INVESTIGATION OF CORROSION RATE KINETICS IN OIL STORAGE TANK USING VARIOUS TYPES OF EPOXY COATINGS

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ABSTRACT

This paper presents the results of corrosivity testing for six types of crude oils collected from six oil fields (lower Zubair, Upper Zubair, Nahr Umr, West Qurna, South Rumaila and North Rumaila) lie in the southern part of Iraq. An immersion test method has been used in studying the six types of coated epoxy (Jotun, Hemple, SPEC Kuwait, Fosroc Jordan, DCP British, and Europe H51-EP22 epoxy coatings) used to coat crude oil storage tanks in the six field regions. The analysis of chemical kinetics between the oil impurities and the active part of coatings towards carbon steel (ASTM A537) show that the lower Zubair field gives lower values of corrosion rate and west Qurna field give higher value and other fields show moderate values. The Europe H51-E22 and Jotun epoxy is the best coating and SPEC Kuwait epoxy show properties not compatible with characteristics of Iraqi crude oil. A mechanism of corrosion of epoxy coatings is developing which suggests that corrosion occurs due to chemical reaction occurs on the surface of coating and depends on temperature, pH and impurities on crude oils. Microscopic examination show that Europe, DCP, and SPEC coating have surfaced pitting, Jotun and Hampel show degradation and Fosroc coats show surface cracking.

KEYWORDS: Crude Oil, Epoxy Coating, Immersion Test, Effective Group, Porosity

INTRODUCTION

Crude oil is one of the most important raw materials for the production of energy and crude oil tanks play a strategic role in its storages. Corrosion is considered the most important factor leading to failures of tanks structures. There are many reasons for crude oil tanks to be effected by corrosion. Firstly, tanks are exposed to very corrosive conditions, crude oil when full; moist atmosphere when empty; cyclic heating and cooling from atmospheric exposure. Secondly, often comes from having large surface and highly stressed areas, such as corners, edges, and welded seam areas. Thirdly, tank coating is a very complex job with many ramifications [1].

Crude oil has a complex composition and it varies widely in its physical/chemical properties. Crude oils do not come out of the ground pure; there are always various by-products. Typically having a variety of impurities such as: water, CO₂, H₂S, various salts (Na⁺, K⁺, Ca²⁺, Cl⁻... etc.) and organic acids. Oxygen (O₂) is not present in produced fluids, but it can be introduced into the oil during the processing operations with fluids that are added. All these corrosive species lead to the corrosion in storage tanks. Various protection mechanisms to control the corrosion in crude oil tanks have been developed including barrier protection, corrosion inhibitors, and cathodic protection. The barrier protection deals with the disconnection of metal surface from the corrosive environment such as coatings on the metal surface using paint and epoxy coats [2].

Epoxy is one of the most common coating materials used in crude oil environment. Due to the chemical groups of cured epoxy structure such as hydroxyl group (–OH), carboxyl group (C = O) and amino group (N–H) that have unpaired
electron, epoxy has exhibited the superior properties when exposed to crude oil environment. The efficiency with which protection is provided is determined by a number of properties of the total coated system, which consists of the coatings film, the metal substrate, and it’s pretreatment [3]. The main goal of this work is to investigate the effect of corrosiveness of various crude oils on various epoxy coatings used for crude oil storage tanks at various fields of south Iraq. A mechanism of corrosion of epoxy coatings has been developed which suggests that corrosion occurs due to chemical reaction on the surface of coatings and depends on temperature, pH and impurities on crude oils. Microscopic testing provides important results which provide a clear indication of types of degradation and corrosion occurring.

**TYPES OF EPOXY COATS**

The epoxy consists of two parts which are mixed shortly before use. The part A (Base) is an epoxy molecule group containing so called epoxy-groups, while the part B is a thinner (Hardener). When the two substances are mixed, a cross linked network is created, resulting in a hard substance that can be very strong. Table 1 shows the six types of commercial epoxy coatings used for crude oil tank lining in the Iraqi markets. The composition of the Europe and Jotun coating is Bisphenol A which is reinforced by various additions. The Hampel coating consists from polyamine adduct curing agent. The DCP is made from polyamide cured epoxy. The Fosroc and SPEC coatings made from amine adduct cured phenolic epoxy (Novolac). These types of coating includes various types of effective groups, Europe and Jotun have hydroxyl group. Hampel, DCP, and SPEC have amine group and Fosroc has amide group. Effective groups play important factors in the cohesion between components of coating and adhesion with the surface.

