# THE CAUSE OF METALLIC CORROSION IN CRUDE OILS

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## *ABSTRACT*

*Metallic corrosion is a severe interrogation regarding most of industrial applications of metals such as the industry of crude oil refining because of the foremost role of metals. The term of corrosion is usually explained as the formation of the metal oxide, sulfide, hydroxide or any compound related with a carboxylic group on the surface due to the impact of the surrounded conditions. The content of sulfur, acidity, mercaptans and salt content are the well ascertained corrosive properties of crude oils also the chemical composition of metals acquit oneself the fundamental preface for the corrosion. The surveillance of the comparison of corrosive capabilities of Murban and Das Blend crude oils in front of seven different types of ferrous metals that used in Sri Lankan refining industry was the dominant intention of this research. The chemical composition of used metals were determined by XRF detector while testing the contents of sulfur, acidities, contents of mercaptans and salt contents with respect to both crude oils simultaneously. Batches of well cleaned and equal sized metal pieces were immersed in both crude oils separately and the corrosion rate of each type of metal piece was determined after 15, 30 and 45 days from the immersion by weight loss method under the observations through the optical microscope. The ferrous and copper concentrations of each crude oil sample were tested while testing the variation of the hardness of each metal as a confirmation stage. According to results there were found relatively higher amount of sulfur, mercaptans, acids and lower amount of salt in Das Blend than Murban although relatively higher corrosion rates of most of metals in the Murban than the Das Blend. The slight reduction of hardness in each metal piece was found while observing significant concentration of ferrous and copper from some of crude oil samples.*

## *KEYWORDS*

*Crude oils, Corrosive properties, Ferrous metals, Weight loss, Corrosion rate, Hardness*

## 1. INTRODUCTION

In the industry of crude oil refining, ferrous metals play a foremost all manner of role. The corrosion is a dominant topic regarding that industry because of the noxious ascendency. Basically it creates some adverse effects in crude oil distillation column head, heat exchangers, transportation tubes and storage tanks. Usually the term of corrosion is defined as the formation of relevant metal oxide, sulfide, hydroxide or any other extrinsic compound related with carboxylic group on the metal surface [1-6]. According to the corrosion of metals in crude oils, the corrosive compounds of crude oils behave as primary lore. The content of sulfur, acidity, content of mercaptans and salt content are the leading corrosive properties of crude oils [2-8]. In the metallic corrosion, the ferrous metal is need to expose to either some kind of oxidizing agent than $Fe^{2+}$ or any system that consisted with oxygen and water [9]. If the system is consisted with salt or organic acids, the rate of above process will be increased in a few times [10-15]. In this research, it was expected to speculate the effect of Murban and Das Blend crude oils on the rate of corrosion in seven different types of ferrous metals which are used in the Sri Lankan crude oil refining industry and suggest the much harmful corrosive compounds present in crude oils that highly effected on the rate of corrosion of those ferrous metals.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Materials

In this experiment two different types of crude oils were selected as samples while selecting seven different types of ferrous metals including three types of carbon steels, three types of stainless steels and Monel which is composed trace amount of iron [1-6]. Those crude oils are somewhat different in their chemical composition namely as Murban and Das Blend.

### 2.2. Corrosive Properties of Crude Oils

Corrosive properties of both crude oils were tested by well defined chemical methods and a brief description of those determinations is given in the Table 1.

Table 1. A descriptive summary of testing corroded aided properties of 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 |

### 2.3. Chemical Composition of Metals

The chemical composition of reach type of metal was determined by the XRF detector as direct readings.

### 2.4. Preparation of the Setup

After cleaning and microscopic test, metal pieces were immersed in both crude oil samples as shown in the Figure 1.

Figure 1. The setup of apparatus.

After 15 days of the immersion a metal piece from each type of metal with respect to both crude oils was taken out and the rate of corrosion in such metals were determined by the weight loss method while observing the corroded surface under 400X lens of optical microscope. The corroded particles were removed by sand papers and isooctane. The initial weight of each metal piece and the weight after removing corrosion from the surface were recorded as readings. The same procedure was repeated for another two batches of samples after 30 and 45 days from the immersed day.

### 2.5. Weight Loss Method

The method of determining the rate of corrosion in metal pieces was the weight loss method based on some advantages such as the applicability of each kind of corrosion and the simplicity [9] [10]. In this method no need to use a complex instrument although need a particular shape for the metal piece. The terms and limitations of weight loss method are given in the following equation.

