Basics of the Metallic Corrosion in Crude Oils

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Abstract: Corrosion is an often-used term regarding the ferrous metals also the general phenomenon of the formation of metal oxides, sulfides, hydroxides or any certain compound on the metal surface itself. There were found the effect of corrosive compounds in crude oils on the metallic corrosion in most of researches up to certain stage. In the current research it was expected to speculate the effect of sulfur, mercaptans, organic acids and salts in both Murban and Das Blend crude oils on the corrosion rates of seven different types of ferrous metals and variations of the hardness of such metals. The corrosive properties of both crude oils were determined by the standard methods and instruments. The chemical compositions of metals were detected by XRF detector. A batch of similar sized metal coupons was prepared, and those metal coupons were immersed in both crude oils separately. The rates of corrosion of those metal coupons were determined by the weight loss method after 15, 30 and 45 days from the immersion also both initial hardness and hardness after corroded of each metal coupon were tested by Vicker's hardness tester. The corroded surfaces were observed by the optical microscope also the ferrous concentration and copper concentration of each crude oil sample were measured by the atomic absorption spectroscopy (AAS) after exposed to metals. There were found relatively lower corrosion rates from stainless steels than other metals, higher corrosion rates of four types of metals in Murban crude oil although it was composed lower amount of sulfur, mercaptans, organic acids and higher amount of salts than Das Blend, higher ferrous concentrations in crude oil samples which were exposed to carbon steels than other crude oil samples whereas high concentrations of copper in crude oil samples relevant to the Monel metal and eventually it was a slight reduction of the initial hardness of each metal coupon due to the corrosion.

Keywords: Ferrous metals, Crude oils, Corrosive properties, Decay, Corrosion rate, Hardness

I. INTRODUCTION

Corrosion is a commonly used term in most of industries that metals play the cardinal role although found as adverse impacts on the durability and properties of metals. Theoretically the term is defined as the formation of metal oxides, sulfides, hydroxides or any certain chemical compound on the metal surface itself also regulated by the surrounding conditions and compounds [1]. The special requirement for the formation of the corrosion the ferrous metal need to expose either stronger oxidation agent than Fe^{2+} or any environment which is consisted water and oxygen also the process will be modified by the salts and organic acids presence in the medium or environment [2-3]. The effect of corrosive compounds in the crude oils on the corrosion rates of metals have been investigated in most of previous researches in the positive manner. In the current research there were expected to investigate the effect of sulfur, mercaptans, organic acids and salts in the crude oils on the corrosion rates of different types of ferrous metals that used in the industry of crude oil refining and the variations of the hardness of metals due to the corrosion of such metals. According the processes of crude oil refining there can be found the corrosion crux based on crude oil distillation column, heat exchangers, transportation tubes and storage tanks.

II. MATERIALS AND METHODOLOGY

A. Materials

There were selected seven different types of ferrous metals which comprised three types of carbon steels, three types of stainless steels and Monel based on the objectives that the investigation of corrosion rates in different types of metals and the testing of the strength of those metals against the corrosive environments. Also, there were selected two different types of crude oils which are slightly different in their chemical compositions based on the objectives of comparison the effect of corrosive properties of such crude oils on the corrosion rates of metals. Those crude oils were Murban and Das Blend.

B. Methodology

The corrosive properties of both crude oils were tested by the standard methods with some of possible illustrations and those methods have been summarized in the Table1.

Table 1. Testing methods for 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

The elemental composition of each type of metal was tested by the XRF detector including ferrous, trace metallic elements and most of non-metallic elements whereas exclusive of carbon in such metals because of the limitations of the instrument. A batch of similar sized metal coupons was prepared from each type of metal and the surfaces of them were cleaned until getting free of any foreign matter on that. Those metal coupons were separately and completely immersed in both crude oils in homogeneous way. A portion of the batch was taken out after 15 days from the immersion and the corrosion rate of each metal coupon was determined by the weight loss method [10]. The portion was comprised seven types of metals with respect to both crude oils. The same procedure was repeated for another two portions of the batch in order to after 30 and 45 days from the immersion. The prepared samples and the setup of the apparatus are shown in the Figure 1.

Figure 1. Samples and apparatus setup

The terms and the mathematical expression of the weight loss method are given in the Equation (1).

