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Ascendancy of the Eager Corrosive Compounds in Crude Oils on the Decay of Metals

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Abstract

Crude oils may be consisted with different types of compounds since the occurrence including the corrosive compounds mostly with the salts, organic acids and sulfur compounds. In the existing research there were expected to investigate the impact of such corrosive compounds on the corrosion rates of seven different types of ferrous metals in both qualitatively and quantitatively as necessary. According to the methodology the chemical compositions of selected metals and selected corrosive properties of two different types of crude oils were measured by the standard methodologies and recommended analytical instruments. In the determination of the corrosion rates of metals a batch of similar sized metal coupons were prepared from selected ferrous metals and the corrosion rates of such metals were determined by the weight loss method while analyzing the corrode metal surfaces through 400X lens of an optical microscope after certain immersion time periods with respect to both crude oils. In addition that the decayed ferrous and copper concentrations from such metals into crude oils while the immersion and variations of the initial hardness of metals were measured. As the major outcomes there were obtained the lower corrosion rates from stainless steels especially with at least 12% of chromium and nickel, relatively higher impact from salts on the metallic corrosion when comparing with other compounds, formations of FeS, Fe₂O₃, corrosion cracks and pitting on the metal surfaces, significant decays of ferrous and copper from some metals and slight reductions of the initial hardness of metals due to the corrosion.

Keywords: Crude oils; Corrosiveness; Ferrous metals; Decay; Weight loss; Corrosion

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Introduction

Crude oils are the valuable resources that applicable in the various industrial usages. As a special adverse incident that the corrosion is found mainly in the metal based industries foremost of the crude oil refining because of the composing of some trace corrosive compounds in such crude oils since the occurrences. Corrosion is basically defined in the material science theories that the formations of the metal sulfides, oxides or hydroxides on the metal surfaces as a results of either chemical or electrochemical process on the metal surfaces with the contribution of either strong oxidizing compound or some system which is containing both water and oxygen [1-12]. The corrosion process and the chemical reactions may be varied with such oxidizing agent or the conditions of the relevant system. According to the corrosion processes some specific corrosion types have been classifiably identified such as the galvanic corrosion, pitting corrosion, general corrosion, thermal corrosion and stress corrosion. According to the chemical compositions and occurrences of crude oils may be composed with some trace amounts of corrosive compounds and those compounds may have the tendency of oxidizing the metals either actively or passively because of the chemical stability and reactivity of such compounds [2-18]. Regarding the previous researches and studies of petroleum oils especially there were investigated the impact of sulfur compounds, salts and organic acids on the corrosion and decay of metals under various supporting conditions [6-18].

In the existing research basically there were expected to analyze the influences of elemental sulfur, Mercaptans, organic acids and salts of two different types of selected crude oils especially in the normal temperature conditions on the corrosion rates of seven different types of selected ferrous metals which are vastly applicable in the industry of crude oil refining to fulfill various tasks under different conditions under both qualitatively and quantitatively.

Materials and Methodology

Based on the requirements and the availability of the materials two different types crude oils were

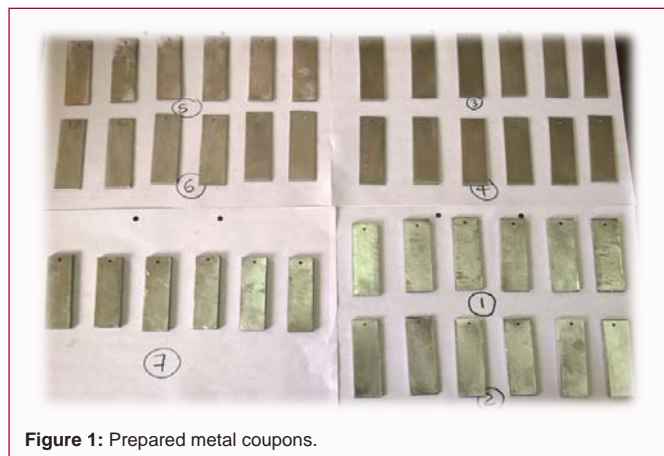


Figure 1: Prepared metal coupons.



