The Impact of the Corrosiveness of Crude Oils on the Metallic Corrosion

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Abstract: Corrosion is a natural phenomenon which is linked with the ferrous metals and the supporting environment as well. Especially it is possible to find in the industry of crude oil refining because of the vast applications of the ferrous metals and the corrosiveness of the crude oils. According to the scope of the current research there were expected to investigate the impact of two different types of crude oils on the corrosion attributes of seven different types of ferrous metals. In the methodology of this research the chemical compositions of selected metals, dominant corrosive properties of both crude oils, corrosion rates of similar sized prepared metal coupons after certain immersion time periods in crude oils, qualitatively analysis of the corroded metals surfaces, decay of metallic elements from metals into crude oils and the reductions of the initial hardness of metal coupons after the corrosion were tested by the standard methodologies and instruments also determined some necessary parameters. The obtained results showed the relatively lower corrosion in stainless steels when comparing with other metals, relatively higher impact from the salts on the metallic corrosion than the impact of the organic acids or possible to occur some effects from unknown compound, formations of FeS, Fe2O3, corrosion cracks and cavities, significant decay of ferrous and copper from some metals in to crude oils and the slight reductions of the initial hardness of metal coupons due to the corrosion.

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1. Introduction

Crude oils are the natural earth resources that found at around specific locations of the earth. According to the chemical compositions of the crude oils they are mostly consisted with a large number of hydrocarbons with some other trace compounds. When considering the properties and the behaviors of other trace compounds the corrosive compounds have gained much attention among other compounds because of the severe impact of such compounds on the decay of metals at the various conditions. The impact of elemental sulfur, active sulfur compounds, organic acids and salts on the decay of metals have been found and emphasized in the most of previous researches [1-15]. The corrosion is simply defined as the decay of metals due to the chemical or electrochemical process on the metals with the aid of surrounding medium and also the formation of metal oxide, sulfide or hydroxide on the relevant metal surface. In other words it is defined as the exposure of the metal to either strong oxidizing agent or the environment which is consisted with both water and oxygen [2-9].

Basically in this research there were expected to speculate the impact of the elemental sulfur, Mercaptans, organic acids and the salts of two different types of crude oils on the corrosion of seven different types of selected ferrous metals with the nature of the corrosion and the strength of such corrosive compounds on the corrosion rates of such metals and also to be distinguished the chemical compounds that formed on the metallic surfaces.

2. Materials and methodology

By considering the variations of the corrosive compounds and the availability two different types of crude oils were selected that namely as Murban and Das Blend. According to the sulfur content of Das Blend crude oils it has been categorized as a “sour” crude oil which considered as a corrosive compound [2],[9],[12],[15]. The elemental sulfur contents, Mercaptans contents, acidities and salt contents of both Murban and Das Blend crude oils were tested quantitatively by the standard methods and instruments as summarized in the Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Readings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content</td>
<td>Respected crude oil samples were directly tested by XRF analyzer.</td>
<td>Direct readings which were given by the XRF analyzer.</td>
</tr>
<tr>
<td>Acidity</td>
<td>Crude oils sample was dissolved in a mixture of toluene and isopropyl and titrated with potassium hydroxide.</td>
<td>End points of the titration</td>
</tr>
<tr>
<td>Mercaptans content</td>
<td>Crude oil sample was dissolved in sodium acetate and titrated with silver nitrate.</td>
<td>End points of the titration</td>
</tr>
<tr>
<td>Salt content</td>
<td>Crude oil sample was dissolved in organic solvent and exposed to the cell of analyzer of salt in crude oils.</td>
<td>Direct readings which were given by the instrument.</td>
</tr>
</tbody>
</table>
In addition seven different types of ferrous metals were selected as the samples by considering the applicability and the tasks of such ferrous metals regarding the industry of crude oil refining as given in the below.

- Carbon Steel (high)- Storage tanks
- Carbon Steel (medium)- Storage tanks
- Carbon Steel (mild steel)- Transportation tubes
- 410-MN: 1.8 420-MN: 2.8 (Stainless Steel)- Pre heaters, crude distillation column
- 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)- Crude distillation units
- 321-MN:1.4 304-MN:1.9 (Stainless Steel)- Hydro treating units
- Monel 400- Heat exchangers, pre heaters

The chemical compositions of the selected ferrous metals were tested by the XRF detector as the percentages of elements that presence in such metal. A batch of similar sized metal coupons were prepared from seven different types of ferrous metals a six metal coupons from each type of metal and forty two metal coupons from all types of metals as shown in the Figure 1.

The surfaces of such metal coupons were cleaned until absence of any heterogeneous compound on the metal surface and the initial weight and the dimensions of each metal coupon were measured by in order of the electronic balance and the micrometer.

