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THE EFFECT OF CRUDE OILS ON THE METALLIC CORROSION AND THE STABILITY OF METALS IN A CORROSIVE ENVIRONMENT

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Abstract

Crude oil is a supreme earth resource that essential in most of industrial applications while having some adverse effects in the crude oil refining process regarding metals such as the corrosion. According to the general definition usually the corrosion is the formation of metal oxides, sulfides, hydroxides or any compound related with carboxylic group. In the environment of crude oils the corrosion is highly depended on the sulfur, organic acids, mercaptans and salts composed in crude oils and also the chemical compositions of such metals. In the current research it was expected to investigate the relative effects of corrosive properties on the rate of corrosion in seven selected types of metals which are frequently used in the Sri Lankan crude oil refining industry and the stability of those metals against the effect of both Murban and Das Blend crude oils regarding the composition and properties. Corrosive properties of both crude oils were determined using in order to XRF analyzer, titration methods and salt analyzer also the chemical compositions of each metal was determined by XRF detector. Batches of equal sized metal coupons from seven types of metal

were dipped in crude oils separately and their corrosion rates were determined after 15, 30 and 45 days while observing through an optical microscope. The metallic concentration in each crude oil sample was tested by AAS. The initial and the hardness after the corrosion were tested in each metal coupon. According to the observed results Das Blend was ahead regarding sulfur content, mercaptans content and acidity even though higher corrosion rates were shown by four types of metals in Murban than the corrosion rate in Das Blend. The slight reductions in the hardness were found in each metal coupon and some significant metallic concentrations were found in both crude oils regarding some metals forever.

Keywords

Crude Oils, Corrosive Properties, Metals, Wight Loss, Corrosion Rate, Hardness

1. Introduction

Metallic corrosion is a foremost phenomenon regarding the crude oil refining industry that usually known as the formation of at least one compound from metal oxides, sulfide, hydroxides or any compound related with carboxylic group (Khana et al., 2009). In the corrosion the essential thing, the ferrous metal need to expose either some stronger oxidizing agent than Fe^{2+} or any environment that consist with oxygen and water (Bolton et al., 1994). Some important corrosive properties of crude oils play a predominant supplementary role for the metallic corrosion and motivate the process of corrosion when interacting with those metals. The content of sulfur, mercaptans, organic acids and the content of salts are the foremost and considerable corrosive properties in crude oils. In the industry of crude oil refining, most of harmful compounds may be removed before the feeding into the distillation column. Basically the metallic corrosion is found in distillation column head, heat exchangers, transportation tubes and storage tanks. In the current research, there were expected to speculate the effect of crude oils and their properties on the rate of corrosion of seven different types of ferrous metals, stability of metals against the corrosion and some variation of the hardness of those metals due to the corrosion.

2. Materials and Methodology

2.1 Materials

2.1.1 Metals

Seven different types of ferrous metals were chosen as the metals samples including three different types of carbon steels, three different types of stainless steels and Monel 400

which has a least composition of ferrous where as it can be used for some tasks regarding the industry of crude oil refining in Sri Lanka.

2.1.2. Crude Oils

Crude oil is a mixture of hydrocarbons and also composed with some accessory compounds that able to give some specific properties to such crude oils. The composition of crude oil could be varied with the geological formation.

In the current research, it was selected two different types of crude oils namely as Murban and Das Blend that slight dissimilar in their chemical compositions that including major corrosive properties of them.

2.2 Methodology

The overall procedure and methodology of this have been subdivided into a few of subtopics and descriptive summaries have been given regarding each topic.

2.2.1. Chemical Composition of Metals

The chemical compositions of seven types of metals were determined by the X-ray fluorescence (XRF) detector after cleaning the surface of each type of metal coupon.

2.2.2. Corrosive Properties of Crude Oils

The corrosive properties of both crude oils were determined by some of essential instruments and well defined methods of analytical chemistry. A brief summary of the testing corrosive properties of both crude oils is given in the Table 1.

Table 1: *Testing of Corrosive properties in both 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

2.2.3. Corrosion Rate and Weight Loss Method

A batch of similar sized metal coupons was prepared from seven different types of metals as six similar metal coupons from each type of metal and prepared two sets of metal coupons from each type of metal. Each set of metal was consisted with three homogeneous

metal coupons and each set was completely dipped separately with respect to both crude oils and each container was closed as shown in the Figure 1.