<table>
<thead>
<tr>
<th>No.</th>
<th>Epoxy Coating</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hampl</td>
<td>Sharjah coating company, U A E</td>
</tr>
<tr>
<td>2</td>
<td>SPEC</td>
<td>Kut Specialties construction chemical factory, Kuwait</td>
</tr>
<tr>
<td>3</td>
<td>Fosroc</td>
<td>Fosroc international company, Jordan</td>
</tr>
<tr>
<td>4</td>
<td>Jotun</td>
<td>Sharjah coating company, U A E</td>
</tr>
<tr>
<td>5</td>
<td>Europe H51-EP22</td>
<td>Master company, Europe</td>
</tr>
<tr>
<td>6</td>
<td>DCP</td>
<td>Don construction production, U K</td>
</tr>
</tbody>
</table>

**SPECIMEN PREPERTION AND COATS**

The test samples were cut from storage tank plate of carbon steel (ASTM A537) which have the following compositions: Fe: 97.58%, C: 0.24%, Mn: 0.035%, S: 0.035%, Cr: 0.025%, Si: 0.5%, Mo: 0.08%, Ni: 0.25%, Cu: 0.35% [4].

The coupons have the dimensions of (25 x 50 x 6) mm. Test coupons were prepared in the college of engineering machine shop. A hole was drilled in the middle of each specimen. The specimens were polished by using a different metallographic grade (180, 500, and 800) of emery paper then cleaned by distilled water and dried in a stream of air at room temperature. A total of 100 coupons were processed for testing. The coating was applied to coats and then left to dry three weeks at room temperature and atmospheric pressure before being exposed to the test. Figure 1 A to H shows the specimens before and after coating.

![Figure 1 Specimens: A-Before Coating, B-Hampel, C-DCP, D-SPEC, E-Europe, F-Fosroc, Jotun](image-url)
CRUDE OIL SAMPLES

The crude oil samples were collected from six various fields located in Basrah region (North Rumaila, South Rumaila, Upper Zubair, Lower Zubair, Nahr Umr and West Qurna). The crude oil heavy metals analysis using spectrophotometer was carried at Basrah Refinery laboratory, south oil company of Iraq. These metals are vanadium, nickel, iron, cadmium, zinc, copper, chromium, aluminum and manganese. The other physical properties and dissolved gases are analysis in the south oil company laboratory. Tables 2 and 3 show material compositions, Viscosity, specific gravity and dielectric constant of crude oils measured laboratory at different temperatures. The heavy metals are measured in ppm wt (mg/kg in the original sample). Table 4 shows dissolved gases of crude oil samples and physical characteristics.

APPARATUS AND TEST PROCEDURE

The equipment used for the experiment were two water baths, Beakers 500ml., Digital pH meter, sensitive weight balance, long pin and nylon thread for suspending the specimens in the beakers. A computerized Carl Zeiss Jena imaging system, using microscope provided by camera smart technical having (22 Mica pixels). Figure 2 shows the equipments used. After taking the initial weight, the coupons were suspended inside the 500 ml Beaker containing crude oil solution balanced with 10% NaOH and 0.1N HCl solution to obtain the pH values for the crude oil solutions were 5. Immersion tests are carried out at temperatures (40°C and 50°C). The temperature regulators using water bathes, for an exposure period of 180 days. After each 15 day of coated coupon immersion, the coupon were extracted from the crude oil and cleaned to remove crude oil deposits and oxide films present and then weight.

Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon in (mm/year) using the expression [5]:

\[
CR = \frac{8.76 \times 10^4}{\rho A_t t} W
\]

Where, W is mass losses in gm.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Fields</th>
<th>North Rumaila</th>
<th>South Rumaila</th>
<th>Zubair - Upper</th>
<th>Zubair - Lower</th>
<th>Nahr - Umr</th>
<th>West - Qurna</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ppm wt</td>
<td>3</td>
<td>1.4</td>
<td>2.25</td>
<td>1.6</td>
<td>2</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Copper ppm wt</td>
<td>5</td>
<td>7</td>
<td>0.8</td>
<td>0.2</td>
<td>9</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Vanadium ppm wt</td>
<td>43</td>
<td>55.7</td>
<td>40.1</td>
<td>31</td>
<td>49</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Nickel ppm wt</td>
<td>8.2</td>
<td>11</td>
<td>10</td>
<td>8.7</td>
<td>10.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Cadmium ppm</td>
<td>0.1</td>
<td>0.17</td>
<td>0.64</td>
<td>0.02</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Zinc ppm wt</td>
<td>0.13</td>
<td>0.07</td>
<td>0.41</td>
<td>0.04</td>
<td>0.08</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>Aluminum ppm wt</td>
<td>0.2</td>
<td>0.16</td>
<td>0.11</td>
<td>0.03</td>
<td>0.06</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Manganese ppm wt</td>
<td>0.10</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2: Water Baths and Computer Imaging System
Table 3: Viscosity, Specific Gravity and Dielectric Constant of Crude Oils

<table>
<thead>
<tr>
<th>Property</th>
<th>North Rumaila</th>
<th>South Rumaila</th>
<th>Zubair Lower</th>
<th>Zubair Upper</th>
<th>Nahr Umr</th>
<th>West Qurna</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cst)</td>
<td>40°C</td>
<td>12.1</td>
<td>17.6</td>
<td>5.8</td>
<td>9.8</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>11.4</td>
<td>13.8</td>
<td>5.3</td>
<td>9.1</td>
<td>15.8</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>40°C</td>
<td>0.8860</td>
<td>0.8952</td>
<td>0.8745</td>
<td>0.9047</td>
<td>0.8572</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>0.8801</td>
<td>0.8707</td>
<td>0.8702</td>
<td>0.8902</td>
<td>0.8503</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>40°C</td>
<td>2.414</td>
<td>2.261</td>
<td>1.921</td>
<td>1.988</td>
<td>2.102</td>
</tr>
<tr>
<td></td>
<td>50°C</td>
<td>2.353</td>
<td>2.207</td>
<td>1.864</td>
<td>1.945</td>
<td>2.006</td>
</tr>
</tbody>
</table>

Table 4: Physical Properties of Crude Oils

<table>
<thead>
<tr>
<th>Properties</th>
<th>North Rumaila</th>
<th>South Rumaila</th>
<th>Zubair Lower</th>
<th>Zubair Upper</th>
<th>Nahr Umr</th>
<th>West Qurna</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>33.8</td>
<td>30.2</td>
<td>34.3</td>
<td>34.1</td>
<td>33.6</td>
<td>32.31</td>
</tr>
<tr>
<td>Carbon residue %</td>
<td>7.3</td>
<td>6.33</td>
<td>5.99</td>
<td>3.95</td>
<td>3.1</td>
<td>8.4</td>
</tr>
<tr>
<td>Sulfur %</td>
<td>3.9</td>
<td>2.92</td>
<td>2.95</td>
<td>1.1</td>
<td>2.1</td>
<td>4.3</td>
</tr>
<tr>
<td>Water content %</td>
<td>1</td>
<td>0.75</td>
<td>0.8</td>
<td>0.2</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>N₂ (g) %</td>
<td>0.13</td>
<td>0.98</td>
<td>0.08</td>
<td>0.09</td>
<td>0.81</td>
<td>0.79</td>
</tr>
<tr>
<td>TAN mgKOH/gm oil</td>
<td>0.37</td>
<td>0.112</td>
<td>0.2</td>
<td>0.06</td>
<td>0.11</td>
<td>0.333</td>
</tr>
<tr>
<td>Salt NaCl ppm</td>
<td>14</td>
<td>13</td>
<td>11</td>
<td>3.8</td>
<td>5</td>
<td>10.81</td>
</tr>
<tr>
<td>Asphaltenes %</td>
<td>2.2</td>
<td>1.45</td>
<td>1.2</td>
<td>0.5</td>
<td>0.77</td>
<td>0.94</td>
</tr>
<tr>
<td>H₂S (g) ppm</td>
<td>1.1</td>
<td>1</td>
<td>2</td>
<td>0.7</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>CO₂ (g) ppm</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2.3</td>
<td>3.5</td>
</tr>
<tr>
<td>O₂ (g) %</td>
<td>1</td>
<td>1.1</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