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

Where;
W = Weight loss of metal coupon in grams
k = Corrosion rate constant (22,300)
D = Metal density in $g/cm^3$
A = Surface area of metal piece ($inch^2$)
t = Immersion/ exposure time (days)
CR= Corrosion rate of metal piece

In this experiment each metal piece was prepared in similar shape and equal dimensions because of dependency of the corrosion rate on the surface area of metals.

### 2.6. Microscopic Analysis

The step of microscopic analysis was performed with the aid of 400X lens of an optical microscope. The surface of each metal piece was observed before the immersion in crude oils and after the corrosion in order to 15, 30 and 45 days.

### 2.7. Metallic Concentration in Crude Oils

The Fe concentrations of crude oil samples that exposed to carbon steels and stainless steels were tested by the atomic absorption spectroscopy (AAS) while testing the Cu concentration of crude oil samples that exposed to Monel metal. In the sample preparation 1 ml of each crude oil sample was diluted with 9 ml of 2-propanol and filtered.

### 2.8. Hardness of Metals

Hardness of each metal piece was tested before the immersion in crude oils and after the corrosion by the Vicker’s hardness tester. According to the principles of Vicker’s hardness tester the hardness of each metal piece was interpreted as an average value with respect to the hardness of several points on the metal surface [4-6].

## 3. Results And Discussion

### 3.1. Corrosive Properties of Crude Oils

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

Table 2. Corrosive properties of both crude oils used in the experiment

| 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 results of corrosive properties of crude oils, the sulfur content, acidity and mercaptans content of Das Blend is higher than Murban while the salt content of Murban is higher than Das Blend. When the elemental sulfur presence in crude oils those sulfur tend to form the sulfides of that relevant metal with the aid of water presence in the crude oils which is known as the process of "localized corrosion" also need some higher temperature in the system [2-8]. The general formula of localized corrosion is given in the following equation.

$$8\ Fe + S8 \rightarrow 8\ FeS$$

Acidity also tends to cause a metallic corrosion because of the effect of organic acids presence in crude oils. Crude oil is a mixture of hydrocarbons that consisted with some trace compounds. According to the formation of crude oils beneath of the earth surface, it could be consisted with some significant amount of naphthenic acids which has a general formula of RCOOH [13] [14]. The general chemical reactions between acids and metals are given in the following equations.

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

$$FeS + 2\ RCOOH \rightarrow Fe\ (COOR)2 + H2S$$

$$Fe(COOR)2 + H2S \rightarrow FeS + 2\ RCOOH$$

Crude oil may contain a few different types of sulfur compounds. Those are mercaptans, thiophenes, sulfoxides, hydrogen sulfides and elemental sulfur. Mercaptan is a compound of active sulfur which has a general formula of "RSH" that cause the metallic corrosion in some higher temperatures nearby $230^0$ C in properly [12-15]. The functional groups of those compounds tend to react with metals and formed specially the metal sulfide.

Salt also much considerable corrosive compound based on the ability of breaking salts into HCl with the aid of water presence in crude oils in some higher temperatures also HCl tend to behave high corrosive compounds when the system is becoming into a system of low temperature. Usually the accumulation of NaCl, $CaCl_2$ and $MgCl_2$ is known as the salt content of any crude oil [2-7]. The formation of corrosion by the salts is explained in the following equations.

$$CaCl2 + H2O \rightarrow CaO + 2HCl$$

$$HCl + Fe \rightarrow FeCl2 + H2$$

$$FeCl2 + H2S \rightarrow FeS + 2HCl$$

Regarding the analysis of corrosive properties of both crude oils, it can be concluded that effect of the sulfur content, acidity and mercaptans content of Das Blend is stronger than Murban while the effect of salt is stronger in Murban than Das Blend based on the assumptions that each process was happened in properly at the room temperature.

## 3.2. Chemical Composition of Metals

According to the results of XRF detector, the chemical compositions of used metals are given in the Table 3.

Table 3. Chemical compositions of metals used in the experiment

| Metal NO. | Metal | Fe (%) | Ni (%) | Cu (%) |
|---|---|---|---|---|
| 1 | Carbon Steel (High) | 98.60 | 0.17 | 0.37 |
| 2 | Carbon Steel (Medium) | 99.36 | - | - |
| 3 | Carbon Steel (Mild Steel) | 99.46 | - | - |
| 4 | 410-MN: 1.8 420-MN: 2.8 (Stainless Steel) | 88.25 | 0.18 | 0.10 |
| 5 | 410-MN: 1.7 420-MN:1.7 (Stainless Steel) | 87.44 | - | - |
| 6 | 321-MN: 1.4 304-MN:1.9 (Stainless Steel) | 72.47 | 8.65 | - |
| 7 | Monel 400 | 1.40 | 64.36 | 33.29 |

Some higher amounts of Fe were found from first three types of metals and moderate amount of Fe were found from fourth, fifth and sixth types of metals while finding a trace amount of Fe and high amount of Cu from Monel metal [1-8].

