Journal of Chemical Engineering & Process Technology

Aluvihara and Premachandra, J Chem Eng Process Technol 2018, 9:4
DOI: 10.4172/2157-7048.1000390

Research Article

Open Access

Fundamental Corrosive Properties of Crude Oils and their Effect on the Ferrous Metals

Suresh Aluvihara[1] **and Jagath K Premachandra**[2*]

[1]*Department of Science and Technology, Uva Wellassa University, Badulla, Sri Lanka*

[2]*Department of Chemical and Process Engineering, University of Moratuwa, Katubedda, Sri Lanka*

[*]**Corresponding author:** Premachandra JK, Department of Chemical and Process Engineering, University of Moratuwa, Katubedda, Sri Lanka, Tel: +94112650281; E-mail: bajagathp@gmail.com

Received date: September 14, 2018; **Accepted date:** October 18, 2018; **Published date:** October 22, 2018

Abstract

Crude oils are predominantly made of organic compounds foremost hydrocarbons, trace compounds and corrosive compounds as well. The interaction between crude oils and ferrous metals causes some severe ascendency on the ferrous metals due to the corrosive compounds in crude oils with the collaboration of the chemical compositions such ferrous metals. In this research it was expected to investigate the effect of both Murban and Das Blend crude oils on the corrosion rates of seven different types of ferrous metals. The contents of sulfur, mercaptans, organic acids and salts in both crude oils were determined by to XRF analyzer, titration methods and salt analyzer while testing the chemical composition of each metal by XRF detector. Batches of similar sized metal coupons were prepared from each type of metal and the corrosion rates of each metal coupon were determined by the weight loss method while after 15, 30 and 45 days from the immersed day while observing the corroded surfaces through the 400X lens of an optical microscope. The hardness of each metal coupon was tested by Vicker's hardness tester before immersion in the crude oil and after corroded. The concentrations of ferrous and copper were tested in each crude oil sample after exposed to the metals by the atomic absorption spectroscopy (AAS). There were found some higher corrosive strength in Das Blend than Murban although found higher corrosion rates from four types of metals in Murban than Das Blend and relatively lower corrosion rates in stainless steels than the other metals. Apart from that there were found significant concentrations of ferrous and copper in some crude oil samples especially regarding carbon steels and Monel. Also, slight reductions of the initial hardness were found from each metal coupon after the corrosion eventually.

Keywords: Crude oils; Corrosive properties; Ferrous metals; Corrosion rate; Hardness

Introduction

Crude oil is a mixture of hydrocarbons, some trace compounds and some corrosive compounds as well. In the industry of crude oil refining there can be found peerless usages of ferrous metals associated with several subsections such as transportation, storage and heating units. Due to the impotence of ferrous metal in the refining industry the corrosion is finding as an adverse phenomenon because of the calamity of the corrosion on the behaviors and the properties of such metals. Usually the term of corrosion is defined as the formation of metal oxides, sulfides or hydroxides compound on the metal surface itself as a results of a chemical oxidation process [1-5]. The corrosion is typically occurring when the ferrous metals are exposing to either some stronger oxidizing agent than Fe^{2+} or any environment that consisted with water and oxygen. That process is modified with the aid of organic acids and salts present in the surrounding medium [2,4]. Basically, most of organic acids, salts, sulfur and active sulfur compounds present in the crude oils tend to cause the metallic corrosion however it is depended on the chemical compositions of such metals with the contribution of environmental conditions foremost the temperature [3]. There were several researches have been performed previously to test the effect of some properties on the metals regarding the corrosion although in the current research there were expected to compare the effects of the organic acids, salts, sulfur and active sulfur compounds of two different crude oils on seven different types of ferrous metals, the variation of the properties of such metals due to the corrosion and the stabilities of such metals against the corrosion [1-15].

Materials and Methods

Materials

In the current research there were chosen seven different types of ferrous metals which are applicable in different tasks while the process of crude oil refining in Sri Lanka. Three different types of carbon steels, three different types of stainless steels and Monel metal were included in the batch of metal coupons [1,3,5]. The types of metals that used in the experiment and their typical applications regarding the industry of the industry of the crude oil refining are given in the below.