MATHMATICAL MODEL

The theoretical values of corrosion rate can be calculated from anodic and cathodic reactions as follows:

Anodic Reaction Description

The mechanism of anodic dissolution of iron has been extensively investigated in acid solutions; the dependence of the dissolution rate on the activity of hydroxyl ion is generally accepted. The mechanism proposed by Bockris et al. [6] is as follows:

\[
\text{Fe} + \text{OH}^- \rightarrow \text{FeOH} + \text{e}^- \quad (2)
\]

\[
\text{FeOH} \rightarrow \text{FeOH}^+ + \text{e}^- \quad (3)
\]

\[
\text{FeOH}^+ \rightarrow \text{Fe}^{2+} + \text{OH}^- \quad (4)
\]

The current density for the Fe dissolution is given by:

\[
i_{Fe}^o = i_{Fe} e^{-\frac{0.15(F-E_{Fe}^o)}{RT}} \quad (5)
\]

The exchange current density can be expressed as follows [7]:

\[
i_{Fe}^o = i_{Fe} a_{OH} a_{H_2O}^{1.6} \quad (6)
\]

The reversible potential is calculated from the Nernst equation and depends on the concentration of (Fe⁺²) ions as follow:
Investigation of Corrosion Rate Kinetics in Oil Storage Tank Using Various Types of Epoxy Coatings

\[ E = E^0 - \frac{RT}{ZF} \ln \left[ Fe^{+2} \right] \]  

(7)

**Cathodic Reaction for CO\textsubscript{2}**

In CO\textsubscript{2} corrosion cathodic process may be due to the reaction of four separate species i.e. H\textsuperscript{+}, OH\textsuperscript{-}, H\textsubscript{2}O and H\textsubscript{2}CO\textsubscript{3}, in acidic solution the reduction of H\textsuperscript{+}, is the dominant cathodic reaction:

\[ H^+ + e^- \rightarrow 0.5H_2 \]  

(8)

According to the basic electrochemical kinetics the current density for H\textsuperscript{+} reduction can be written as [8]:

\[ \frac{1}{i_H} = \frac{1}{i_{H,a}} + \frac{1}{i_{H,lim}} \]  

(9)

The activation current density for the reduction portion can be written as follows:

\[ i_{H,a} = i_H^0 \left( -0.5F(E-E^0_H) / RT \right) \]  

(10)

So, the exchange current density is given by Smart and Bockris [6]:

\[ i_H^0 = i_{H,a} \left( a_{H^+} a_{H_2O} \right) \]  

(11)

The limiting current densities Eq.22 can be calculated as:

\[ i_{H,lim} = K_m F a_H \]  

(12)

Where, the values of \( K_m \) can be calculated if the flow regime, diffusion coefficient of H\textsuperscript{+} ions and solution viscosity are known. In addition to the reduction of H\textsuperscript{+} ions, the direct reduction of water is also considered, i.e. [7]:

\[ H_2O + e^- \rightarrow 0.5H_2 + OH^- \]  

(13)

The water reduction does not exhibit limiting current density because there are no diffusion limitations for the transport of H\textsubscript{2}O molecules to the surface. Thus the current density can be express as:

\[ i_{H_2O} = i_{H_2O}^0 \left( -0.5F(E-E^0_{H_2O}) / RT \right) \]  

(14)

Thus the exchange current density is given by the following equation [9]:

\[ i_{H_2O}^0 = i_{H_2O,a} \left( a_{H^+} a_{H_2O} \right) \]  

(15)

At (pH > 4) reduction of carbonic acid (H\textsubscript{2}CO\textsubscript{3}) becomes the dominant cathodic process and carbonic acid results from the hydration of dissolved CO\textsubscript{2}, i.e.