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

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

The corroded metal surfaces were cleaned by sand papers and isooctane while observing those surfaces through the 400X lens of an optical microscope. The metal coupons were weighed by the analytical balance.

The ferrous concentrations and copper concentrations of crude oil samples were tested by the atomic absorption spectroscopy (AAS) in each crude oil sample after exposed to the metals at the end of the experiment of corrosion rate determination. Because there were observed some invisible weight losses regarding most of metals during the determination of the corrosion rates. Therefore, the atomic absorption spectroscopic analysis (AAS) stage was performed. According to the methodology of sample preparation for the AAS analysis 1ml of each crude oil sample was diluted with 9 ml of 2-propanol.

Based on the confirmation of the formation of the corrosion the qualitative analysis stage was performed. The visible appearances of each metal coupon were observed by the 400X lens of an optical microscope before immersion in the crude oils and after corroded. The changes were identified with the aid of physical appearances of such corrosion compounds.

The 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 Vicker's hardness tester there were tested at least three points on the metal surface at once and the average value was interpreted as the hardness of metal at that moment [3].

III. RESULTS AND DISCUSSION

C. Corrosive Properties of Crude Oils

The obtained values for the corrosive properties for both crude oils in relevant experiments are given in the Table 2.

According to the obtained results for the corrosive properties of both crude oils there were identified higher amount of sulfur, mercaptans, organic acids and lower amount of salts in Das Blend than Murban.

Table 2. Corrosive properties of 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

Sulfur seized a major character in the metallic corrosion. Because crude oils usually contain different sulfur compounds such as elemental sulfur, mercaptans, thiophenes, sulfoxides and hydrogen sulfides also called as active sulfur compounds. Most of them have been identified as corrosive compounds because of the presence of fractional or functional groups which are able to react with metals and tend to be formed the metallic corrosion also the process is known as the "sulfidation" [2] [6] [8]. Although it is a process that depending on the temperature and a proper chemical reaction can be expected at about 230^0C or above that temperature. The general reaction between elemental sulfur and metals has been given in the equation (2).

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

According to the geological formation of crude oils there can be consisted some amount of organic acids in the crude oils also called as "naphthenic acids" which are having a general formula of RCOOH [2] [4]. The total amount of organic acids presence in some crude oil is known as the acidity of such a crude oil also plays a major role in the corrosion [9]. The general chemical reactions of the formation of the corrosion due to the organic acids are given in the Equation (3), Equation (4) and equation (5).

$$Fe + 2\ RCOOH \longrightarrow Fe\ (RCOO)_2 + H_2 \quad (3)$$

$$FeS + 2\ RCOOH \longrightarrow Fe\ (COOR)_2 + H_2S \quad (4)$$

$$Fe\ (COOR)_2 + H_2S \longrightarrow FeS + 2\ RCOOH \quad (5)$$

Salts are considerable corrosive properties in crude oils because due to the chemical reaction of salts and salts at some higher temperatures. The summation of NaCl, $MgCl_2$ and $CaCl_2$ in some particular crude oil is known as the total salt content of such crude oil [7]. At some enough higher temperatures salts tend to be broken into HCl. However HCl is not behaved as a corrosive compound in the gas phase although during the reduction of the temperature of the system some of HCl molecules tend to be reacted with the moisture present in the system and produced hydrochloric acids while the formation of hydrogen sulfide simultaneously the formation of metal sulfides as explained in the Equation (6), Equation (7) and Equation (8).

$$CaCl_2 + H_2O \longrightarrow CaO + 2HCl \quad (6)$$

$$HCl + Fe \longrightarrow FeCl_2 + H_2 \quad (7)$$

$$FeCl_2 + H_2S \longrightarrow FeS + 2HCl \quad (8)$$

Therefore, the corrosive strength of Das Blend was stronger than the corrosive strength of Murban accordance to the contents of such corrosive compounds in both crude oils based on the assumptions of the proper progress of such chemical processes with the temperature and other important environmental conditions.

D. Chemical Compositions of Metals

The elemental compositions of the seven types of metals according to the readings of XRF detector are given in the Table 3.