Carbon Steel (High)- Transportation tubes, storage tanks.

Carbon Steel (Medium)- Transportation tubes, storage tanks.

Carbon Steel (Mild Steel)- Heat exchanges.

410-MN: 1.8 420-MN: 2.8 (Stainless Steel)- Crude distillation unit.

410-MN: 1.7 420-MN: 1.7 (Stainless Steel)- Crude distillation unit.

321-MN: 1.4 304-MN: 1.9 (Stainless Steel)- Crude distillation unit.

Monel 400-Heat exchangers.

Beside of that different two types of crude oils were selected which are slightly different in their chemical composition. Murban and Das Blend are the two different types of crude oils and the Das Blend has been identified as a "sour" crude oil because of the high sulfur content of that crude oil which is a major corrosive compound that presence in crude oils [2,8,15].

Methodology

The entire procedure of the whole research has been discussed in separate sub topics in order of the performed and the necessity.

Composition test of metals: The elemental compositions of each type of metal coupon were tested by the digital XRF detector including the major metals, trace metals and most of doping nonmetals as well excluding carbon as a percentage [1-5]. The XRF detector is an instrument that able to measure the composition of materials based on the principle of the diffraction of X-ray while penetrating the bulk of such material. According to the working principle of XRF detector the cleaned surface of the material needs to be either touched or even exposed to the detector of the instruments and the digital readings are given as results.

Property test of crude oils: The major corrosive properties of both Murban and Das Blend crude oils were tested by the standard test methods [11,14,15]. A brief introduction about the tests of some important corrosive properties of both crude oils and the standard test methods is given in the Table 1.

Property	Method	Readings
Sulfur content	Crude oil samples were directly used to the XRF analyzer.	Direct readings from the digital display in ppm
Acidity	Each crude oil sample was dissolved in a mixture of toluene and isopropyl and titrated with potassium hydroxide.	End point of such titrations and calculated the concentration of acids
Mercaptans content	Each crude oil sample was dissolved in sodium acetate and titrated with silver nitrate.	End point of the titration and calculated the Mercaptans content
Salt content	Each crude oil sample was dissolved in organic solvent and exposed to the cell of analyzer.	Direct readings from the digital display

Table 1: Test methods of the corrosive properties of crude oils.

Determination of the corrosion rates: A batch of similar sized metal coupons was prepared from seven different types of metals in same dimensions as six metal coupons from each type of metal and the surfaces of them were cleaned by the sand papers as shown in the Figure 1.

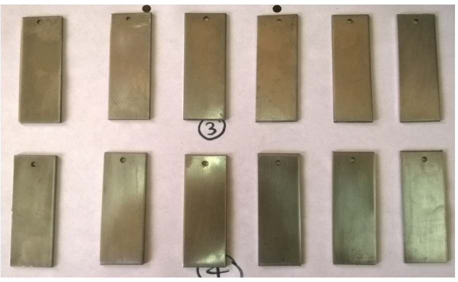

Figure 1: Prepared metal coupons.

Each metal coupon was completely dipped in Murban and Das Blend crude oil samples separately according to the type of metal as three homogeneous metal coupons per on crude oil container under the normal environmental conditions such as the room temperature as shown in the Figures 2 and 3.

Figure 2: Metal coupons.

Figure 3: Set of apparatus.

After 15 days from the immersion a metal coupon from each crude oil container was taken out. The corrosion rates of those metal coupons were determined by the weight loss method while observing the corroded surfaces through the 400X lens of an optical microscope and corroded surfaces were cleaned by sand papers and isooctane and measured the final weight by the electronic balance accordance to the necessity of the calculations. Weight loss method is a manual method of determining the rate of corrosion accordance to any type of metal and simple method with a few of limitations [10]. The mathematical expression and the terms of the weight loss method are explained in the Equation 1.

