variation of the Corrosion rates of Metal Coupons with the Exposure Time Period in Murban

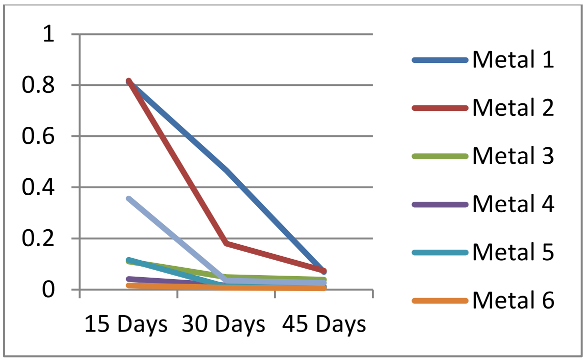
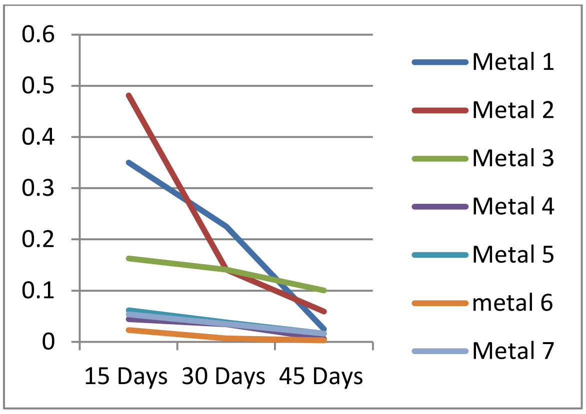


Fig 3(b): Variation of the Corrosion Rates of Metal Coupons with the Exposure Time Period in Das Blend



According to the qualitative analysis the microscopic observations interpret some essential evidences for the formation of the corrosion. A few some significant microscopic observations have been shown in the Figure 4.

Fig 4 (a): Corroded Surface of 410-MN: 1.8 420-MN: 2.8 (Stainless Steel) in Murban

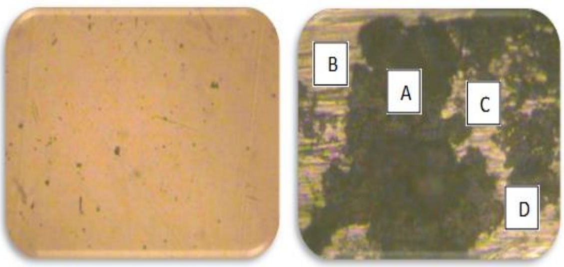
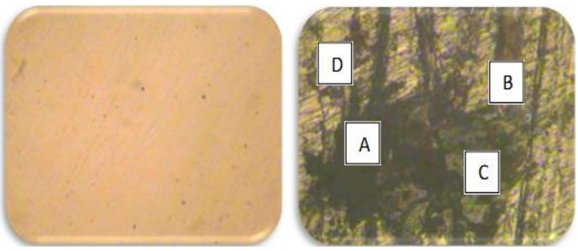


Fig 4 (b): Corroded Surface of 410-MN: 1.8 420-MN: 2.8 (Stainless Steel) Corroded Surface of Carbon Steel (Mild Steel) in Das Blend



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

In this discussion the analysis is based on the physical properties and visible features foremost the color [3]. The observations and the relationship between the references have been listed in the Table 5.

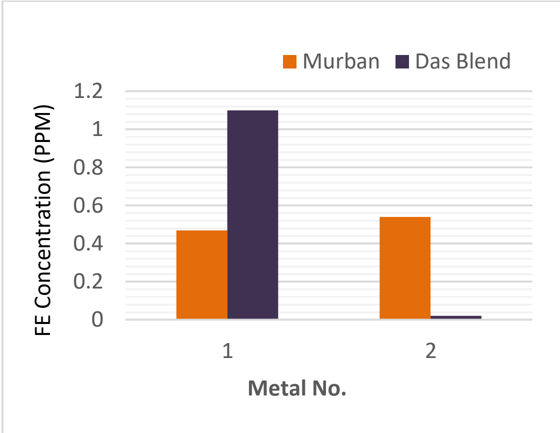
Table 5: Visible Features of Corrosive Compounds

Compound	Appearances	Observations
FeS	Black, brownish black, property of powder, pitting, cracks	Observed most of features in each metal piece.
Fe_2O_3	Rusty color	Observed rarely.
CuS	Dark indigo/ dark blue	Unable to specify.

Apart from that there were observed some important features on the corroded metallic surface such as the pitting corrosion which is unique feature that formed where the less or lack areas of other corrosive compounds. In most of observations that there can be concluded the formations of FeS because of the acceptable optical features. During the microscopic observations and corrosion rate calculations there were observed some invisible weight losses in some metal coupons specially form carbon steels and Monel. Therefore, the ferrous and copper concentrations in each crude oil sample were measured by the atomic absorption spectroscopy (AAS) after interaction of the metal coupons.

The ferrous concentrations of crude oil samples which were interacted with carbon steels and stainless steels have been given in the Figure 5.

Fig 5: Ferrous Concentrations in Crude Oil Samples



According to the analysis of atomic absorption spectroscopic (AAS) there were observed high amounts of ferrous in both Murban and Das Blend crude oil samples which were exposed to carbon steels (high) and carbon steels (medium) although there was not observed any amount of ferrous in any crude oil sample with respect to neither carbon steels (mild steels) nor stainless steels.