Figure 1: Apparatus Setup

A metal coupon from each set was taken out and the corrosion rates of those metal coupons were determined by relative weight loss in order to after 15, 30 and 45 days from the immersion. The corroded surface was observed under the 400X lens of an optical microscope. The corroded surfaces of metal coupons were cleaned by sand papers and isooctane. The weight loss method is some simple and direct method that undependable on the type of corrosion and applicable in each type of corrosion (Oparaodu & Okpokwasili, 2014). The terms and the mathematical expression of weight loss method are given in the Equation 1.

$$CR = \frac{W}{(D \times A \times t)} \times k \quad (1)$$

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

2.2.4. Microscopic Analysis

As qualitative analysis of the corrosion compounds on the surfaces of metal coupons the microscopic analysis part was performed. In fact that it was a confirmation step of the formation of the corrosion on the surfaces of metal coupons. The surface of each metal coupon was observed through the 400X lens of an optical microscope before the immersion in crude oils and after corroded.

2.2.5. Decay of Metals in Crude Oils

The ferrous concentrations of crude oil samples which were interacted with carbon steels and stainless steels were tested by the atomic absorption spectroscopy (AAS) at the same time tested the copper concentration of crude oil samples which were interacted with Monel metal due the necessity of evidences and confirmation steps for the invisible weight loss of metal pieces in the crude oils that identified while the determination of corrosion rate in metal coupons.

2.2.6. Hardness of Metals

Beside of the formation of corrosion on metals the initial hardness and hardness after the corrosion were tested in each metal coupon by the Vicker's hardness tester as a step of confirmation of the changes on the surfaces of metal coupons simultaneous to the corrosion. According to the procedure regarding the hardness testing the hardness of each metal coupon was interpreted as the average value after testing at least three points on the metal surface at once.

3. Results and Discussion

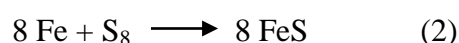
3.1 Corrosive Properties of Crude Oils

The observed results regarding the corrosive properties in both crude oils are given in the Table 2.

Table 2: Corrosive Properties in 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

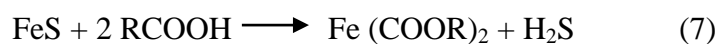
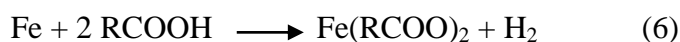
According to the observed results higher amounts of sulfur, mercaptans and organic acids were found from Das Blend crude oil than the Murban crude oil whereas higher amount of salts was found in Murban crude oil than the Das Blend crude oil. The elemental sulfur and some sulfur compounds are some corrosive compounds that tend to create the corrosion compounds on the metals. Mercaptans also some active sulfur compound that cause the metallic corrosion which has a formula of RSH. Usually the process is known as the “sulidation” which is tending to befall the temperature above 230⁰C in proper (Fahim, Alsahhaf & Elkilani, 2010). The general reaction between ferrous and sulfur is given in the Equation 2.



Salt play an eager role in metallic corrosion that found in crude oils as NaCl, CaCl₂ and MgCl₂. Specially during heating processes of crude oils and approaching to towards higher temperatures those salts are broken into HCl molecules although does not behave as a corrosive compound. When reducing the temperature HCl molecules tend to react with moisture and formed hydrochloric acids and hydrogen sulfide (Badmos, Ajimotokan & Emmanuel, 2009). FeS is the major corrosion compound regarding the above mechanism and it has some distinguish visible features. The reproducing reactions of HCl are given in the Equation 3, Equation 4 and Equation 5.



The role of acids in the metallic corrosion is considered significantly regarding the environment of crude oils because crude oils consisted with some amount of naphthenic acids which is depended on the geological formation of the particular crude oil that having a general formula of RCOOH also known as the acidity of crude oils (Fahim, Alsahhaf & Elkilani, 2010). The general formulas of the cause of metallic corrosion due to the presence of acids are given in the Equation 6, Equation 7 and Equation 8 (Davis & Davis, 2003), (Afaf et al, 2007).



The Das Blend crude oil has some higher strength in causing metallic corrosion than Murban crude oil according to the sufficiency of corrosive properties in Das Blend crude oil.

3.2. Chemical Compositions of Ferrous Metals

The chemical compositions of used metals in the experiment according to the XRF detector are given in the Table 3.