\[ CO_2 + H_2O \rightarrow H_2CO_3 \]  

(16)

The H\textsubscript{2}CO\textsubscript{3} reduction is under chemical reaction control so,
The activation current is given by [12]:

\[
i_{iH_2CO_3} = i_{H_2CO_3}^{o} \exp \left( \frac{(-o_{H_2CO_3}E + E_H^o)}{RT} \right)
\]

(18)

The exchange current density for \( H_2CO_3 \) reduction can be expressed as:

\[
i_{H_2CO_3}^{o} = i_{H_2CO_3}^{0.5} H_2CO_3^{0.5} \]

(19)

Following Nesic et al. [10] the limiting current density can be expressed as follows:

\[
i_{H_2CO_3,lim} = F \cdot a_{H_2CO_3} \cdot \left( D_{H_2CO_3} K_{H_2CO_3} K_{H_2CO_3}^{f} \right)^{0.5}
\]

(20)

Where,

\[ D_{H_2CO_3} = 10^{-5} \text{ cm}^2/\text{s}, \quad K_{H_2CO_3} = 1.7 \times 10^{-3} \]

The values of \( K_{H_2CO_3}^{f} \) at any temperature are calculated from the expression developed by Nesic et al. [8]:

\[
K_{H_2CO_3}^{f} = 10^{169.2 - 53 \log(T) - \left[ \frac{11715}{T} \right]}
\]

(21)

For all partial process the generalized Arrhenius equation can be expressed as follows [11]:

\[
i_{T} = i_{T_0} \exp \left( -\frac{\Delta G}{RT} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right)
\]

(22)

And the applied current density is:

\[
i = \frac{zF_1}{A_w} \exp \left( -\frac{\Delta G}{RT} \right)
\]

(23)

According to mixed potential theory:

\[ \Sigma I_{\text{cathod}} = I_{\text{anode}} = I_{\text{corr}}. \]

(24)

Then, Faraday’s law used to calculate the corrosion rate (CR) in mm/year for uniform corrosion as follows [9]:

\[ CR = 3.27 \times 10^{-3} \times I_{\text{corr}} \times E_w \]

(25)

**Calculation of Crude Oil Activity**

Bromley, show a method for the calculating of activity coefficient (\( \gamma_i \)) as follows [11]:
\begin{equation}
\log \gamma_i = -\frac{A_d[Z_i^+Z_j^-\sqrt{I} \left(1 + 1.5\right)^{-2}]^{2}I + B_dI}{1 + \sqrt{I}} + \frac{BB[Z_i^+Z_j^-]}{1 + \frac{1.5}{Z_i^+Z_j^-I}}
\end{equation}

And,
\begin{equation}
BB = 0.06 + 0.6B_d
\end{equation}

The ionic strength I and Debye-Huckel constant A_d are calculated as follows:
\begin{equation}
I = \frac{1}{2} \sum m_iZ_i^2
\end{equation}

\begin{equation}
A_d = \frac{2\pi N_A \rho \epsilon}{3} \left(\frac{e}{\sqrt{4\pi \delta D_i \epsilon_{r_i} \kappa_b T}}\right)^3
\end{equation}

The Bromley constants are calculated as:
\begin{equation}
B = B^+ + B^- + \delta^+ \delta^-
\end{equation}

The individual ion values for B and \( \delta \) coefficients for the equation (29) are given in table 5.

<table>
<thead>
<tr>
<th>Cation</th>
<th>B*</th>
<th>( \delta^+ )</th>
<th>Anion</th>
<th>B*</th>
<th>( \delta^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H^+</td>
<td>0.0875</td>
<td>0.103</td>
<td>Cl</td>
<td>0.0643</td>
<td>-0.06</td>
</tr>
<tr>
<td>Na^+</td>
<td>0.00</td>
<td>0.028</td>
<td>NO_3^-</td>
<td>-0.025</td>
<td>0.27</td>
</tr>
<tr>
<td>K^+</td>
<td>-0.045</td>
<td>-0.079</td>
<td>SO_4^-</td>
<td>0.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>NH_4^+</td>
<td>-0.042</td>
<td>-0.02</td>
<td>CO_3^-</td>
<td>0.028</td>
<td>-0.67</td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>0.0374</td>
<td>0.119</td>
<td></td>
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<tr>
<td>Al^{3+}</td>
<td>0.052</td>
<td>0.12</td>
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</tr>
<tr>
<td>Mn^{2+}</td>
<td>0.037</td>
<td>0.21</td>
<td></td>
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</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.057</td>
<td>0.157</td>
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</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**