The copper concentrations of crude oil samples which were interacted with Monel have been given in the Figure 6.

Fig 6: Copper Concentrations in Crude Oil Samples

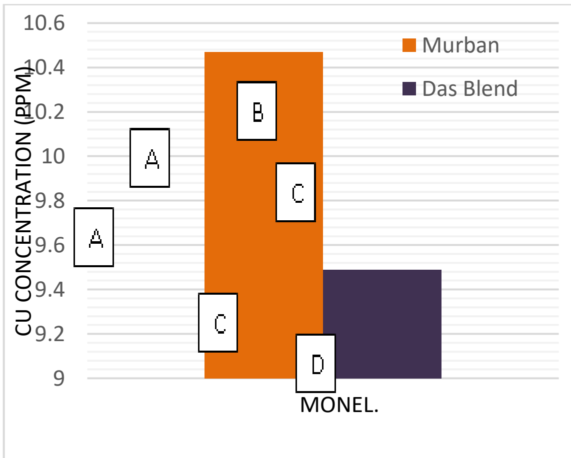
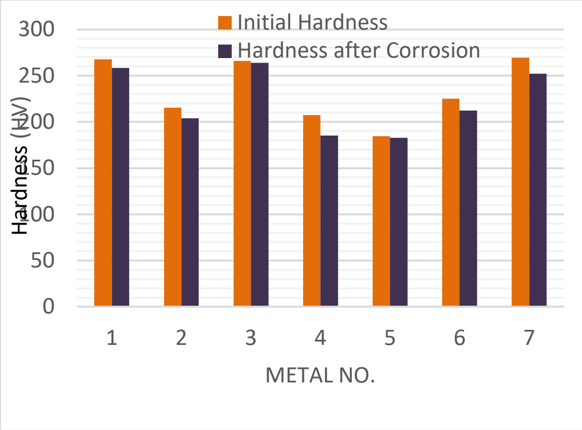


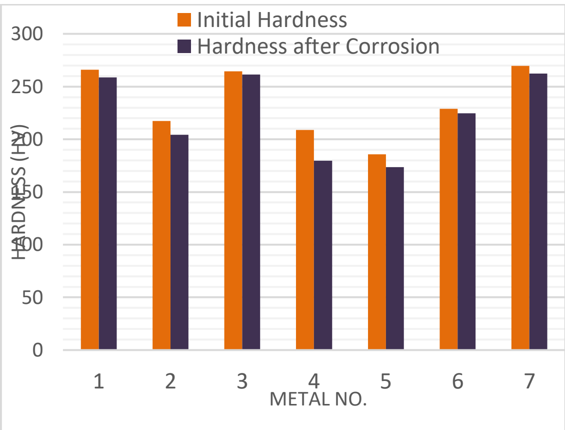
Fig 7: Variations of the Hardness of Metals in Murban Crude Oil



Furthermore the atomic absorption spectroscopic (AAS) results showed significant copper concentrations in both Murban and Das Blend crude oil samples which were exposed to the Monel metal coupons. Corrosion is known as the formation of metal sulfide, oxide or hydroxide on the metallic surface and also those corrosive compounds tend to be removed from the relevant metal surface as the post corrosion incident due to the repulsive and attractive forces between the between the successive electrons and protons [3]. The recent matter for the high concentrations of ferrous in some crude oil samples is emphasized as the formation of the metallic corrosion on the surfaces of such metals moreover. The variations of the hardness of metals in the Murban crude oil have been given in the Figure 7.

The variations of the hardness of metals in the Das Blend crude oil have been given in the Figure 8.

Fig 8: Variations of the Hardness of Metals in Das Blend Crude Oil



According to the variations of the initial hardness values of metal coupons due to the corrosion there can be identified a slight reduction of the initial hardness in each metal coupon. This distribution cannot be interpreted as any relationship in between the hardness and the corrosion rates of metals although a slight reduction of the initial hardness in each metal coupon was identified. The hardness of the metal may be varied with the position where it has been tested randomly. Due to the formation of corrosive compounds on the metallic surface instantly those compounds tend to be removed from the initial surface. Therefore, an instability situation is formed automatically on the metallic surface [1] [2]. Under this kind of situation the reduction of the initial hardness of the metal coupon is a possible phenomenon even though it is impossible to be predicted the variation of the hardness quantitatively.

4.0 Conclusions

As the results there were found least corrosion rates from 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) in both Murban and Das Blend crude oils while carbon steels were showing some relatively higher corrosion rates in both crude oils. When comparing the corrosion rates of metals with respect to both crude oils four types of metals showed higher corrosion rates in Murban crude oil than the corrosion rates of same metals in Das Blend crude oil although Das Blend crude oil is much stronger in corrosive properties. According to the microscopic analysis there were observed the formation of FeS in most of metals. There were found some higher ferrous concentrations in both Murban and Das Blend crude oil samples which were interacted with carbon steels and any ferrous concentration was not found in any crude oil sample which was interacted with stainless steel and also found some significant copper concentrations in both crude oil samples which were exposed to Monel metal. Finally there were indicated the slight reductions of the initial hardness of metal coupons due to the formation of corrosion on the metal surface itself.

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