Table 3: Chemical Compositions of used Metals

Metal	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cr (%)	Cu (%)	P (%)	Mo (%)	Si (%)	S (%)	Ti (%)	V (%)
(1)Carbon Steel (High)	98.60	0.43	-	0.17	0.14	0.37	0.12	0.086	0.09	-	-	-
(2)Carbon Steel (Medium)	99.36	0.39	-	-	-	-	0.109	-	0.14	<0.02	<0.04	-
(3)Carbon Steel (Mild Steel)	99.46	0.54	<0.30	-	<0.07	-	-	-	-	-	<0.19	<0.07

(4) 410- MN: 1.8 420- MN: 2.8 (Stainl ess Steel)	88.25	0.28	-	0.18	10.92	0.10	0.16	-	0.11	-	-	-
(5) 410- MN: 1.7 420- MN: 1.7 (Stainl ess Steel)	87.44	0.30	-	-	11.99	-	0.18	-	0.09	-	-	-
(6) 321- MN:1. 4 304- MN:1. 9 (Stainl ess	72.47	1.44	-	8.65	17.14	-	0.18	-	0.12	-	-	-

Steel)												
(7)Monel 400	1.40	0.84	0.11	64.36	<0.04	33.29	-	-	-	-	-	-

The results showed higher amount of ferrous in carbon steels, moderate amount of ferrous in stainless steels and trace amount of ferrous in Monel 400 with other alloy metallic elements (Khana et al., 2009).

3.3. Corrosion Rates of Metals

The average corrosion rates of seven different types of metals with respect to Murban and Das Blend crude oils are given in the Figure 2.

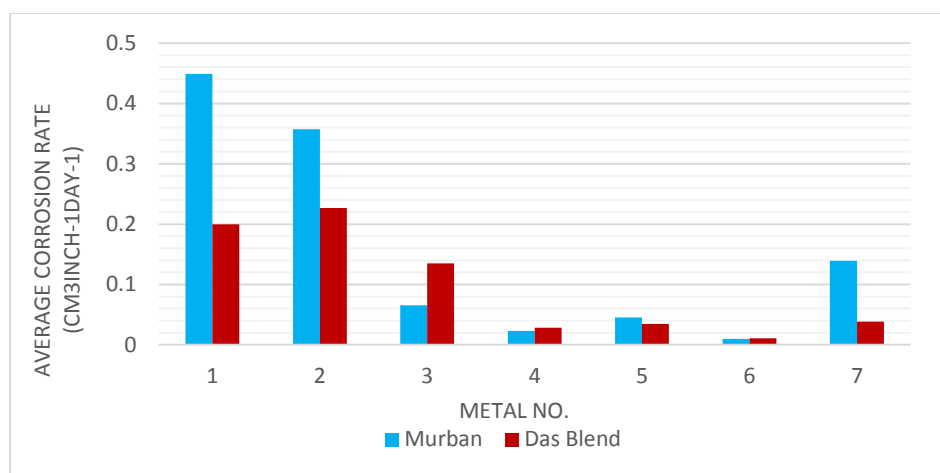


Figure 2: Average Corrosion Rates of Metals

According to the distribution of the average corrosion rates of metals with respect to both crude oils carbon steels showed some relatively higher rates of corrosion regarding both crude oils and stainless steels showed relatively lower corrosion rates regarding both crude oils while an intermediate corrosion rates were found from Monel 400 in both crude oils. There were found that higher corrosion rates of four types of metals in Murban crude oil than the corrosion rate in Das Blend crude oil. When comparing the corrosion rates regarding the type of metal stainless steels showed lower corrosion rates among others specially the 321 MN:1.4 304-MN:1.9 (Stainless Steel) showed the least corrosion rates in both crude oils among the seven different types of metals. According to the chemical composition it was composed with ~ 8% of Ni and ~ 18% Cr while the amount of Fe was remaining ~72%.

According to the theoretical explanation about the Cr and Ni composition of stainless steels it tends to create a self-corrosive protection film when the amount of Cr is present at least 12% and sufficient amount of Ni (Singh et al., 2006). Therefore, with respect to above theory the least corrosion phenomenon was proved properly.