The prepared metal coupons were immersed in both crude oils separately as three homogeneous metal coupons from each crude oil container as shown in the Figure 2.

![Figure 1 Prepared metal coupons](image1)

![Figure 2 Apparatus setup](image2)
After 15 days from the immersion one metal coupon from each crude oils sample was taken out that altogether as a batch of fourteen metal coupons which is represented both the all of metal types and two crude oil types. The corroded metal surfaces of such metal coupons were observed through the 400X lens of an optical microscope and the corrosion compounds were analyzed qualitatively. As the key task of the current research the corrosion rates of such metal coupons were determined by the relative weight loss method. The mathematical expression and the terms of that expression are given in the Equation 1 [9], [10].

\[
CR = \frac{W \times k}{(D \times A \times t)}
\]

Where, \( W \) is the weight loss in grams, \( k \) is the constant (22,300), \( D \) is the metal density in g/cm\(^3\), \( A \) is the area of metal piece in inch\(^2\), \( t \) is the exposure time in days and \( CR \) is the corrosion rate of metal piece in cm\(^3\) inch\(^{-2}\) day\(^{-1}\).

The corroded metal surfaces were cleaned by the sand papers and isoctane and the final weight of each metal coupon was measured by the electronic balance according to the requirements of the determination of the weight loss of metal coupon due to the corrosion and the determination of the corrosion rate ultimately.

The same procedure was repeated twice again for another two similar batches of metal coupons in order of after 30 and 45 days from the immersion to determine the corrosion rates of such metal coupons. Finally there were calculated interpreted the average corrosion rates of each metal type with respect to each crude oil by considering the obtained values for the corrosion rates after 15, 30 and 45 days from the immersion.

Apart from the essential experiments the decayed ferrous and copper concentrations from each metal type into each crude oil sample was measured by the atomic absorption spectroscopy (AAS). According to the sample preparation methodology for the instrument 1 ml of each crude oil sample was diluted with 9 ml of 2-proponol and filtered.

Also the variations of the initial hardness of metal coupons were measured by the Vicker’s hardness tester. As the compulsory measurements the initial hardness and the hardness after formation of the corrosion on the metal surface of each metal coupon were measured by the Vicker’s hardness tester.

3. Results and discussion

The obtained results have been discussed under several paragraphs in the below.

According to the analysis of the chemical compositions of the selected ferrous metals by the XRF detector the elemental compositions of such metals are shortlisted in the Table 2.
Table 2 Elemental compositions of metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
<th>Cr (%)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Carbon Steel (High)</td>
<td>98.60</td>
<td>0.17</td>
<td>0.14</td>
<td>0.37</td>
</tr>
<tr>
<td>(2) Carbon Steel (Medium)</td>
<td>99.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3) Carbon Steel (Mild Steel)</td>
<td>99.46</td>
<td>-</td>
<td>&lt;0.07</td>
<td>-</td>
</tr>
<tr>
<td>(4) 410-MN: 1.8 420-MN: 2.8 (Stainless Steel)</td>
<td>88.25</td>
<td>0.18</td>
<td>10.92</td>
<td>0.10</td>
</tr>
<tr>
<td>(5) 410-MN: 1.7 420-MN: 1.7 (Stainless Steel)</td>
<td>87.44</td>
<td>-</td>
<td>11.99</td>
<td>-</td>
</tr>
<tr>
<td>(6) 321-MN:1.4 304-MN:1.9 (Stainless Steel)</td>
<td>72.47</td>
<td>8.65</td>
<td>17.14</td>
<td>-</td>
</tr>
<tr>
<td>(7) Monel 400</td>
<td>1.40</td>
<td>64.36</td>
<td>&lt;0.04</td>
<td>33.29</td>
</tr>
</tbody>
</table>

By referring the obtained results that there can be found relatively higher ferrous concentrations in carbon steels, moderate ferrous concentrations in stainless steels and trace ferrous concentration in Monel metal. In addition that there can be seen the trace elements of chromium and nickel in stainless steels. According to the conceptual expectation of the doping of such metals with some trace metals there were expected to enhance the strength of such metal and the reduction of the corrosion of such metals in the corrosive environments. The combination of the chromium composition of 12% with sufficient amount of nickel is known as a successful corrosive protection film for the stainless steels [1],[3],[4],[5].

The obtained results for the analysis of corrosive compounds in both Murban and Das Blend crude oils have been given in the Table 3.
According to the investigation results of the corrosive compounds of both crude oils Das Blend crude oil was composed relatively large amount of organic acids, Mercaptans, elemental sulfur and relatively lower amount of slats when comparing with such contents of Murban crude oil. In the analysis of the impact of such corrosive compounds the most important thing that need to mention about the required conditions for the occurrences of the corrosion of metals with the aid of such compounds such as the temperature. The real discussion of the corrosion processes has been emphasized in this chapter.