Figure 2: Apparatus setup.

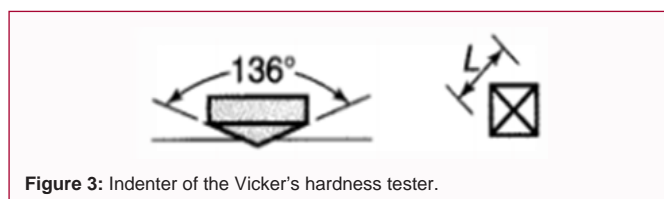


Figure 3: Indenter of the Vicker's hardness tester.

chosen as the corrosive aided liquids and those crude oils are namely as Murban and Das Blend. Those crude oils are slightly different in their chemical compositions most probably may be including the corrosive properties. By referring the literature sources it was decided to investigate the elemental sulfur contents, Mercaptans contents, organic acid contents and salt contents of such crude oils. A descriptive summary about such investigations has been given in the Table 1.

Beside of that there were selected seven different types of ferrous metals which are vastly applicable in the industry of crude oil refining for various tasks under different conditions such as different temperatures. The chemical compositions of such metals were detected by the X-ray fluorescence technique as the percentages of metallic elements and most of non metals excluding carbon. The selected metals and their usages have been given in the below.

- Carbon Steel (High) – Transportation tubes, pre heaters
- Carbon Steel (Medium)- Storage tanks , transportation tubes
- Carbon Steel (Mild Steel)- Storage tanks, heat exchangers
- 410-MN: 1.8 420-MN: 2.8 (Stainless Steel)- Heat exchangers
- 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)- Crude distillation columns
- 321-MN:1.4 304-MN:1.9 (Stainless Steel)- Crude

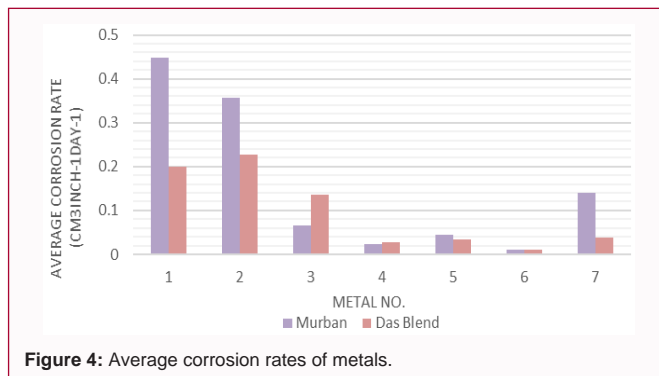


Figure 4: Average corrosion rates of metals.

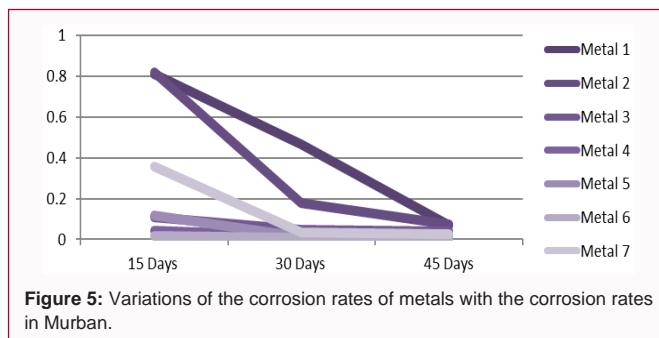


Figure 5: Variations of the corrosion rates of metals with the corrosion rates in Murban.

distillation columns

- Monel 400- Pre heaters, desalting unit

A batch of similar sized metal coupons were prepared from the selected ferrous metals as six metal coupons from each metal types and altogether forty two metal coupons from all metal types. As the further requirements each metal coupon was well cleaned by the sand papers and isooctane until free of any heterogeneous compounds on the surface and also the dimensions and the initial weight of each metal coupon were measured by in order of micrometer and analytical balance. The prepared metal coupons were shown in the Figure 1.

The prepared metal coupons were immersed in both crude oils samples separately as three homogeneous metal coupons per each crude oil beaker at the same occasion as altogether fourteen crude oils beakers that including seven Murban crude oil beakers and seven Das Blend crude oil beakers as shown in the Figure 2.