When considering the corrosion rate with respect to both crude oils it was found some higher corrosive tendency regarding the Das Blend crude oil than the Murban crude oil even though most of metals showed relatively lower corrosion rates in Das Blend crude oil than the corrosion rate in the Murban crude oil. In the analysis of obtained results it can be suggested the effect of salts in the crude oils on the metallic corrosion was stronger than the overall effect of sulfur, mercaptans and organic acids in crude oils on the metallic corrosion specially in the room temperature for as much as some of corrosive mechanisms are raised at some higher temperatures such as the “sulfidation” (Speight et al., 1999).

3.4. Microscopic Review

According to the microscopic analysis of corroded metallic surfaces some captures of the corroded surface of carbon steel (mild steel) are given in the Figure 3.

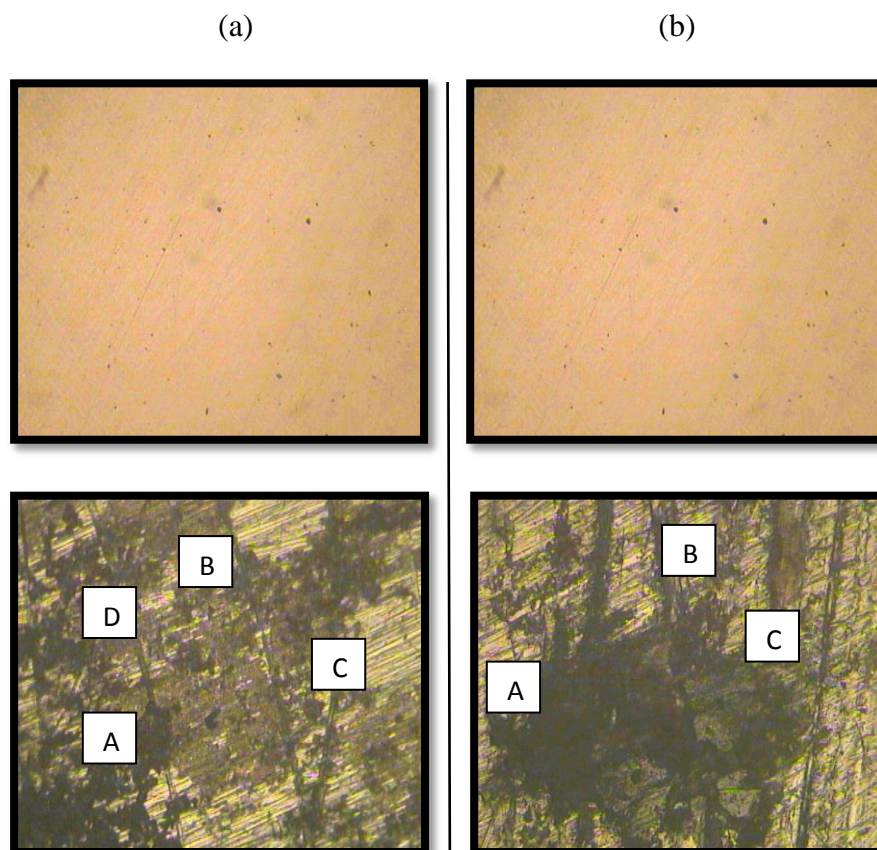


Figure 3: Corroded Surface of Carbon Steel (Mild Steel) in (a) Murban and in (b) Das Blend

According to the captured images of corroded metal surfaces some specific features were identified based on their visible appearances foremost the color (Calister et al., 2003).

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

Some distinguish appearances of corrosion compounds and specific observations regarding the qualitative analysis are given in the Table 4.

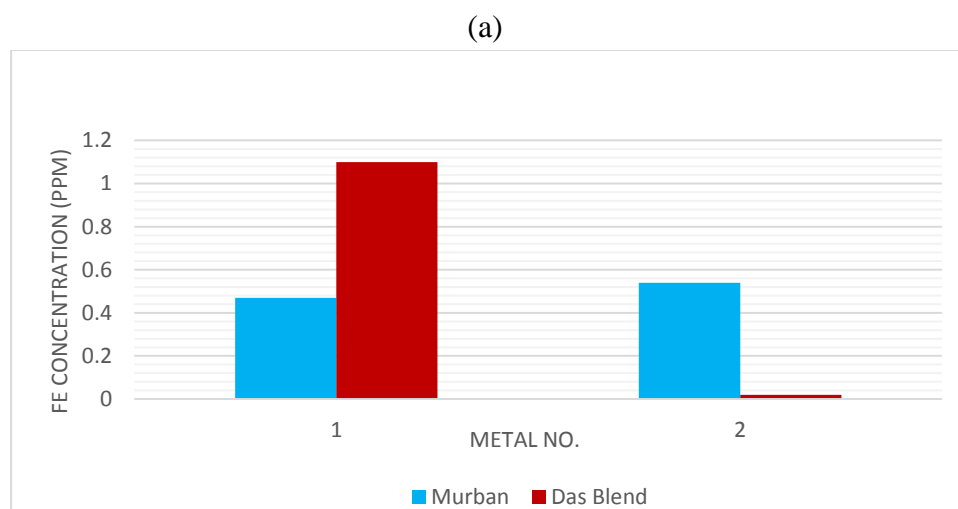
Table 4: Appearances of Corrosive Compounds