## 3.3. Corrosion Rates of Metals

The average rate of corrosion in each metal piece was determined and interpretation with respect to the type of metal and the type of crude oil is given in the Figure 2.

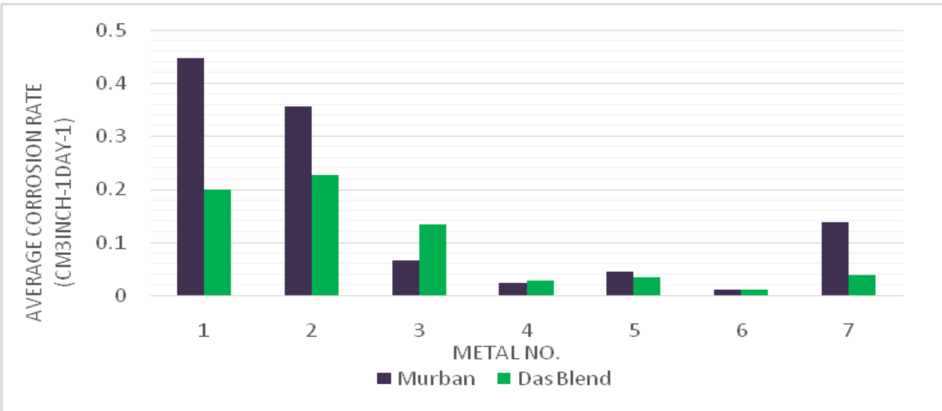



Figure 2. Average corrosion rates of metals in both crude oils

According to the interpretation of the average corrosion rates of metals, the first three types of metals showed relatively high corrosion rates in both crude oils and fourth, fifth and sixth types of metals showed relatively low corrosion rates with respect to both crude oils while Monel was showing a moderate corrosion rates in both crude oils. When comparing the corrosion rates of metals with respect to the type of crude oil, four types of metals showed higher corrosion rates in Murban crude oil than Das Blend while three types of metals were showing higher corrosion rates in Das Blend than Murban although according to the results of the strength of corrosive properties of both crude oils, there was found some higher possibility of corrosion in Das Blend than Murban by considering the progress of corrosive compounds in both crude oils with the conditions of the system foremost the temperature [2-15]. By referring the obtained results, it can be concluded the progress of the salts in the metallic corrosion is more intensive than the progress of sulfur content, acidity and mercaptans content of crude oils in the metallic corrosion in most of occasions. However, it can be suggested some slight effect of much trace and volatile compounds regarding some occasions on the rate of corrosion such as the presence bacteria in crude oils as explained in the following equation [2-7].

$$SO_4^{2-} + H_2 \rightarrow H_2S + H_2O$$

### 3.4. Microscopic Analysis

The important features and changes of the surface of each metal piece were identified clearly under the microscopic analysis. Some of distinguish properties regarding the metallic corrosion were observed in each metal piece as given in the Figure 3.