The mechanism of corrosion phenomena in the immersion crude oil solution is discussed to show the effects of pH and temperature on corrosion rate.

Figures 3 A to F show comparisons of the general corrosion rate obtained from the experimental immersion tests and mathematical models, (depending on the equations 18, 21, 26, and 32) as functions of temperatures and pH values for the uncoated and coated specimens of Europe coatings only.

The results showed good agreements between the corrosion rates obtained from the mathematical model calculations and experimental results using an uncoated carbon steel ASTM A537. Both theoretical and experimental corrosion rates for the uncoated coupons were very high comparison with the results obtained from coated coupons. This is due to the resistance of a coated coupon against the crude oil impurities, which is higher than that of uncoated coupon. The layer of a coating relative to the uncoated coupon has prevented the direct contact between crude oil impurities (CO_2, H_2S, O_2, N_2, salts ... etc.) and the metal surface. These impurities are considered the main reason for corrosion problems. The rate of a chemical reaction between these impurities and the metal surface may be accelerated due to the change in the concentrations of impurities. However, when the concentration of impurities increases, the rate of corrosion will increase and this is identical with the previous results which have been obtained by various researchers.
Figures 4 and 5 show the general corrosion rate obtained from testing six types of coatings in the six kinds of crude oil that are collected from various fields. The corrosion rates obtained are examined at temperatures (40°C and 50°C) and pH value is 5 for a total period of six months. The results indicate that the best protection was provided by the Europe H51-E22 and Jotun epoxy which exhibit low corrosion losses, and provide better overall performance than other coatings and deemed a viable corrosion control system, whereas SPEC Kuwait epoxy exhibits the greatest amount of weight loss due to corrosion compared to other types of epoxy coats. This attributed to the composition of each types of coating and reactivity of effective groups found. In Europe coating, the components are very cohesive with other and resistance to corrosion compare to others.

The lower Zubair crude oil has lower values of corrosion rates and the west Qurna crude oil has large values of the corrosion rates. The other types of crude oil showed moderate values between these results. This is attributed to the influence of impurities in the crude oil. The lower Zubair crude oil has lower impurities and material concentration as shown in table 2 compared to other crude oils. The maximum CO₂ and H₂S concentrations are observed in west Qurna and north Rumalia crude oil samples, while lower Zubair and Nahr Umr crude oils have minimum concentration.

It was observed that all the coated coupon experience gain in the weight that's decrease occurs during the immersion test at some points in different curves; this attributed to the absorption of water and dissolved gases into the coating epoxy.

The mechanisms of corrosion have started by the reaction of crude oil impurities and coating surface, then, the reaction occurred at the metal–coating surface and lead to initiation of pitting. The possible reactions occur in coating surfaces depend on the compositions of coating and can be summarized as follows:

The reactions of Bisphenol A with various impurities in crude oil are summarized by the following reactions:

\[
\text{Reactions of Bisphenol A with impurities: } \\
\text{(31) } \text{OH}^{-} + \text{OH}^{+} \\
\text{(32) } \text{H}_{2}\text{O} + \text{H}^{+} \\
\text{(33) } \text{H}^{+} + \text{H}_{2}\text{S} \\
\text{(34) } \text{CO}_{2} + \text{OH}^{+} \\
\text{(35) } \text{O}_{2} + \text{H}_{2}\text{O}
\]
The above chemical equations illustrate the nature of an electrochemical reaction Bisphenol A. During the reactions, electrons are transferred to the crude oil solution, i.e., an oxidation process occurs together with a reduction process. During this, the bond force between coating components are broken and this causes loss of cohesion between the coating components.