Compound	Appearances	Observations
FeS	Black, brownish black, property of powder, pitting, cracks	Observed most of features in each metal piece.
Fe ₂ O ₃	Rusty color	Observed rarely.
CuS	Dark indigo/ dark blue	Unable to specify.

These observations can be used as a confirmation stage of the formation of the corrosion compounds on the surfaces of metal coupons.

3.5. Metallic Concentrations in Crude Oils

The ferrous concentration in crude oil samples that interacted with carbon steel, stainless steel and the copper concentration of crude oil samples that interacted with Monel metal are given in the Figure 4.



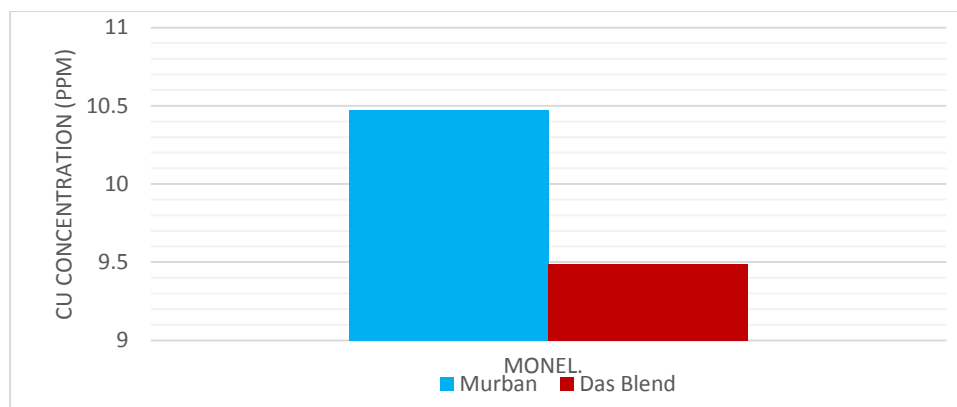
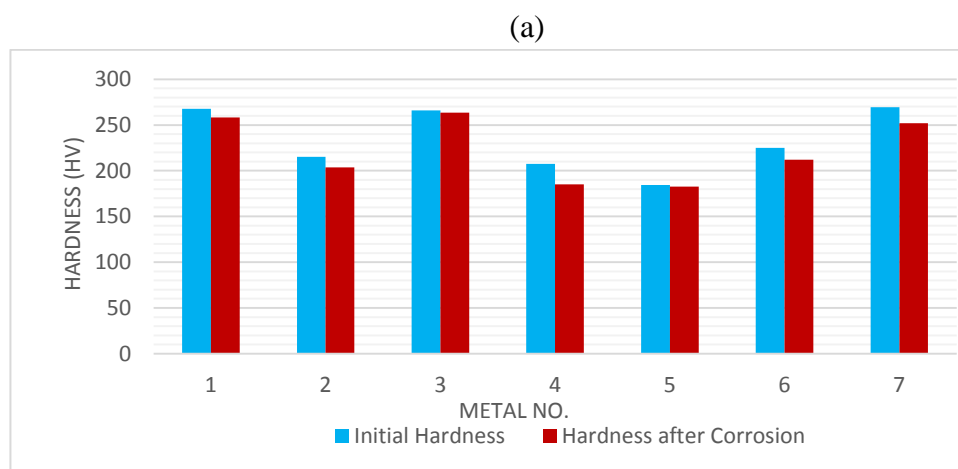