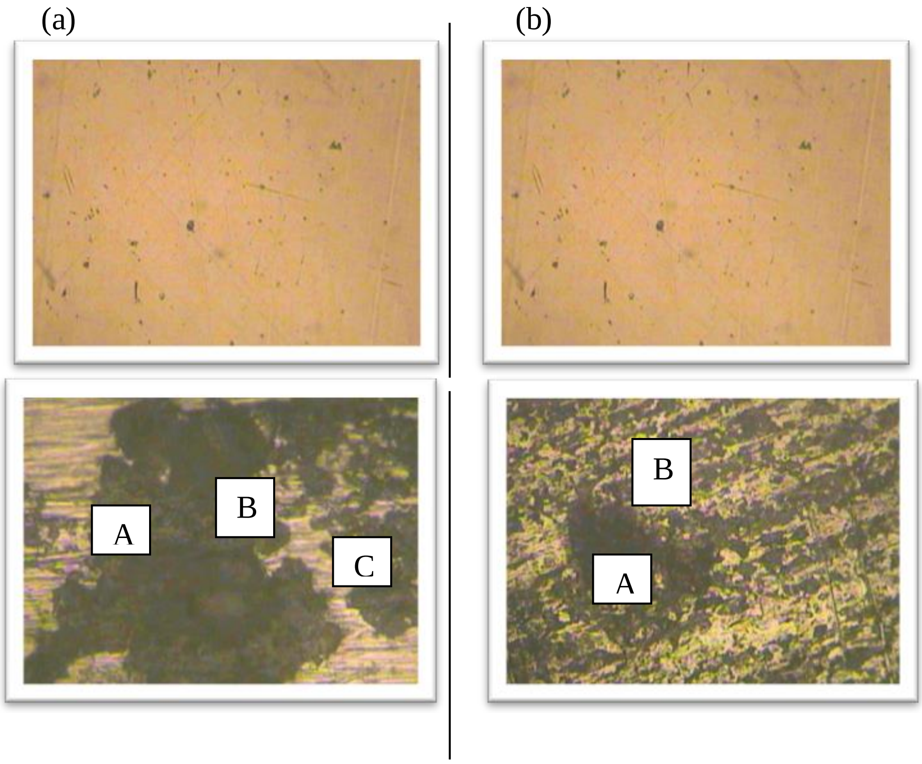



Figure 3. Corroded surface of 410-MN: 1.8 420- MN: 2.8 (Stainless Steel) in (a) Murban and (b) Das Blend.

The analysis of microscopic was based on the visible and tangible features of corrosion compounds of ferrous metals also it was a type of qualitative analysis. Some important corrosion compounds and their appearances are shortlisted in the Table 4 [1-6].

Table 4. Corrosion compounds and appearances

| 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. |

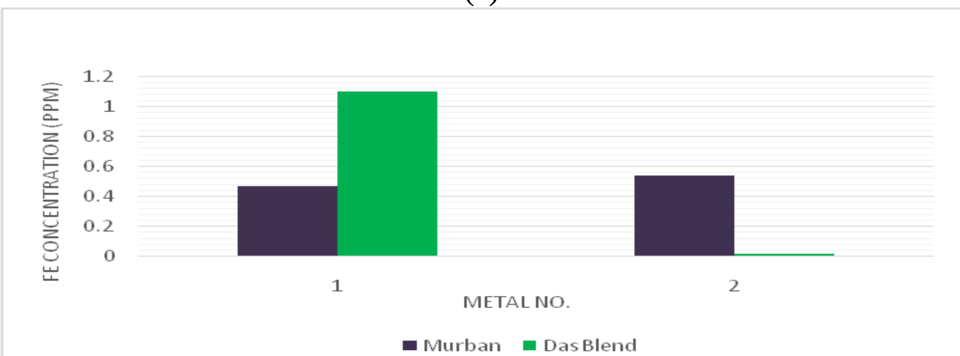
- A- Ferrous Sulfide and Trace Compounds
- B- Pitting Corrosion
- C- Corrosion Cracks

According to the observed results that there were found some pitting corrosions in most of metal surfaces and cavities were identified from some metal pieces. Especially in some stainless steel surfaces corrosion cracks were identified. Those corroded features can be used as the confirmation evidences for the formation of metallic corrosion that explained previously.

### 3.5. Decay of Metals in Crude Oils

The ferrous concentrations in crude oils samples which were exposed to stainless steel and carbon steel and copper concentrations in crude oil samples which were exposed to Monel metal are given in the Figure 4.

(a)




(b)