The reaction between amines and water, hydrogen sulfide, hydroxyl ion, hydrogen ion, carbon dioxide, chloride ion, and hydrochloric acid are:

\[
2 \text{R-} \text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{R-} \text{NH}_3^+ + \text{OH}^- \quad (36)
\]

\[
\text{R-} \text{NH}_2 + \text{H}_2\text{S} \rightarrow \text{R-} \text{NH}_3^+ + \text{HS}^- \quad (37)
\]

\[
\text{R-} \text{NH}_2 + \text{OH}^- \rightarrow \text{R-} \text{NH} + \text{H}_2\text{O} \quad (38)
\]

\[
\text{R-} \text{NH}_2 + \text{H}^+ \rightarrow \text{R-} \text{NH}_3 \quad (39)
\]

\[
\text{R-} \text{NH}_2 + \text{CO}_2 \rightarrow \text{R-} \text{NH}_2\text{COO}^- \quad (40)
\]

\[
\text{R-} \text{NH}_2 + \text{Cl}^- \rightarrow \text{R-} \text{NH}_2\text{Cl}^- \quad (41)
\]

\[
\text{R-} \text{NH}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{R-} \text{NHCOO} + \text{H}_2\text{O} \quad (42)
\]

All the reactions that include broken bonds in molecular structure are accompanied by generation of heat. The heat generation causes an increase in the temperature of coating, which makes the coats soften more. Also, it affects on the properties of epoxy coating especially porosity, cohesion bond, hardness, viscosity and coating permeability.

The increase of the temperature leads to the expansion of coating, which increases pore volume and this increases porosity. Through the coating porosity; the impurities of crude oil include: water, chloride ion and dissolved gas permeates through the coats and reach the interface between coating and metal.

As temperature increases the porosity of the coating has increased, this leads to the penetration of impurities of crude oil inside the coating voids and increases the reaction rate between molecular structures. The break bond between molecular structures leads to reduce the cohesion and strength between compounds of epoxy coatings which contributes to increase the corrosion rates.

The property of a porous material which permits the passage of water and oxygen through it is called permeability which affects the barrier properties of coating. The permeability depends primarily on the structure (cross-linking) and the chemical composition and properties of the epoxy. With small value of permeability, the protection ability of the coating is improved. More cross linking reduces the coating’s moisture permeability and increases its long term resistance to water. The Bisphenol A epoxy coating has a low resistance to permeability of (0.5 gm/cm\(^2\)/mm/Pa.S) and increase with increase temperature while the polyamine epoxy coating has medium resistance to permeability of (0.4 gm/cm\(^2\)/mm/Pa. S), these values decrease with increasing temperature because it has morphological heterogeneity. The Novolacs epoxy coating has high resistance to permeation of (0.2-0.25 gm/cm\(^2\)/mm/Pa.S). This information is obtained according to the manufacturing Company.

The results indicate that the best protection was provided by the Europe and Jotun coatings which exhibit low
corrosion losses, and provide better overall performance than the other coatings and deemed a viable corrosion control system. Whereas SPEC Kuwait epoxy exhibits the greatest amount of weight loss due to corrosion compared to the other types of coats. This is attributed to the composition of each type of coating and reactivity of the effective groups found. The effective groups are hydroxyl group in Europe and Jotun coatings, amide group in DCP, amine group in other coatings. A hydroxyl group strongly improves the barrier properties and lowers the permeability of dissolved gases than other effective groups. Also the glass fibers in Europe coating make the components very cohesive and increase the resistance to corrosion rates in comparison with other types of coatings.

The immersion test results show that the lower Zubair crude oil has the lowest values of corrosion rates while the west Qurna crude oil has large values of the corrosion rates. The other types of crude oil show moderate values between these results. This is attributed to the effect of many factors that influence the crude oils such as: impurities, dissolved gases including CO$_2$, H$_2$S, O$_2$, water chemistry and salts in the crude oils.

**MICROSCOPIC INSPECTION AFTER TEST**

The microscopic inspection is important in order to observe any change on the surface appearance. Figure 6 represents the surface microstructures of some specimens after exposure to the crude oils. The images were taken from the surface areas of the specimens after the immersion test at a temperature 50$^\circ$C and the value of pH is equal to 5.