Figure 4: (a) Fe Concentration and (b) Cu Concentration in Crude Oils

According to the results for the metallic concentrations in crude oils there were found some of significant concentration of ferrous in both crude oil samples which were interacted with carbon steel (high) and carbon steel (medium). There weren't shown any amount of ferrous in any crude oil sample that interacted with carbon steel (low) or stainless steels although there were found some higher concentrations of copper regarding the both crude oil samples which were interacted with Monel 400. In the mechanism of the occurrence of corrosion the metal oxide, sulfide, hydroxide or any extrinsic compounds tend to be discarded to the outward from the parent surface due to the ascendancy of repulsive and attractive forces in between successive electrons and protons (Calister et al., 2003). These observations also complied with some equitable results that observed regarding the rate of corrosion of metals and also verified the accuracy of those results forever.

3.6. Deviations of the Hardness

The values of the hardness of each metal coupon before the immersion in crude oils and after corroded with respect to both crude oils are given in the Figure 5.



(b)

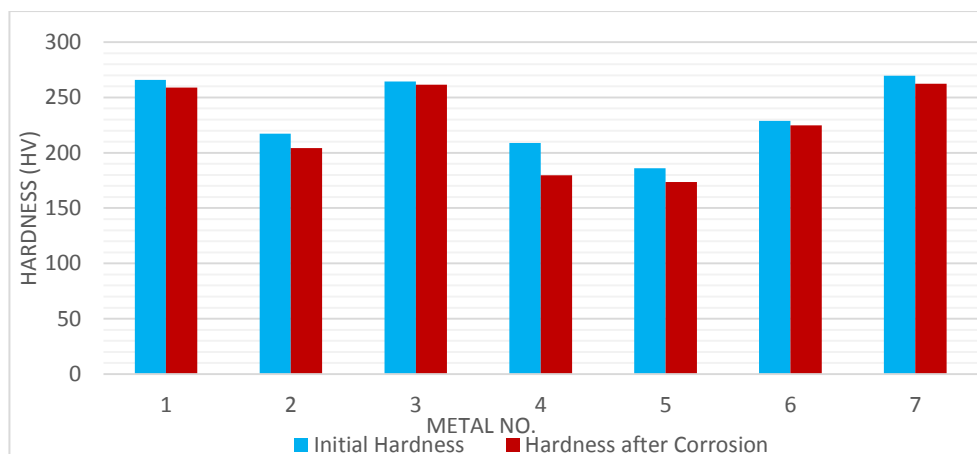


Figure 5: Deviation of the Hardness of Metals in (a) Murban and in (b) Das Blend

The slight reduction of the initial hardness was found from each metal coupon after the corrosion in both crude oils according to the interpretation of the values of hardness of each metal before and after the corrosion although it showed some of asymmetric variations in the hardness. According to the behaviors of corrosion compounds they are removed from the metal surface while creating some unstable conditions on the parent metal surface at different points (Khana et al., 2009). The hardness is depending on the conditions of the particular point where it is tested. The reduction of hardness can be emphasized with the effect of corrosion on the metal and the unstable surface with some asymmetric distribution of the hardness (Fahim, Alsahhaf & Elkilani, 2010). These results provided considerable evidences for the cause of metallic corrosion more over.

4. Conclusion

According to the observed results Das Blend crude oil is much stronger regarding the corrosive properties than Murban crude oil because it showed high sulfur content, acidity and mercaptans content while Murban showing higher salt content than Das Blend although there were found higher corrosion rates regarding four types of metals in Murban crude oil than the corrosion rate in Das Blend the same metal. When comparing the corrosion rates with the type of metal some relatively higher corrosion rates were found from carbon steels while least corrosion rates were finding in 321-MN:1.4, 304-MN:1.9 (Stainless Steel) with respect to both crude oils. Apart from that according to the AAS analysis some higher concentrations of Fe were found from crude oil samples that interacted with carbon steel (high) and carbon steel (medium) nevertheless found Fe concentrations form any crude oil sample that interacted with any other metal specially any type of stainless steel. In the microscopic analysis there were found some important features regarding the cause of corrosion such as

FeS, corrosion cracks and pitting corrosion based on their visible appearances. There were found some significant Cu concentration in both crude oil samples that interacted with Monel metal can be concluded the formation of CuS. The significant concentration of ferrous and copper can be used as confirmation evidences of the metallic corrosion forever. Beside of that a slight reduction of the original hardness of each metal coupon was found after the corrosion.

5. Acknowledgement

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