Table 3. Elemental compositions of metals

Metal	Fe (%)	Mn (%)	Co (%)	Ni (%)	Cr (%)	Cu (%)	P (%)	Mo (%)	Si (%)	S (%)	Ti (%)	V (%)
(1)CarbonSteel (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 (Stainless Steel)	88.25	0.28	-	0.18	10.92	0.10	0.16	-	0.11	-	-	-
(5) 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)	87.44	0.30	-	-	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)Mone 400	1.40	0.84	0.11	64.36	<0.04	33.29	-	-	-	-	-	-

Above results showed relatively high percentages of carbons in three types of carbon steels and moderate amounts of carbons in three types of stainless steels whereas composed significant percentages of nickel and copper based on the purposes of enhancements of some essential properties in the industrial usages such as the hardness, corrosive resistance and the strength [1] [3]. Monel metal was composed trace amount of ferrous while composed higher amount of copper and nickel.

E. Corrosion Rates of Metals Metallic Concentrations in Crude Oils

The average corrosion rate value of each type of metal with respect to both crude oils has been summarized in the bar chart of the Figure 3.

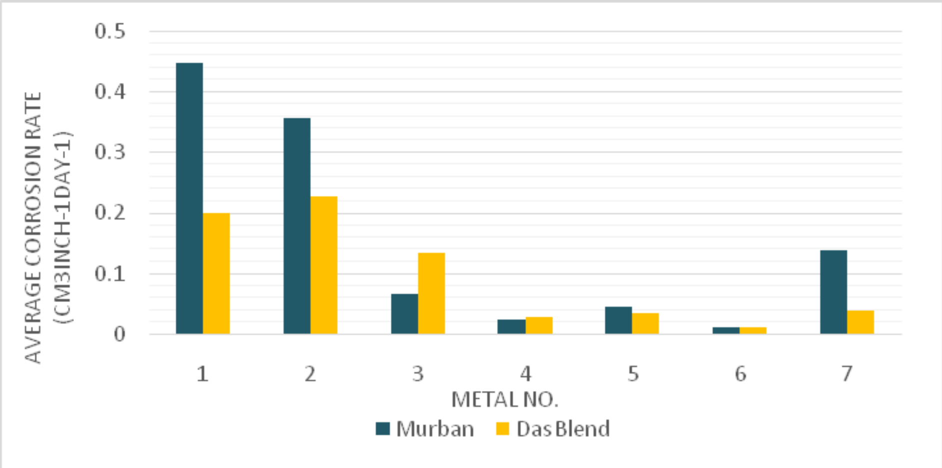


Figure 3. Corrosion rates of metals in both crude oils

According to the obtained results for the rates of corrosion of ferrous metals with respect to both crude oil the least corrosion rates were obtained from 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) while finding relatively lower corrosion rates from three types of stainless steels, relatively higher corrosion rates from three types of carbon steels and intermediate corrosion rates from Monel regarding both crude oils. When comparing the chemical composition of stainless steels all of them were composed in nickel, chromium and some other trace metals. According to the theoretical concept chromium and nickel are able form a corrosive protection film on the metal surface itself when the presence of chromium at least 12% and enough nickel [1] [4] [5]. The three types of stainless steels used in this experiment were composed 12%, 13% and 18% of chromium with sufficient content of nickel. The least corrosion rates were observed from stainless steel which was having 18% chromium and ~8.65% nickel. Therefore, it can be concluded the corrosive protection ability of stainless steels is increased with the chromium and nickel contents. Also, Monel showed some intermediate corrosion rates in both crude oils while it was having trace amount of ferrous and it can be emphasized that there might be formed another metallic compound relevant with copper and nickel apart from the ferrous [5].

When comparing the corrosion rates of metals with respect to both crude oils it was found higher corrosion rates of four types of metals in Murban crude oils than the corrosion rates of such metals in Das Blend crude oil while Das Blend was having higher amount of elemental sulfur, mercaptans, organic acids and lower amount of salts than the Murban crude oil. Therefore, it can be reached for the conclusion that the improper progress of “sulfidation” process at normal temperatures and the contribution of salts in the metallic corrosion were stronger than the contribution of organic acids in the metallic corrosion at the environmental conditions [2] [4] [7].

F. Microscopic Observations

The microscopic analysis was a supplementary stage for the analysis of formed corrosion compounds and determination of corrosion rates of metals. There were observed some of distinguish visible properties of such corrosive compounds as shown in the Figure 4.

