Characterization of Corrosion Behavior of Low Carbon Steel Oil Pipelines by Crude Oil

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Abstract

Corrosion and erosion–corrosion in weld joints of petroleum pipelines were investigated by the studying the corrosion of carbon steel in crude oil and water extraction from oil. The experimental work tests of erosion–corrosion were done using special device which was designed according to (G 73) ASTM. The work tests were achieved using traditional weight loss technique to measure weight loss rates in (mpy) Unit, the tests above were done in pumped media and pumped media had constant pressure of 1 bar, flow rate $Q = 36$ L/min, temperature $25\, ^\circ\mathrm{C}$ and $\mathrm{pH} = 6.56$ for erosive-corrosive media. Weight loss method was used in which test specimens of carbon steel, with a known weights, were immersed in the oil for a total exposure time of 60 days and for 10 days in water. Metallographic observations and micro-hardness measurements were also performed on specimens taken from the parent metal, heat affected zone and weld metal. The obtained results clearly indicate a degradation of the mechanical properties of steel welds.

Keywords: Crude, Oil, Internal Corrosion, Welded Joint.

Introduction

Since 1950 the corrosion weldment has been investigated, whoever in today’s corrosion play a major problem to different engineering projects. Structure failure of low carbon steel weldment certified to selective attacked as result of different zone of a weldment for example fusion zone corroded rather than heat affected zone H.A.Z or parent material. The preferential corrosion of weldment can attributed to same factors: the different in composition of metal itself and wire or electrode, microstructure and shape or geometry of weld. In welding process parent material and weld wire mixed to gather by rapidly heating to melting temperature and then cooling to room temperature, the high cyclic of heating and cooling produces (phase change), thus the heat affected zone (HAZ) and the weld metal (WM) may contain one or more of the following structures: ferrite, pearlite, bainite and martensite. Farther more residual stress development during welding can cause stress corrosion crack. Geometrical parameters such as excess root penetration can lead to erosion (impingement) corrosion downstream of the weld. In general, the surface discontinuity generated by the weld reinforcement may lead to turbulence in a flowing system. One of the main thread in pipeline transmission crude oil is internal corrosion. Crude oil is non corrosive the presence of water and sediment makes it corrosive media. the density different between crude oil and water case that water separate at the bottom and contact the pipe wall. The primary factors that effected the internal corrosion in flow rate when a low flow rate facilitates separation of water droplets and stagnation in the bottom of the tube which facilitates the occurrence of pitting corrosion whereas in the case of higher flow rate cause erosion corrosion due to remove the internal layers of the tube especially in the weld joint (as a result of excess penetration of root pass ) and areas of impact or change in the flow direction such as the valves. According to ASTM G205, the corrosivity of crude oil containing water can be understood in terms of three properties: the corrosivity of water in the presence of crude oil, type of the emulsion formed between oil and water, and the wettability of steel surface. It is a widely held view that water and oil are immiscible, but under certain conditions, they can form emulsion, two kinds (o/w and w/o). O/W emulsion means that oil is the continuous phase (less corrosive and has low conductivity) and vice versa for W/O emulsion. Wettability can be characterized by measuring the contact angle. The contact angle is determined by the surface tensions (surface free energies) of the three phases.

Material and Methods

Material and Mechanical Tests: The chemical composition of the mild steel is represented in Table-1. Standard V-groove butt configurations an included angle of 60° was employed to weld these similar metals and having root face of 4 mm and land face 2 mm, the SMAW parameter shown in Table-2. Metallographic inspection was carried out on the composite region [parent metal + HAZ+ weld] of the weldment as shown in Figure-1. The specimens working of the weldments and parent material were polished using the emery sheets of Si C with grit size varying from 220 to 1000 and followed by disc polishing using diamond (grain size1µm) to obtain a mirror finish to the sample. Electrolytic etching nital (2% HNO$_3$ with 98% alcohol) was employed to study the microstructure of mild steel 1020. Further the samples were cute to different dimensions to achieve various
mechanical tests. Hardness studies were conducted on the composite region of the weldment by keeping weld as center using Vicker’s Microhardness tester employing a load of 1000g and 10 s dwell time at the regular intervals of 0.25mm.