$CR=W \times K/D \times A \times t$……….(1)

Where;

W=Weight loss due to the corrosion 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.

The same procedure was repeated for another two sets of metal coupons which were remained in the crude oil containers in order of 30 and 45 days from the immersion to determine the corrosion rates of such metal coupons and finally the average corrosion rates of each metal type was calculated with respect to each Murban and Das Blend crude oils by considering the obtained values for the corrosion rates of three metal coupons from each metal types after 15, 30 and 45 days from the immersion with respect the relevant crude oil [10].

Microscopic analysis: Corroded metal surfaces were observed through the 400X magnification lens of the laboratory optical microscope as a qualitative analysis of the corrosion subsequently after getting out of the metal coupons from the crude oils and their visible features were observed with the references to identify the corrosion compounds which were formed on the surfaces of the metal coupons with the aid of their visible features foremost the color and the changes of surface such as the cavities [1,3-5].

Metallic concentration test in crude oils: The concentrations of ferrous in crude oil samples which were exposed to both carbon steels and stainless steels were tested separately by the atomic absorption spectroscopy (AAS) while testing copper concentrations of crude oil samples which were exposed to the Monel as a confirmation test of the formation of the corrosion in those metal coupons. According to the methodology of testing 1 ml of each crude oil sample was diluted with 9 ml of 2-propanol and filtered out the precipitate.

Hardness test: Hardness is an important physical property regarding the conditions of the surface of metal although may be varied [1,3]. Both initial hardness and hardness after the corrosion of each metal coupon were tested by the Vicker's hardness tester. According to the working principles of the Vicker's hardness tester there were tested the hardness of at least three points on each metal coupon at once and the average values were calculated and interpreted as the hardness of each metal coupon with respect to each occasion.

Results and Discussion

Chemical compositions of metals

The elemental compositions of each type of metal according to the results of XRF detector are given in the Table 2.

Metal	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cr (%)	Cu (%)	P (%)	Mo (%)	Si (%)	S (%)	Ti (%)	V (%)
(1) Carbon Steel (High)	98.6	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 (Stainless Steel)	88.25	0.28	-	0.18	10.92	0.1	0.16	-	0.11	-	-	-
(5) 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)	87.44	0.3	-	-	11.99	-	0.18	-	0.09	-	-	-
(6) 321-MN:1.4 304-MN:1.9 (Stainless Steel)	72.47	1.44	-	8.65	17.14	-	0.18	-	0.12	-	-	-
(7) Monel 400	1.4	0.84	0.11	64.36	<0.04	33.29	-	-	-	-	-	-

Table 2: The elemental compositions of metals.

According to the obtained results regarding the chemical compositions of metals there were found some higher amounts of ferrous in carbon steel, moderate amount of ferrous in stainless steel and trace amount of ferrous in Monel while containing higher amounts of nickel and copper. Especially in stainless steels some significant amounts of nickel and chromium were added based on the purposes of enhancing properties and the reduction of the corrosion as well [1,3].

Corrosive properties of crude oils

The results regarding the experiments for the corrosive properties of both Murban and Das Blend crude oils are given in the Table 3.

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

Table 3: Corrosive properties of crude oils.

The above results showed some emphatics in the corrosive tendency of Das Blend. Because Das Blend was composed higher amounts of organic acids, sulfur and mercaptans than Murban while Murban was showing greater amount of salts than Das Blend.

Salts present in crude oils are known as the summation of NaCl, $CaCl_2$ and $MgCl_2$. Due the chemical reaction between those salts and water at some high temperatures salts tend to be broken into HCl and those HCl molecules become into high corrosive compounds due to the reaction with the moisture when the system is approaching to low temperatures and formed the hydrochloric acids and hydrogen sulfides which are known as high corrosive compounds although the contribution of hydrogen sulfide in the metallic corrosion cannot be considered as much because of its gas phase and evolving ability [7]. Finally, the metal sulfides are formed on the metal surfaces due the chemical reactions that given in the Equation 2, Equation 3 and Equation 4.