Hence, after fifteen days from the immersion one metal coupon from each crude oil container was taken out altogether as a batch of fourteen metal coupons from all crude oil beakers at once and the corroded metal surfaces of such metal coupons were observed under 400X lens of an optical microscope. According to the determinations of the corrosion rates of such metal coupons the corroded metal surfaces were cleaned by the sand papers and isooctane and the final weight of each metal coupon was measured by the analytical balance. Ultimately with the aid of necessary data and obtained results the corrosion rates of metal coupons were determined by the weight loss method as explained in the below [9,10].

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

Where;

W = weight loss due to the corrosion in grams,

k = constant (22,300),

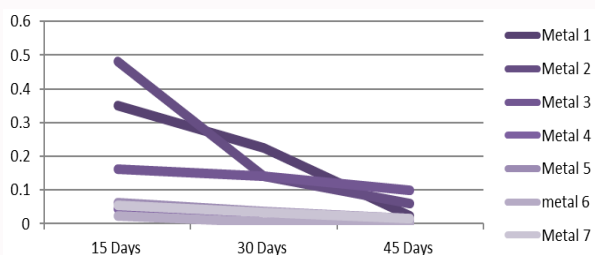


Figure 6: Variations of the corrosion rates of metals with the corrosion rates in Das Blend.

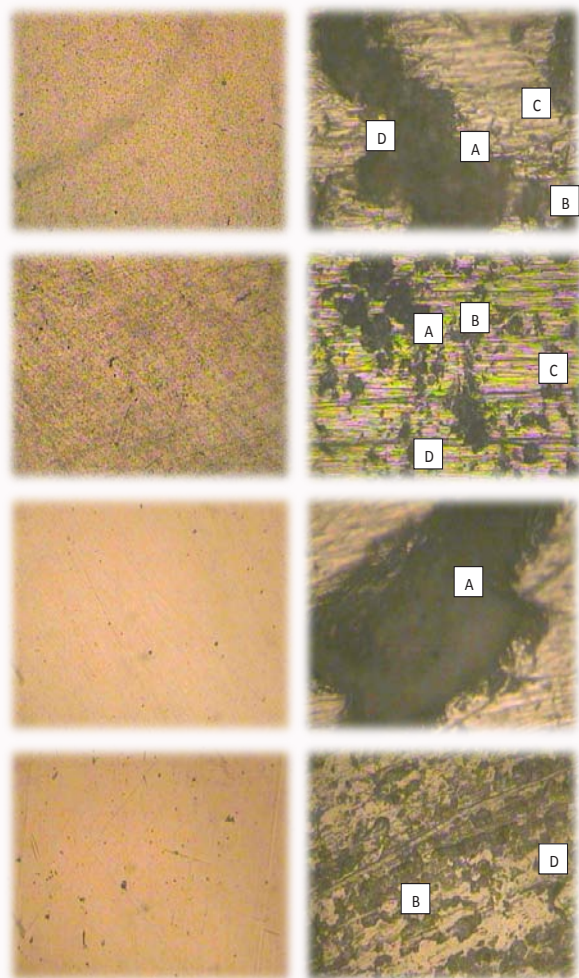


Figure 7: Corroded metal surfaces.

D = metal density in g/cm^3 ,

A = area of metal piece (inch^2),

t = time (days),

CR= Corrosion rate of metal piece.

By following the same procedure the corrosion rates of another two similar batches of metal coupons in order of after thirty and forty five days from the immersion were determined.

In addition to that experiments the decay of some metallic elements from such metal into crude oils during the interactions were measured by the atomic absorption spectroscopy (AAS) because

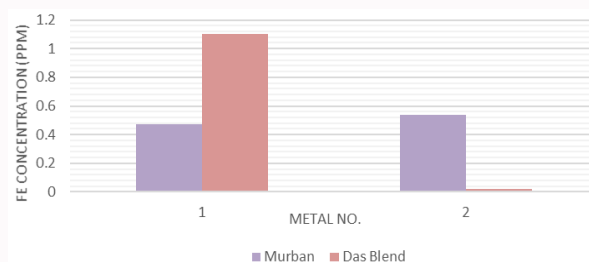


Figure 8: Decayed ferrous concentrations from metals into crude oils.