The microscopic examination of the Europe, DCP and SPEC coated coupons show cavities besides many pits covering most of the coated surface of the coupons. There are many reasons for pitting of coatings, first the cavities and pits already present on the coat surface of the coupon are due to local corrosion as a result of long exposure of epoxy coating coupon to the crude oil. The oxide film is form on coating surface due to chemical reaction between coating and various component found on crude oil. The breakdown of the oxide films by chlorides will initiate pitting. The chemical reaction on the surface causes changes the surface area of specimen coating and causes the formation of bubbles in the film coating and due the effect of heat applied, which forms cavities. The second results from water found in crude oil penetrated through the epoxy lining and initiated localized corrosion attack at the coupon surface and the coating/metal interface and lead to the breakdown of the coating.

Microscopic examinations of Jotun and Hampel coated coupons show chemical and physical degradation on the surfaces and this accompanied by structural changes, which lead to the deterioration of the coating materials. Molecules at a higher temperature have more thermal energy and a collision frequency is greater at higher temperatures. This lead to bond dissociation between compounds atoms and then molecular weight of coating and results these dissociates into ions in the solution. The degradation changes the chemical structures and generation a various types of radicals, this lead to causes the embrittlements in coatings, reduction in molecular weight due to chain scission process and loss of mechanical properties.

The Fosroc epoxy coating specimen's show many grooves and cracks of different size occurring on the surface of the specimen as indicated in the figure 6-E. The reason for cracking behavior is attributed to many factors especially elasticity of compositions materials, internal stress, and thermal stress. These factors effects on the molecular weight of the coating and causes weakly cross link density. After exposure to the crude oil solutions and raise the temperature of solution, the coating begins to expand and due to low elasticity, the coating becomes brittle and cracks begins to initiation and propagation through the surface coating.

Also it can be seen that changes in the surface morphology of the coating and color of the corrosion surface of the coated coupons for all types of epoxy which were examined. This attributed to the chemical reactions occurs at the
coatings surface between various impurities in the crude with coatings.

CONCLUSIONS

It was found that epoxy coatings can provide considerable protection, as well as a physical barrier against corrosive crude oil and various elements in which the metal are exposed. The following remarks can be made about this work:

- Crude oil has a significant effect on the corrosion of steel, and these effects are significantly different for different crude oils.
- Type of coating affects the speed and quality of the corrosion rate.
- Europe and Jotun epoxy coatings are the best coat for the tank lining in all position tested. SPEC coating have large values of corrosion rate, while other types gave moderate values of corrosion rates.
- Lower Zubair crude oil gave lower values of corrosion rate and west Qurna crude oil gives the largest values.

ACKNOWLEDGEMENTS

The authors express thanks to staff of the chemical engineering laboratories, Basrah University and stuff engineer at Basrah petroleum refinery. Also the authors would also like to thank Dr. Rudolf Dolling from the Bank Elektronik - Intelligent Controls GmbH, Germany for his help and useful remarks.

REFERENCES


NOMENCLATURE

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Figure 3: Comparison of Analytical and Experimental Corrosion Rates vs. Temperatures at pH = 5 for:
A- Lower Zubair, B- Upper Zubair, C- Nahr Umr, D- South Rumaila, E- North Rumaila, F- West Qurna
Figure 4: Comparison the Corrosion Rate vs. Time Obtained from Immersion Test for Different Crude Oil at pH = 5 and T = 40°C for: A- Europe, B- Jotun, C- Hampel, D- DCP, E- Fosroc, F-SPEC Coating

Figure 5: Comparison the Corrosion Rate vs. Time Obtained from Immersion Test for Different Crude Oil at pH = 5 and T = 50°C for: A- Europe, B- Jotun, C- Hampel, D- DCP, E- Fosroc, F-SPEC Coating
Figure 6: Surface Morphologies after Immersion Test in Lower Zubair Crude Oil at pH = 5 and T = 50°C for: A- Jotun, B- Hampel, C- DCP, D- SPEC, E- Europe, F- Fosroc