$CaCl_2+H_2O \rightarrow CaO+2HCl$……….(2)

$HCl+Fe \rightarrow FeCl_2+H_2$……….(3)

$FeCl_2+H_2S \rightarrow FeS+2HCl$……….(4)

According to the naturally occurrence of crude oils those crude oils may be consisted with some significant amount of organic acids also known as "naphthenic acids" which has a general formula of RCOOH [2,9,15]. The total amount of both organic acids and naphthenic acids in some crude oil is known as the "acidity" of such crude oil also found as a corrosive compound. In some previous researches there were investigated some effects of organic acids on the metallic corrosion although there cannot be correlated these two properties [15]. The general reactions between metals and those acids are given in the Equation 5, Equation 6 and Equation 7.

$Fe+2RCOOH \rightarrow Fe(RCOO)_2+H_2$……….(5)

$FeS+2RCOOH \rightarrow Fe(COOR)_2+H_2S$……….(6)

$Fe(COOR)_2+H_2S \rightarrow FeS+2RCOOH$……….(7)

Crude oils may be contained with different types of sulfur compounds such as mercaptans, thiophenes and elemental sulfur. The formation of the corrosion on metal surfaces due to the direct interaction between the sulfur and metal is known as the process of "localized corrosion" which is highly depended on the temperature that usually occurred at about 80°C [11,14,15]. Also sulfur compounds which are having fraction or functional group tend to react with metallic compounds and formed the corrosion especially in some higher temperatures above 230°C properly also the process is called as the "sulfidation" [2,6]. Mercaptans also an active sulfur compound can cause the metallic corrosion which has a general formula of "RSH". The general chemical reaction between sulfur and metals is given in the Equation 8 and Equation 9.

$S8_{(s)}+8H_2O_{(l)} \rightarrow 6H_2S_{(aq)}+2H_2SO_4$……….(8)

$8Fe+S8 \rightarrow 8FeS$……….(9)

By referring the theoretical explanations regarding the nature of the corrosion of ferrous metals in the crude oils there can be concluded and assumed the formation of the FeS regarding the all possible mechanisms of the formation of the corrosion.

Corrosion rates of metals

The average corrosion rates of metal coupons with respect to both crude oils are given in the Figure 4.

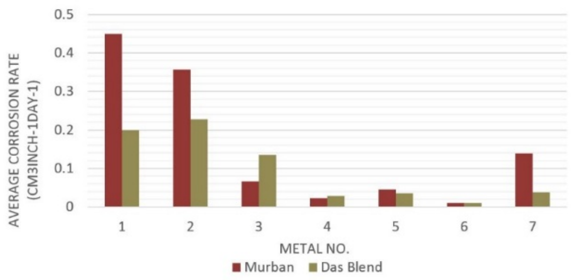

Figure 4: Corrosion rates of metal coupons in both crude oils.

According to the rates of corrosion of metals in both crude oils there were found relatively high corrosion rates from carbon steels and moderate corrosion rates from Monel in both crude oils. The least corrosion rates were found from 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) in both crude oils. According to the chemical composition of 321-MN: 1.4304-MN: 1.9 (Stainless Steel) it was composed 18% of chromium and nearly 8% of nickel. Regarding a theoretical concept of the doping of metals with nickel and chromium at some particular composition those two elements tend to form a self-protection film against the corrosion and the minimum amount of chromium for that is about 12% with sufficient amount of nickel [1,3,5]. Also, in this research the least corrosion rates were found from the metals that the chromium content was in order to 18%, 12% and 11%. When consider about the corrosion rates of 410-MN: 1.7 420 -MN: 1.7 (Stainless Steel) showed some higher corrosion rates among other stainless steels since it was composed ~12% of chromium and lack of nickel. Although some lower corrosion rates were shown 410- MN: 1.8 420-MN: 2.8 (Stainless Steel) since it was composed ~11% of chromium and ~0.2% of nickel. By referring such observations there can be reached to some opinion that the necessity of both chromium and nickel in the recommended level to have the optimal performances of the self-corrosive protection layer against the corrosive environment [1,3,5,6].