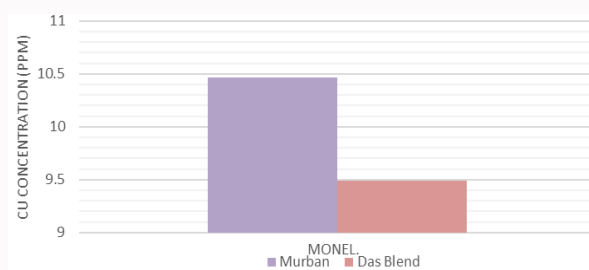


Figure 9: Decayed copper concentrations from metals into crude oils.

during the determinations of the corrosion rates of metal coupons there were observed some invisible weight loss from some of metal coupons. Based on the analysis of such incident this experiment was performed. According to the sample preparation of for such experiment 1 ml of each crude oil sample was diluted with 9 ml of 2-propanol and filtered.

As the final stage of the research the variations of the initial hardness of metal coupons after the corrosion of metal coupons were measured by the Vicker's hardness tester. The working principles of such instruments have been shown in the Figure 3 and Equation 2.

$$HV = 1.854 * P^2 / L^2 \quad (2)$$

Where;

P= Applied Load on the surface of metal,

L= Diagonal length of square,

HV= Hardness.

By considering the accuracy of the measurements and the working methodology of the instrument the hardness of at least three positions of each metal coupon were measured for one measurement. As the essential readings the initial hardness and hardness after the formations of the corrosion on each metal coupon were measured.

Results and Discussion

According to the analysis of the chemical compositions of metals by the X-ray fluorescence the obtained results have been interpreted in the Table 2.

Basically above results showed the higher amount of ferrous in carbon steels, moderate amount of ferrous in stainless steels and trace amount of ferrous in Monel metal. In addition to that there were observed some trace amounts of d-block metals in trace amounts such as nickel, copper, chromium and molybdenum from stainless steels. The purposes doping of the ferrous metals with some d-block metals are the enhancements of the qualities of such metals as given in the below [1,3-5].

Table 1: Investigations of the corrosive properties of crude oils.

Property	Method	Readings
Sulfur content	Directly used the crude oil samples to the XRF analyzer.	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

Table 2: Chemical compositions of metals.

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	0.09	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 3: 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

- Improve the strength and hardness of such metals
- Reductions of the corrosive tendency of that metals

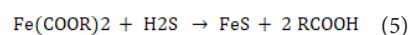
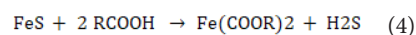
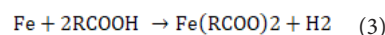
Regarding the reductions of the corrosion rates of metals usually the combination of at least 12% of chromium and sufficient amount of nickel tend to be created some corrosive protection film on the metal surfaces which is act as a corrosive barrier [1,3-6].

The obtained results for the investigations of the corrosive compounds of both crude oils have been interpreted in the Table 3.

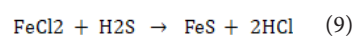
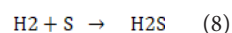
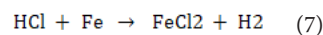
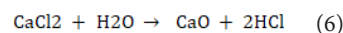
By considering the obtained results that there were observed relatively higher amounts of elemental sulfur, Mercaptans, organic acids and lower amount of salts in Das Blend when comparing with such values of Murban. The important thing that when estimating the impact of corrosive compound on the metallic corrosion that it must be considered about the requirements of supporting conditions for such corrosion reactions foremost of the temperature also with the magnitude of the concentration of such compounds.

Organic acids are the trace compounds that found in crude oils since the occurrences because of the abundance of such organic compounds in the beneath of the earth. The crude oils are also known as the naphthenic acids which are having a chemical formula of

"RCOOH". Most these acids are strong oxidizing agents. The chemical reaction processes between such organic acids and the metals have been given in the following chemical reactions [2,4,9,12,15].