**Chemical Analysis of corrosive solution:** A chemical analysis of both the two mediums has been made. Analysis of water phase present in the crude oil was determined with the results are given in Table-3. The main ions detected were chloride (CL⁻), bicarbonate (HCO₃⁻) and sulphate (SO₄²⁻) where chloride (CL⁻) has been known as aggressive ion. Water was identified to have pH of 6.34 or basic condition and water content (%) ~45%. Analysis of crude oil: Chemical composition of the crude oil was determined with the results are given in Table-4. The density of crude oil (0.8944) g/cm³ and pH (6.56).

**Immersion Test:** Immersion corrosion were conducted in crude oil and water extraction from it. Specimens were cut to the dimensional (30×18×6) mm with a whole diameter of (2mm). The corrosive media are oil and water extracted from the oil. The weight loss of the metal specimen during the corrosion test calculated by the Equation-1 given below

\[
\text{Weight loss (mpy) = } \frac{\text{Weight of specimen before test} - \text{Weight of specimen after test}}{\text{Surface area of specimen} \times \text{Dwell time} \times \text{Weighting factor}}
\]

**Table 1**

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>AL</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.179</td>
<td>0.009</td>
<td>0.398</td>
<td>0.011</td>
<td>0.01</td>
<td>0.017</td>
<td>0.005</td>
<td>0.025</td>
<td>0.060</td>
<td>0.005</td>
<td>0.019</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

**Erosion-Corrosion Test:** Jet impingement tests were conducted using device which was manufactured and designed according to (G 73) ASTM as show in Figure-2. The device consist of: 1. Tank Perspex, 2. 1H.P motor, 3. P.V.C pipe, 4.outlet gas pipe, 5. effective media, 6. Metal specimen, 7. jet nozzle. The investigational work tests were achieved using traditional

The nozzle is 4 mm in diameter and positioned at a fixed distance of 5 mm from the specimen. Thickness loss measurements were taken based on the surface area of the sample (540 mm²) exposed to the jet. Tests were conducted for 2 h and specimens were weighed before and after the test to determine the total weight loss. The specimen is weighted again after the specified (10) minutes of exposure to the medium. The weighting is carried out after the specimens are cleaned with distilled water and a brush.

**Open Circuit Potential Measurements:** The potentials of carbon steel electrodes were measured conventional three-electrode electrochemical cell with and saturated calomel electrode (SCE) as reference electrode, platinum (Pt) grid as auxiliary electrode and material as worker electrode were used. The measurements of OCP were obtained with a PAR 263 potentiostate.

**Polarization Measurements:** Corrosion rate of the steel pipeline was measured using a three-electrode cell with saturated calomel electrode (SCE) as the reference electrode, platinum (Pt) grid as auxiliary electrode and material as worker electrode were used. To simulate actual corrosion process, the water phase extracted from crude oil was used as the electrolyte.
Table-2
SAW parameters

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Current I (A)</th>
<th>Voltage V (volt)</th>
<th>Heat input (KJ/mm)</th>
<th>Root g (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First pass E6010</td>
<td>Ac 120</td>
<td>20</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Second pass E7018</td>
<td>DC 150</td>
<td>50</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Corrosion Rate (mpy) = \( \frac{534 \, \Delta W}{\rho \, \Delta t} \)  \hspace{1cm} (1)

Where: \( \Delta W \): different in weight loss (mg), \( \rho \): density of coupon material (g/cm\(^3\)), \( A \): area (in\(^2\)), \( t \): time of exposure (h).

Table-3
The main ions detected of water phase present in crude oil

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water extraction from crude oil (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>142360</td>
</tr>
<tr>
<td>bicarbonate (HCO(_3)-)</td>
<td>534</td>
</tr>
<tr>
<td>sulphate (SO(_4)-2)</td>
<td>40</td>
</tr>
<tr>
<td>chloride (Cl(^-))</td>
<td>7742</td>
</tr>
</tbody>
</table>

Table - 4
The composition of crude oil

<table>
<thead>
<tr>
<th>Element composition</th>
<th>Crude oil (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>85.62</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>12.1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Results and Discussion

Hardness Measurement: The results of Vickers micro hardness tests carried out at different regions of the weld cross-section specimen shown in Figure-3. We have found that maximum hardness values are situated in the area of weld metal and HAZ. The variation in properties across the weld can be attributed to several factors, mainly to residual stresses just after welding. However, other factors can contribute to this hardening like phase composition, grain size, and metallic inclusions. We have observed that bands of coarse grains grow along a certain preferred crystallographic directions\(^{15}\).