Sulfur is a dominant corrosive compound that found in crude oils as various forms such as the fractions and the functional groups may be in various phases such as the elementals sulfur, hydrogen sulfide, thiophenes, sulfoxides and Mercaptans. Most of them are corrosive compounds and the Mercaptans are the highly corrosive compounds which are having a chemical formula of “RSH”. The corrosion process due to the Mercaptans is known as the “sulfidation” which is tend to be happened at about 230°C properly and the corrosion process due to the elemental sulfur is known as the “localized corrosion” which is also happened above 80°C properly [2],[6],[9],[15]. The general chemical reaction of the above processes is given in the Equation 2.

\[ 8 \text{Fe} + S_8 \rightarrow 8 \text{FeS} \quad (2) \]

Organic acids also the considerable corrosive compounds that presence in crude oils since the geological formation of such crude oils. The organic acids are known as the “naphthenic acids” in some particular references with the general chemical formula of “RCOOH” [9], [11], [12]. It’s is possible to be presented large number of various naphthenic acids in some crude oil and the summation of such acids is known as the terms of “acidity” or “total acid number (TAN)”. The general chemical reactions of the naphthenic acids with the metals have been given in the Equation 3, Equation 4 and Equation 5.

\[ \text{Fe} + 2 \text{RCOOH} + \text{H}_2 \rightarrow \text{Fe(RCOO)_2} \quad (3) \]
\[ \text{FeS} + 2 \text{RCOOH} + \text{H}_2\text{S} \rightarrow \text{Fe(COOR)_2} + \text{H}_2\text{S} \quad (4) \]
\[ \text{Fe(COOR)_2} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2 \text{RCOOH} \quad (5) \]

### Table 3 Corrosive properties of both crude oils

<table>
<thead>
<tr>
<th>Property</th>
<th>Murban</th>
<th>Das Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content (Wt. %)</td>
<td>0.758</td>
<td>1.135</td>
</tr>
<tr>
<td>Salt content (ptb)</td>
<td>4.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Acidity (mg KOH/g)</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Mercaptans content (ppm)</td>
<td>25</td>
<td>56</td>
</tr>
</tbody>
</table>
Salts play a significant character regarding the metallic decay because of the solubility of the salts in the water. Especially NaCl, MgCl₂ and CaCl₂ are the types of salts that found from crude oils and the total content of such salt is known as the salt content of such crude oil [2], [4], [7]. Usually when the temperature of the system is increasing such salts tend to be broken into HCl molecules although do not behave as corrosive compounds. When decreasing the temperature of such system the existing HCl molecules tend to react with the water or moisture and formed the highly corrosive hydrochloric acids and simultaneously begin the process of the corrosion of metals as shown in the chemical reactions in Equation 6, Equation 7 and Equation 8.

\[
\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl} \quad (6)
\]

\[
\text{HCl} + \text{Fe} \rightarrow \text{FeCl}_2 + \text{H}_2 \quad (7)
\]

\[
\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{HCl} \quad (8)
\]

In the comparison of the contributions of the corrosive compounds of the crude oils the impact of sulfur and sulfur compounds which is impossible to expect in properly because of the requirements of higher temperature. Therefore, the impact of both organic acids and salts can be compared with the obtained results.

The average corrosion rates of the selected types of metals with respect to both crude oils have been interpreted in the Figure 3.

\[
\begin{align*}
\text{Figure 3} & \quad \text{Average corrosion rates of metals} \\
\text{The above results showed the lower corrosion rates from stainless steels, moderate corrosion rates from Monel metal and the relatively higher corrosion rates from carbon steels. When comparing the chemical compositions of stainless steels 321-MN:1.4304-MN:1.9(Stainless Steel) was composed \sim 18\% of chromium and \sim 8\% of nickel which is a sufficient amounts for the formation of the self corrosive protection layer on the metal surface that required \sim 12\% of chromium with sufficient amount of nickel. According the expectation of the lower corrosion rates from stainless steels the obtained results showed the performances of the self corrosive protection layer in the recommended compositions and the necessity of both nickel and chromium for the corrosive protection layer because 410-MN: 1.7 420-MN: 1.7(Stainless Steel) has \sim 12\% of chromium and lack of nickel and also it was shown relatively higher corrosion rates among stainless steels [1], [3], [4], [5], [8].}
\end{align*}
\]
In the comparisons of the corrosion rates of metals with respect to the both crude oils there were found that four types of metals have been decayed highly in Murban crude oils since the other metals were highly decaying in Das Blend crude oil. When comparing the concentrations and the progresses of corrosive compounds in both crude oils the improper progresses of sulfur and active sulfur compounds are impossible to consider rather because of the requirements of high temperatures for that. Therefore, with the available observations that there can be concluded the impact of salts on the corrosion of metals is greater the impact of organic acids on the metallic corrosion especially at the room temperatures [2]-[15].