When comparing the corrosive properties of both crude oils there were found some higher corrosive tendency from Das Blend crude oil than the Murban crude oil although four types of metals showed higher corrosion rates in Murban crude oil than the Das Blend crude oil. Therefore, it can be concluded the effect of salts on the corrosion was higher than the overall effect of organic acids, sulfur and mercaptans on the corrosion due to the less progressiveness of the both processes of "sulfidation" and "localized corrosion" in room temperatures and other conditions [2,6,8,15].

The variations of the rate of corrosion of each metal type with the exposure time in the respect crude oil are given in the Figures 5 and 6.

Citation: Aluvihara S, Premachandra JK (2018) Fundamental Corrosive Properties of Crude Oils and their Effect on the Ferrous Metals . J Chem Eng Process Technol 9: 390. doi:10.4172/2157-7048.1000390

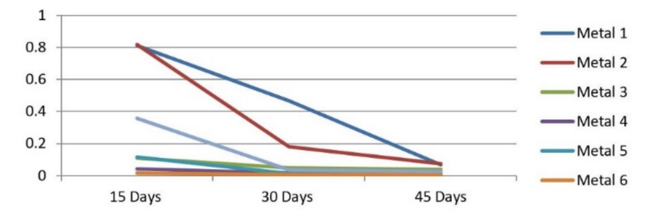

Figure 5: Variations of the rates of corrosion of metal coupons with the exposure time in Murban.

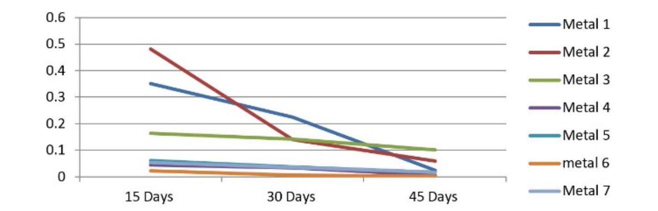

Figure 6: Variations of the rates of corrosion of metal coupons with the exposure time in Das Blend.

Metal 1- Carbon Steel (High).

Metal 2- Carbon Steel (Medium).

Metal 3- Carbon Steel (Mild Steel).

Metal 4- 410-MN: 1.8 420-MN: 2.8 (Stainless Steel).

Metal 5- 410-MN: 1.7 420-MN: 1.7 (Stainless Steel).

Metal 6- 321-MN: 1.4 304-MN: 1.9 (Stainless Steel).

Metal 7- Monel 400.

Above results showed some reductions of the rates of corrosions in each metal when increasing the exposure time. According with these experimental results it can be used as the proven stage of the weight loss method that the inversely proportional relationship in between the rate of corrosion and exposure time [10].

Qualitative analysis of corrosion

There were observed some features of corrosion compounds regarding most of metals while observing some distinguish properties of such compounds including color, cracks and pits on the corroded metal surface [1,3,6]. Some special features that identified during the microscopic analysis are given in the Figures 7 and 8.

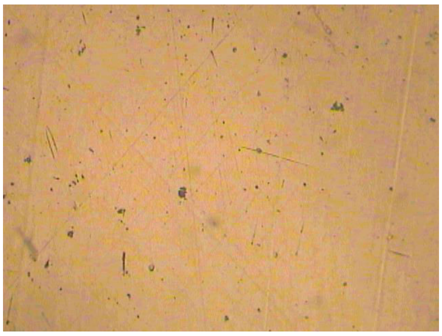

Figure 7: Corroded surface of 410-MN: 1.8 420- MN: 2.8 (Stainless Steel) in Murban.

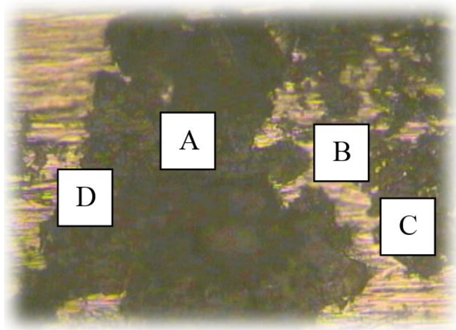

Figure 8: Corroded surface of 410-MN: 1.8 420- MN: 2.8 (Stainless Steel) in Murban. A: Ferrous Sulfide and Trace Compounds; B: Pitting Corrosion; C: Corrosion Cracks; D: Ferrous Oxides and Trace Compounds.