Static Corrosion Measurement: uniform corrosion and pitting corrosion was observed in all the test coupons immersed in the media (water extraction from crude oil and crude oil)\(^{16,17}\) as show in Figure-4(A,B). Furthermore the corrosion rate measurements as a function of time are as shown in Figure- (5 and 6) in crude oil and water extraction from crude oil respectively. Corrosion rate of samples slowly increases as a result of formation of porous Fe\(_2\)O\(_3\), which is not protective in nature\(^{12}\). The most important one is water chemistry What is interesting in the curves is that the dissolved Fe ions in the water were higher than in the crude oil for both cases: in the absence and presence of inhibitor. It was attributed the conductivity nature of water, i.e. more electrons can be moved between the metal and the corrosion solution. In addition to that, water layer has a high ratio of salts as reported earlier in Table-3, HCO\(_3\), SO\(_4\)-2, and Cl, whereas, the crude oil layer has very low electrical conductivity\(^{20}\).

Erosion: Corrosion Rate: Erosion-corrosion produces the maximum weight loss rate which comes from two effects, one mechanical resulting from the high velocity of the erosive medium with slurry which produces cavitation and impingement\(^{18}\). It produces effect like horse-shoe traces which are a distinctive characteristic of erosion-corrosion as show in Figure-7. The horse-shoe-like areas are dark, distinctive and oriented toward flow direction of the erosive-corrosive medium. The other is electro-chemical resulting from there action between the medium and the specimen. Figure-8 shows the effect of erosion-corrosion on corrosion rate. This type of corrosion produces great weight loss as a result of removing large and clear-cut metal portions due to impingement erosion and corrosion\(^{19}\).

Open circuit potential: The open circuit potential is a parameter which indicates the thermodynamically tendency of a material to electrochemical oxidation in a corrosive medium. It can be seen that the values of potential were higher than the base metal and that means the corrosion has slowly occurred. The welded metal erodes to protect the weldment area while the
base metal erodes upon touching the corrosion solution. The noticeable decreasing and increasing in the curve was attributed to form a protecting thin layer and it has been broken because of the accumulated corrosion products after a period of immersion it stabilizes around a stationary value. This potential may vary with time because changes in the nature of the surface of the electrode occur (oxidation, formation of the passive layer or immunity).

![Microstructure showing (a) base metal, (b) Weld metal in water extraction from crude oil](image)

**Figure-4**

Microstructure showing (a) base metal, (b) Weld metal in water extraction from crude oil

![Corrosion rate of specimens in water extracted from crude oil](image)

**Figure-5**

Corrosion rate of specimens in water extracted from crude oil

![Corrosion rate of specimens in crude oil](image)

**Figure - 6**

Corrosion rate of specimens in crude oil
Figure-9 shows the OC curves (the relationship between potential (mV) and time (mn)) for all the samples immersed in corrosion solution (water extraction from crude oil) at 25°C. 

Microstructure of specimen A) non-welded and B) welded after erosion corrosion test

![Figure-7]

**Figure-7**

**Figure-8**

Erosion Corrosion rate of specimens in crude oil

![Figure-8](image)

**Figure-9**

Open circuit potential of both specimens

![Figure-9](image)
Tafel Extrapolation Method: It was used to calculate corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) for two specimens (with and without welding). Through point of intersect the both Tafel lines that makes possible the estimation of the corrosion current density by the extrapolation of the Tafel slopes with corrosion potential. This method which used to calculate corrosion rates in (water extraction from crude oil) solution. Figure-10 (A and B) for metal and weldment respectively shows that samples in solution. For metal $I_{corr}$ (38.18 $\mu$A/cm$^2$) and $E_{corr}$ (-627.5 mV) whereas for welding $I_{corr}$ (20.11 $\mu$A/cm$^2$) and $E_{corr}$ (-614 mV). The current density was quite large which tells that the base metal has rapidly corroded. That has been assigned to the weak default ability of low carbon steel to resist corrosion. Also, the Cl- has great penetration in the metal causing corrosion and also increases the conductivity of the solution.

Conclusion

This work represents a contribution to the study of the effect of shielded metal arc welding on industrial low carbon steel (0.179 wt. % C). The findings from this study make several important contributions to the corrosion research and thus identified the following conclusions: The welding and HAZ regions have been found to be of high hardness than the base metal. The welding area has shown a higher corrosion resistance than base metal before the stress relieving heat treatment because the base metal has worked a sacrificial metal to protect the welding area and more hardness which means more resistance the impingement behavior of the fluid flow. Corrosion rate by erosion corrosion is greater than the corrosion rate by pure corrosion for all specimens.
References