When considering the foremost corrosive compounds in crude oils salts play a dominant background in the destruction of metals that usually found in the forms of NaCl, MgCl₂ and CaCl₂. Mainly at some particular temperatures such salt molecules tend to be broken into HCl molecules which are showed some inert conditions at the lower temperatures although tend to react with water or even the moisture presence in the crude oils when decreasing the temperature. As the products of such reactions it is possible to form the hydrochloric acids which are having strong corrosive ability because this one is a strong acid and easily ionization. The general chemical reactions for that process have been given in the following chemical reactions [2,4,7,13,17].



Sulfur compounds are mostly found corrosive compounds in crude oils because of the high abundance of sulfur in the interior parts of the earth in various forms. According to the chemical compositions of the crude oils there were found various sulfur compounds and

Table 4: Corrosion rates of metals in Murban.

Metal	Corrosion Rate after 15 Days (cm ³ inch ⁻¹ day ⁻¹)	Corrosion Rate after 30 Days (cm ³ inch ⁻¹ day ⁻¹)	Corrosion Rate after 45 Days (cm ³ inch ⁻¹ day ⁻¹)	Average Corrosion Rate (cm ³ inch ⁻¹ day ⁻¹)
(1) Carbon Steel (High)	0.811971	0.466425	0.068794	0.4490632
(2) Carbon Steel (Medium)	0.817791	0.180339	0.073358	0.3571623
(3) Carbon Steel (Mild Steel)	0.10973	0.048244	0.038592	0.0655217
(4) 410-MN: 1.8, 420-MN: 2.8 (Stainless Steel)	0.041784	0.016075	0.011801	0.02322
(5) 410-MN: 1.7, 420-MN: 1.7 (Stainless Steel)	0.11626	0.011968	0.007574	0.0452676
(6) 321-N:1.4, 304-MN:1.9 (Stainless Steel)	0.016612	0.007453	0.005599	0.009888
(7) Monel 400	0.356263	0.034877	0.026729	0.13929

Table 5: Corrosion rates of metals in Das Blend.

Metal	Corrosion Rate after 15 Days (cm ³ inch ⁻¹ day ⁻¹)	Corrosion Rate after 30 Days (cm ³ inch ⁻¹ day ⁻¹)	Corrosion Rate after 45 Days (cm ³ inch ⁻¹ day ⁻¹)	Average Corrosion Rate (cm ³ inch ⁻¹ day ⁻¹)
(1) Carbon Steel (High)	0.350249	0.224901	0.024738	0.1999627
(2) Carbon Steel (Medium)	0.481055	0.140654	0.05911	0.2269396
(3) Carbon Steel (Mild Steel)	0.162883	0.141093	0.100635	0.1348702
(4) 410-MN: 1.8 420-MN: 2.8 (Stainless Steel)	0.044146	0.034035	0.006149	0.0281102
(5) 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)	0.053701	0.034841	0.016363	0.0349681
(6) 321-MN:1.4 304-MN:1.9 (Stainless Steel)	0.022894	0.006503	0.002825	0.0107404
(7) Monel 400	0.061554	0.037655	0.016067	0.0384254

Table 6: Visible appearances of corrosion 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, property of powder	Unable to specify.

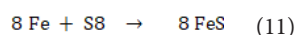
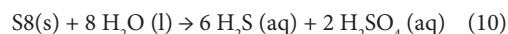
Table 7: Decayed metallic concentrations from metals into crude oils.

Metal	Crude Oil	Fe Concentration/ ppm	Cu Concentration / ppm
Carbon Steel	Murban	0.47	-
(High)	Das Blend	1.1	-
Carbon Steel	Murban	0.54	-
(Medium)	Das Blend	0.02	-
Carbon Steel	Murban	-0.08	-
(Mild Steel)	Das Blend	-0.48	-
410-MN: 1.8 420- MN: 2.8	Murban	-0.65	-
(Stainless Steel)	Das Blend	-0.78	-
410-MN: 1.7 420-MN: 1.7	Murban	-0.71	-
(Stainless Steel)	Das Blend	-0.79	-
321-MN:1.4 304-MN:1.9	Murban	-0.44	-
(Stainless Steel)	Das Blend	-0.17	-
Monel 400	Murban	-	10.47
	Das Blend	-	9.49