A descriptive summary of the corrosion compounds that formed on the metal surfaces and appearances of them is given in the Table 4 [1,3].

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.

Table 4: Appearances of corrosion compounds.

There can be concluded that the observations of at least one feature regarding each metal and pitting corrosion and corrosion c racks were found in most of stainless steels. Beside of that there observed some cavities on some of metals and according to the optical features of corrosion there can be concluded the formation of FeS regarding the carbon steel and stainless steel [1-9]. According to the Monel metal there can be concluded the formation of CuS as a result of the interaction between crude oil and the metals although unable to distinguish from FeS only with the visible appearances.

Decay of metals into the crude oils

The concentrations of ferrous and copper in crude oil samples after exposed to the metals are given in the Figures 9 and 10.

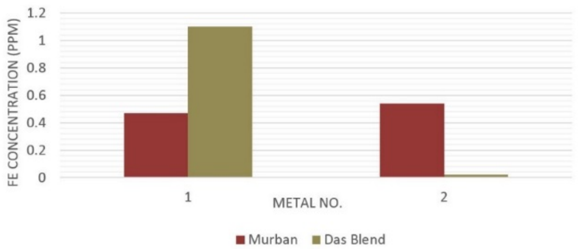

Figure 9: Fe concentrations in crude oil samples after interacted with metals.

Figure 10: Cu concentrations in crude oil samples after interacted with metals.

According to the above results of atomic absorption spectroscopy (AAS) some significant concentrations of ferrous were found from both Murban and Das Blend crude oil samples which were exposed to the high carbon steel and medium carbon steel while there were not found any concentration of ferrous crude oil samples which were exposed to neither mild steel nor any type of stainless steel. Apart from that high amounts of copper were found from both Murban and Das Blend crude oil samples which were exposed to Monel. After the formation of corrosive compounds on the surfaces of the metals those compounds tend to be removed from the relevant metal surface by the repulsive and attractive forces in between successive electrons and protons [1,3,6]. The invisible weight loss of the metal also can be explained with this theory and these results can be used as the confirmation evidences of the formation of corrosion.

Effect on the hardness of metals

The values of the hardness of each metal coupon before the immersion in crude oils after corrosion have been interpreted in the Figures 11 and 12.

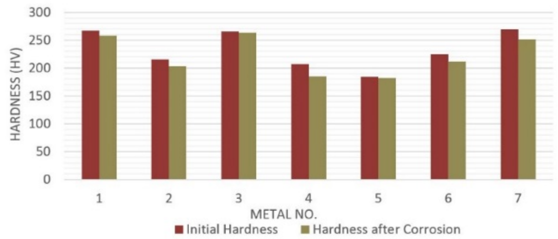

Figure 11: Variations of the hardness of metal coupons after corroded in Murban.

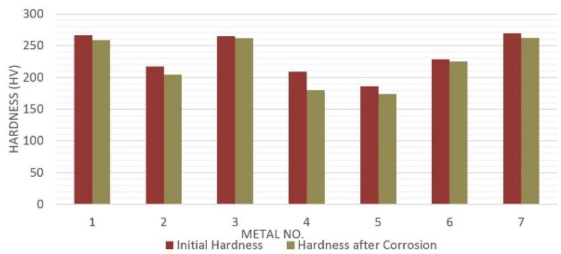

Figure 12: Variations of the hardness of metal coupons after corroded in Das Blend.