The distributions of the corrosion rates of ferrous metal coupons with the exposure time against the both Murban and Das Blend crude oils have been interpreted in order of Figure 4 and Figure 5.

![Figure 4 Variations of the corrosion rates of metals with the exposure time in Murban](image)

![Figure 5 Variations of the corrosion rates of metals with the exposure time in Das Blend](image)

The above distribution showed the similar sequence between the corrosion rates of the metals and the exposure time as the inversely proportional relationship. These results can be used for the confirmations of the validity of the weight loss method for various types of materials that the inversely proportional relationship of such parameters [9]-[10].

According to the microscopic analysis of the corroded metals surfaces some important features have been identified qualitatively and some of them are shown in the Figure 6.
The specific and distinguished features of the corroded metals surfaces that observed under the microscopic analysis have been emphasized in the below.

- A- Black/ brownish black compounds
- B- Rusty/ reddish brown compounds
- C- Corrosion cracks
- D- Pits/ cavities

According to the above observations and properties of such observations there can be concluded the formation of some specific corrosion compounds on the metallic surfaces as explained in the Table 3 [1], [3], [5].

<table>
<thead>
<tr>
<th>Compound</th>
<th>FeS</th>
<th>Fe₂O₃</th>
<th>CuS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearances</strong></td>
<td>Black, brownish black, property of powder, pitting marks, cracks</td>
<td>Rusty color</td>
<td>Dark indigo/ dark blue</td>
</tr>
<tr>
<td><strong>Observations</strong></td>
<td>Observed most of features in each metal piece.</td>
<td>Observed rarely.</td>
<td>Unable to specify.</td>
</tr>
</tbody>
</table>

By referring the features of basic corrosion compounds that there can be concluded the formations of FeS, Fe₂O₃, corrosion cracks and pitting corrosion with the aid of the qualitative analysis.
As a special observation some black color compound was identified on the corroded Monel surfaces that similar with FeS and also referring the features of CuS it can be concluded as the CuS although it is possible to recommend an advanced compositional analysis technology for the better results such as the X-ray diffraction (XRD).

According to the analysis of the decayed ferrous and copper concentrations into crude oils from the metals that the obtained results have been shown in the Figure 7 and Figure 8.

![Figure 7 Decayed ferrous concentrations into crude oils](image)

![Figure 8 Decayed copper concentrations into crude oils](image)

The above results showed the significant decay of ferrous from carbon steel (high) and carbon steel (medium) into both crude oils during the interactions with the metals. The highest corrosion rates also found from these two types of metals with respect to both Murban and Das Blend crude oils. Also the significant decays of copper from Monel metal into both crude oils were observed. After formation of the corrosion compounds on the metal surfaces such heterogeneous compounds are tended to be removed from the initial metal surfaces due to the effects of the repulsive and attractive forces in between the successive electrons and protons of such chemical compounds [1], [4], [5]. The decay of metals into crude oils is usually explained under this principle and these observations can be used as the confirmation stages for the formation of the corrosion in the current experiment.

The variations of the initial hardness of metals after formations of the corrosion on the metal surfaces have been shown in the Figure 9 and Figure 10.
Basically there were identified a slight reductions of the initial hardness of most of metal coupons due to the formations of the corrosion on the metal surfaces. After the formations of the corrosion compounds on the metal surfaces such compounds tended to be removed from the metal surfaces due to the repulsive and attractive forces between the successive electrons and protons of such compounds while generating the unstable conditions on the existing metallic surface [1],[4],[5]. The reductions of the hardness may be a result of the electron transactions and the heterogeneous conditions on the metallic surfaces due to the formation of the corrosion.

Figure 9 Variations of the initial hardness of metals in Murban crude oil

Figure 10 Variations of the initial hardness of metals in Das Blend crude oil
4. Conclusion

As the elemental results of the research there were obtained the relatively lower corrosion rates from stainless steels and least corrosion rates from stainless steels which was composed ~18% of chromium and ~8.6% of nickel because of the performances of the self corrosion protection film of stainless steels ~12% of chromium with sufficient amount of nickel. The Das Blend crude oil was composed with relatively higher amount of elemental sulfur, organic acids, Mercaptans and lower amount of salts than Murban crude oil. The higher impact from the salts on the metallic corrosion was found when comparing with other compounds and the less progresses of the sulfur and active sulfur compounds were found in the lower temperatures. The formations of FeS, Fe₂O₃, corrosion cracks and pitting corrosion were found according to the qualitative analysis. In addition the significant decay of ferrous and copper concentrations and the slight reductions of the initial hardness of the metal coupons were observed.

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References