most of them are corrosive compounds such as elemental sulfur, Mercaptans, sulfoxides, hydrogen sulfides and thiophenes because of the higher reactivity of the functional groups and fractions of such compounds. Mercaptans are the recognized corrosive compound which is having a chemical formula of "RSH". It is possible to abide a

few of different chemical processes regarding the corrosion of metals due to the sulfur compounds because of the various functions of such compounds and the dissimilarity of the behavior of such functional groups [2,4,7,11,14,15,17,18].

The corrosion process due to the impact of elemental sulfur is known as the "localized sulfur" which is usually happened at about 80°C in properly and the corrosion process due to the Mercaptans is known as the "sulfidation" which is usually happened at about 230°C properly. The initiation chemical reactions that relevant with such chemical processes have been given in the following chemical reactions.



The important thing that considering about the impact of some corrosive property on the metallic corrosion that it must be considered about the requirements of the supporting conditions for that process foremost of the temperature simultaneously with the consideration of the magnitude of the concentration of such corrosive compound in the crude oil.

According to the determinations of the corrosion rates of metal coupons by the weight loss method the obtained results have been interpreted in the Table 4 and Table 5.

The concluded interpretation of the average corrosion rates of

metals have been shown in the Figure 4.

According to the average corrosion rates of that there were observed relatively higher corrosion rates from carbon steels, intermediate corrosion rates from Monel metal and mild steels and the lower corrosion rates from stainless steels with respect to both crude oils. Among the corrosion rates of stainless steels 321-MN: 1.4 304 - MN: 1.9 (Stainless Steel) showed least corrosion rates in both crude oils. When comparing the chemical compositions of such 321-MN: 1.4 304-MN: 1.9 (Stainless Steel) was composed 18% of chromium and 8.65% nickel which are much enough amounts for the self corrosive protection layer against the corrosion. Therefore, it is possible to emphasize the high performances of the corrosion protection ability of stainless steels when having sufficient amounts of both nickel and chromium [1,3-6,17].

When considering the variations of the corrosion rates of metals with respect to the crude oils four types of metals showed their higher corrosion rates in Murban crude oils while other three types of crude oils were showing their higher corrosion rates in Das Blend crude oils. In the considerations of the corrosive properties of bath crude oils and the obtained results it can be suggest that there might be highly impacted by the salts on the metallic corrosion at the lower temperatures when comparing with the corrosive impact of other corrosion compounds mainly the sulfur content that also having lower impacts at the lower temperatures [2-18].

By referring the variations of the corrosion rates of metals with the exposure time in both Murban and Das Blend crude oils the relevant analyzed results have been shown in the Figure 5 and Figure 6.

Above variation curves showed some similarities that the reductions of the corrosion rates of metals with their exposure time period in crude oils. By considering these variations and the explanations of the weight loss method that it is possible to conclude the applicability of weight loss method for the various materials because similarly it was found the inversely proportional relationship between the two parameters of corrosion rate and the exposure time of some metal. Also it is able to explain that the further corrosion process will be disturbed variously by the early formed corrosion compounds on the metal surfaces in the same rate forever [1,3,5,9,10,17].

According to the qualitative analysis of the corroded metal surfaces by the 400X lens of an optical microscope there were observed some kinds of various features in both identifiable and non identifiable with the visible features mainly with the color as shown in the Figure 7.

Regarding the observations mostly identified corrosion compounds and their distinguished features have been discussed in the Table 6 [1,3,5,6,14,15].