According to the variations of the initial hardness of the metals there were observed a slight reduction of the initial hardness after the formation of the corrosion on the surfaces of those metals. After the formation of corrosion compounds on the metal surfaces the stability of metal surface will be reduced due to the tendency of removing those compounds also the reduction of the hardness might be happened due to this phenomenon [1,3,5]. Beside of that there were identified an asymmetric distribution of the hardness and same as an asymmetric variation in hardness. Therefore, these observations can be used as the confirmation evidences for the formation of the corrosion.

Conclusion

According to the observed results there were found higher amounts of ferrous in carbon steels, moderate amount of ferrous in stainless steels and trace amount of ferrous in Monel while containing higher amount of nickel and copper. The Das Blend crude oil was much stronger accordance to the compositions of sulfur, meracaptans, and oraganic acids than Murban while having less salt content than Das Blend. There were found some relatively higher corrosion rates regarding carbons steels in both crude oils and lower corrosion rates were found from Stainless steels. Also, Monel showed a moderate corrosion rates in both crude oils and four types of metals showed higher rates of corrosion in Murban crude oil since Das Blend was stronger than Murban accordance to their corrosive properties. Therefore, it can be concluded the effect of slats on the corrosion is higher than the overall effect of sulfur, mercaptans and organic acids. Beside of that there were observed some visible appearances under the microscopic observations that including corrosion cracks, pitting corrosion and color changes which were most similar to FeS and CuS. The significant concentrations of ferrous in crude oil samples that exposed to carbon steel, nullity of any amount of ferrous in crude oil samples that exposed to stainless steel and great concentrations of copper in crude oil samples that exposed to Monel also expressed some linkage with the rate of corrosions and the reductions of hardness of metals provide some important evidences for the formation of the corrosion forever.

Acknowledgement

The great assistances of the laboratory staff at the Ceylon Petroleum Cooperation Refinery, the staff of the chemistry laboratory at the Uva Wellassa University and the staff of material laboratory at the University of Moratuwa on the success of this research project must be appreciated always.

References

1. Khana OP (2009) Materials Science and Metallurgy. Dhanpet Rai and Sons Publication, New Delhi, India.
2. Fahim MA, Al-Sahhaf TA, Elkilani A (2010) Fundamentals of petroleum refining. Amsterdam: Radarweg Press, Netherlands, Europe.
3. Callister WD (2003) An Introduction of Materials Science and Engineering. John Wiley & Sons, New York, USA.
4. Davis ME, Davis RJ (2003) Fundamentals of chemical reaction engineering. Courier Corporation. McGraw-Hill, US.
5. Singh R (2006) Introduction to basic manufacturing process and workshop technology. New Age International.
6. Bolton W (1994) Engineering materials technology. BH Newnes Limited, London, England.
7. Badmos AY, Ajimotakan HA, Emmanuel EO (2009) Corrosion in petroleum pipelines. New York Science Journal 2: 36-40.
8. Speight JG (1999) The chemistry and technology of petroleum. CRC Press. Boca Raton, Florida.
9. Afaf GA (2007) Corrosion Treatment of High TAN Crude. Doctoral Thesis. University of Khartoum, Sudan.
10. Oparaodu KO, Okpokwasili GC (2014) Comparison of percentage weight loss and corrosion rate trends in different metal coupons from two soil environments. International Journal of Environmental Bioremediation & Biodegradation 2: 243-249.
11. Usman AD, Okoro LN (2015) Mild Steel Corrosion in Different Oil Types. International Journal of Scientific Research and Innovative Technology 2: 9-13.
12. Elnour MM, Ahmed M, Ibrahim T (2014) Study the Effects of Naphthenic Acid in Crude Oil Equipment Corrosion. Journal of Applied and Industrial Sciences 2: 255-260.
13. Rickard D, Luther GW (2007) Chemistry of iron sulfides. Chemical Reviews 107: 514-562.
14. Fang H, Young D, Nesic S (2008) Corrosion of mild steel in the presence of elemental sulfur. International Corrosion Conference and Expo.
15. Bota GM, Qu DM, Nesic SM, Wolf HA (2010) Naphthenic acid corrosion of mild steel in the presence of sulfide scales formed in crude oil fractions at high temperature. International Corrosion Conference and Expo.