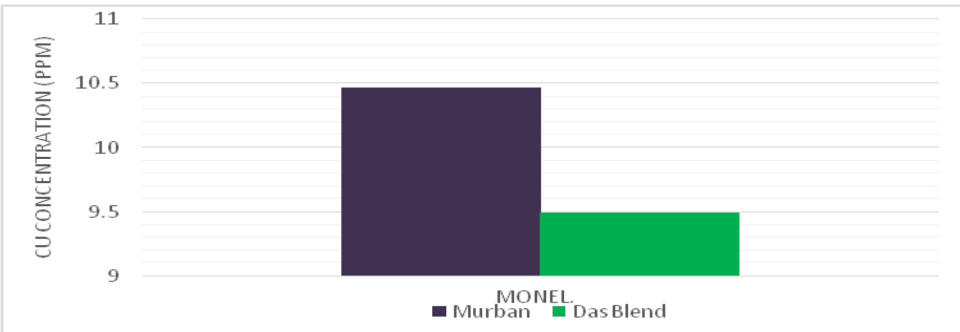


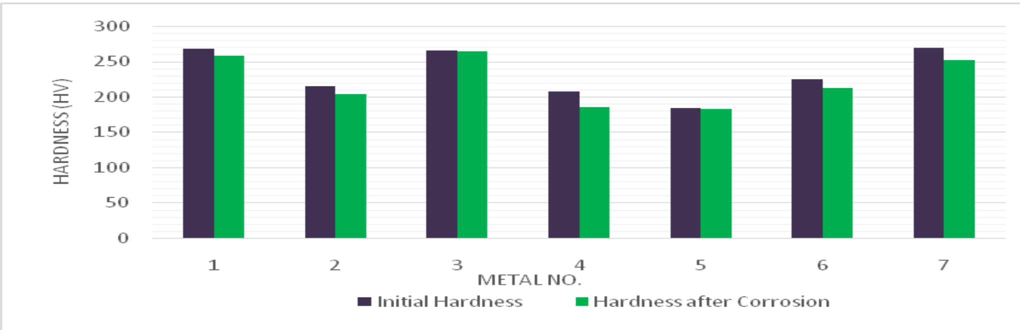

Figure 4. (a) Fe concentrations and (b) Cu concentration in both crude oils with respect to metals

During the determination of corrosion rates of metals by the weight loss method, there were found some invisible weight loss in some of metal types. According to the results of atomic absorption spectroscopy (AAS) there were found some significant concentration of Fe in both crude oil samples which were exposed to the first two types of metals also showed higher rate of corrosion in front of both crude oils. There was not found any amount of Fe in crude oil samples which were exposed to stainless steels and Monel that showed lowest corrosion rates in both crude oils although there were found some higher amount of Cu from crude oil samples which were exposed to the Monel metal. Due to the formation of metallic oxides, sulfides and hydroxides and their tendencies to removing form the initial metal surface the metals tend to decay into the crude oils because of the effect of attractive and repulsive forces between successive electrons and protons [1-6]. In the first two types of metals that process was happened rapidly while the formation of any copper compound regarding Monel metal as CuS.

### 3.6. Variation of the Hardness of Metals

A graphical representation of values of hardness before the immersion in crude oils and after the corrosion in each metal piece due to the corrosion is given in the Figure 5.

(a)




(b)

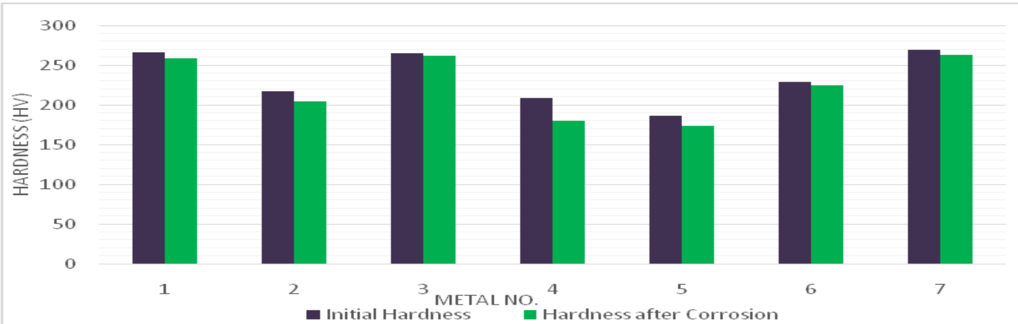



Figure 5. Variation of the hardness of metals in (a) Murban and (b) Das Blend

The observed results showed slight reduction in hardness regarding each metal piece with respect to both crude oils even though difficult to interpret any correlation between the rate of corrosion and the reduction of hardness. After the formation of corrosion compounds on the metallic surface such as metal oxides and sulfides tend to remove from the relevant surface due to the attractive and repulsive forces between successive electrons and protons while creating instability on the metal surface [1-5]. There can be concluded the reduction of the hardness was caused by the metallic corrosion of such metals in this experiment also can be used as an evidence for the happening of corrosion in each type of metal.

## 4. CONCLUSION

According to the obtained results there were found higher sulfur content, acidity, mercaptans and lower amount of salt in the Das Blend than the Murban even though some relatively higher rates of corrosion were found in four types of metals which were exposed to Murban crude oils than Das Blend crude oils. Also there can be concluded the contribution of salts in metallic corrosion is stronger than the contribution of sulfur, mercaptans and acids together. The processes of the contribution of sulfur and mercaptans in the metallic corrosion were not happened properly at the room temperature. The tendency of the cause of metallic corrosion is relatively higher in carbon steels which are having some high amount of Fe than others and also Monel showed higher rate of corrosion regarding the Cu while having a trace amount of Fe. The results that relevant to the microscopic analysis confirmed the formation of FeS in most of occasions by the appearances and features. The Fe and Cu concentrations that found from crude oil samples and reductions of harness in most of metal pieces provide notable evidences for the cause of metallic corrosion forever.

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