- A- Ferrous Sulfides (FeS)
- B- Ferrous Oxides (Fe_2O_3)
- C- Corrosion Cracks
- D- Pitting Corrosion/ cavities

As the important results of the microscopic analysis of the metallic corrosion that there were identified and distinguished ferrous sulfides (FeS) in most of observations due to the corrosive compounds of crude oils, ferrous oxides (Fe_2O_3) rarely due to the water and oxygen presence in crude oils, corrosion cracks and cavities on the metal

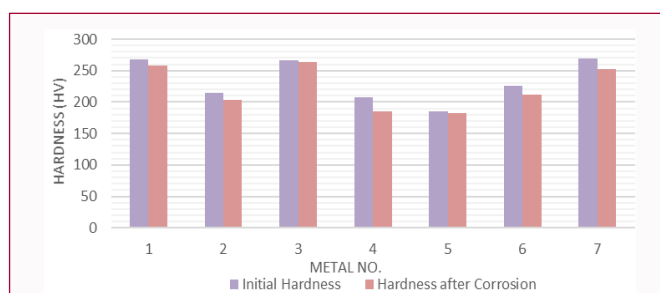


Figure 10: Variations of the initial hardness of metals in Murban.

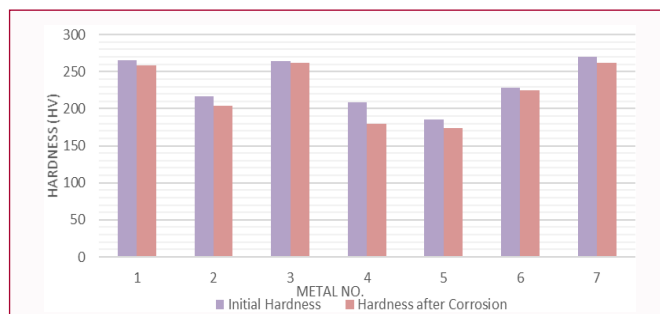


Figure 11: Variations of the initial hardness of metals in Das Blend.

surfaces due to the decay of materials during the process of corrosion. As the special incident there were observed some black color corrosion compounds that similar with ferrous sulfides although it is not be able to suggest as CuS only with the visible features [1,3,14,15]. Therefore, it is better to recommend some compositional analysis of the corrosion compounds such as the X-ray diffraction (XRD) for further analysis.

The relevant results for the analysis of the decays of the metals during the corrosion by the atomic absorption spectroscopy (AAS) have been interpreted in the Table 7.

The concluded results of the above interpreted results have been given in the Figure 8 and Figure 9.

The above concluded results showed relatively higher decay of ferrous from carbons steels also found highest corrosion rates from such metals and significant decay of copper from Monel metal that found intermediate corrosion rates in both crude oils. In addition that it was not found any decay of neither copper nor ferrous from any of ferrous metal during the corrosion into crude oils where the least corrosion rates were found. The incident of the decay of metallic elements from some metal into crude oils during the corrosion is possible to explain with the theory of electron repulsive [1,3,4,5,6]. After the formations of the corrosion compounds on the metal surfaces such compounds tend to be removed from the metal surfaces due to the attractive and repulsive forces between the successive electrons and protons of relevant compounds and this is the most feasible reason for the decay of metal into crude oils while the corrosion.

According the analysis of the variations of the initial hardness of metals due to the corrosion by the Vicker's hardness tester the obtained results have been shown in the Figure 10 and Figure 11.

According to the above graphs mainly there were found some little reductions of the initial hardness of most of metals after the formations of the corrosion on the metal surfaces. The incident

is possible to describe with two possible theoretical concepts as discussed in the below [1,3,5].

- After formations of the corrosion compounds on the metal surfaces such compounds tend to be removed either partially or completely from the metal surfaces due to the repulsive and attractive forces between the successive electrons and protons while creating some instability on the metal surfaces which is affecting to the mechanical properties such as the hardness
- Contaminations of the metal surfaces by the corrosion compounds and become into a heterogeneous surface and also the original features may be varied

Conclusion

As the basic outcomes of the current research there were obtained some lower corrosion rates in stainless steels basically having at least 12% of chromium with sufficient amount of nickel, relatively some higher impact from salts when comparing with the impact of other corrosive compounds in the room temperatures, formations of the ferrous sulfides (FeS), ferrous oxides (Fe₂O₃), corrosion cracks and pitting on the metal surfaces, significant decays of ferrous from some of carbon steels and significant decay of copper from Monel metal and also little reductions of the initial hardness of metals due to the corrosion.

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