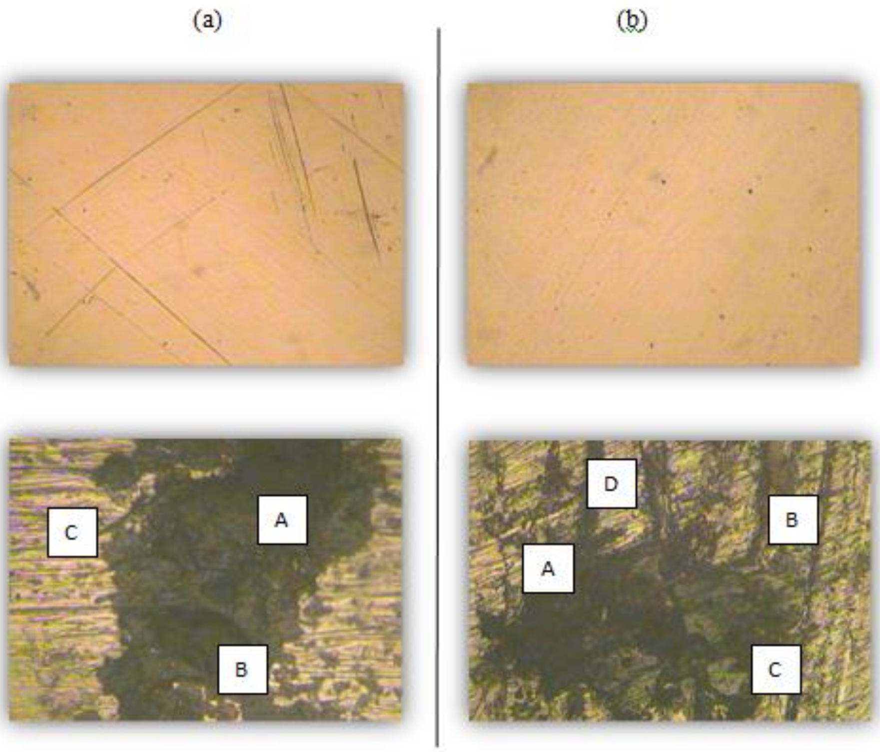


Figure 4. (a) Corroded surface of 410-MN: 1.7 420- MN: 1.7 (Stainless Steel) in Murban and (b) Corroded surface of Carbon Steel (Mild Steel) in Das Blend

A-Ferrous Sulfides and Trace Compounds

B- Corrosion Cracks

C- Pitting Corrosion

D- Ferrous Oxides

Based on the microscopic obsrvations and references there can be idendentified and distinguished some of specific corrosion com pounds on most of metals [3]. A description about the visible appearances of the corrosion compounds and the current oservations are given in the Table 4.

Table 4. Corrosion compounds and their visible appearances

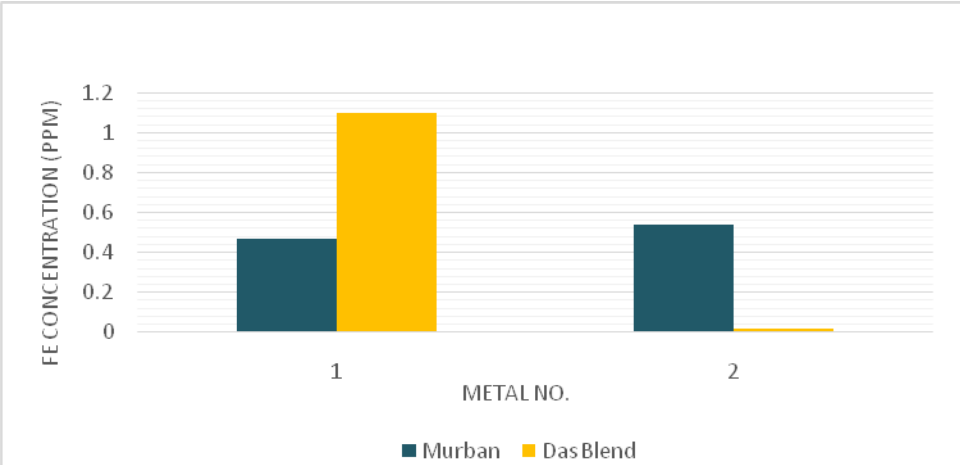
Compound	Appearances	Observations
FeS	Black, brownish black, property of powder, pitting, cracks	Observed most of features in each metal piece.
Fe_2O_3	Rusty color	Observed rarely.
CuS	Dark indigo/ dark blue	Unable to specify.

Apart from the major observations there were identified some accessory features that simultaneous to the basic corrosion such as corrosion cracks and pitting corrosions especially on the surfaces of stainless steels. According to the Monel metal most probably it can be concluded the formation of CuS on such metal surfaces although quite different to be distinguished from ferrous compounds only with the aid of visible analysis.

G. Decay of Metals in Crude Oils

According to the analysis of atomic absorption spectroscopy (AAS) the ferrous concentrations and copper concentrations of each crude oil sample with respect to the exposed metal are shown in the Figure 5.

(a)



(b)

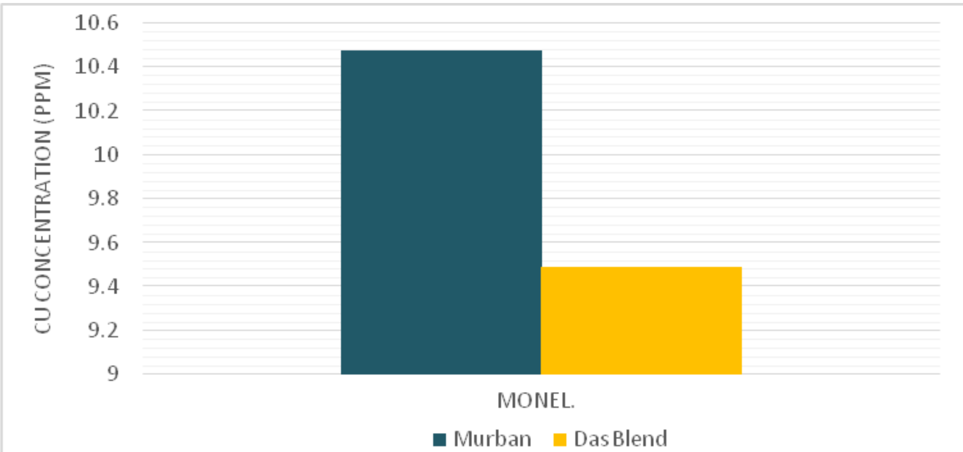


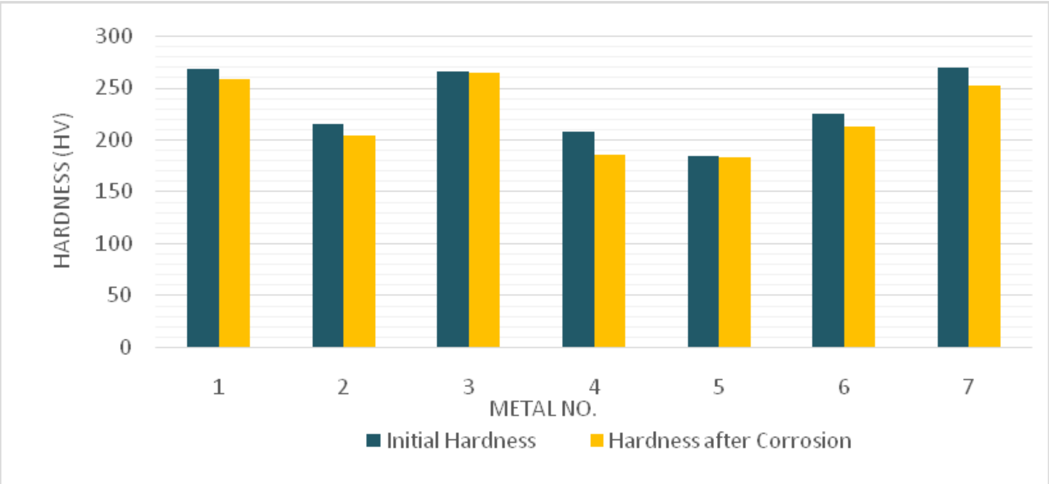
Figure 5. (a) Ferrous concentrations and (b) copper concentrations in crude oil samples after exposed to the metals

The obtained results for the analysis of atomic absorption spectroscopy (AAS) showed a perspicuous distribution of both ferrous and copper concentrations in crude oil samples because of the similarity of acceptability between the distributions of corrosion rates and metallic concentrations in crude oils after interacting with such metals as the higher ferrous concentration and higher corrosion rates regarding carbon steels. Also, least corrosion rates and absence of any amount of ferrous in crude oil samples regarding any type of stainless steel. Apart from that there were found some significant concentrations of copper in both crude oil samples which were exposed to Monel also ~33% of copper content was found in Monel metal. Usually corrosion is known as the formation of relevant metal oxides, sulfides, hydroxides or any certain compound on the metal surface itself and after formation of such compound it tends to remove from the metal surface due to the repulsive and attractive forces between successive electrons and protons [3]. The invisible weight loss and the metal concentration in crude oil samples can be linked with that incident and these observations can be used as a confirmation stage of the formation of the metallic corrosion furthermore.

H. Variations of the Hardness

The values of the initial hardness and the hardness after the corrosion of each metal type with respect to both crude oils are shown in the Figure 6.

(a)



(b)

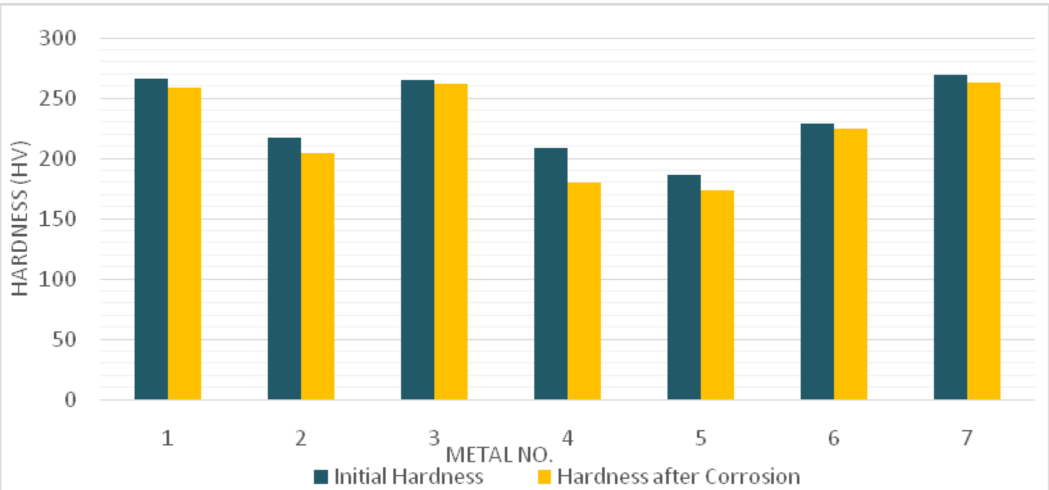


Figure 6. Variations of the hardness of metals in (a) Murban and (b) Das Blend

By referring the obtained results for the initial hardness and hardness after corrosion of metal coupons basically it was able to identify a slight reduction of the initial hardness of each metal coupon after the corrosion although unable to express neither linear correlation nor any relationship between the reduction of the hardness and the exposure time period. After the formation of corrosion compounds on the surfaces of metals the stability of the metal surface will be reduced due to the tendency of removing those corrosion compounds from the initial metal surface and also the reduction of the hardness can be emphasized a result of that instability of metal surface due to the corrosion [1] [2] [3]. The asymmetric hardness variation and the asymmetric formation of the corrosion explained the nature of the formation of corrosion forever.

IV. CONCLUSION

According to the obtained results eventually there were found the least corrosion rates of 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) in both Murban and Das Blend crude oils because of the corrosive protection ability of that metal due to the chemical composition of ~18% chromium and ~8% nickel whereas higher corrosion rates were found from carbon steels and Monel also some significant ferrous concentrations were found in both crude oil samples that interacted with carbon steels although there was not observed any concentration of ferrous in both crude oil samples that interacted with any type of stainless steel and significant copper concentrations were found in both crude oil samples which were interacted with Monel metal. There were observed higher corrosion rates of four types of metals in Murban crude oil than the corrosion rates of such metals in Das Blend crude oil even though Das Blend crude oil was contained higher amounts of elemental sulfur, mercaptans sulfur, organic acids and lower amount of salts than Murban crude oil. The formations of FeS, corrosion cracks and pitting corrosion were observed through the microscopic analysis and the slight reduction of the initial hardness was observed from each metal coupon due to the corrosion while the confirmation of the happening of metal corrosion in the crude oils.

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This volume is dedicated to Late Sh. Ram Singh Phanden, father of Dr. Rakesh Kumar Phanden.

