Evaluation of the Corrosion Rate of Different Types of Marine Ship Steel using Potentiostatic Test Method in Arabian Gulf Sea Water

Abstract - The effect of flow velocity and chemical composition of Arab gulf sea water on the corrosion behavior of three different types of steel (DNV/EH40, AB/FH32 and ABS DQ47) used in building of marine ship hull structures investigated by using electrochemical Potentiostatic test method. The results indicate that the general corrosion rate under flow condition is larger than that obtained under static case. Increasing the velocity of sea water leads to increase the corrosion rates for certain limit and then began to decrease. NV/EH40 steel exhibited a significantly lower values of corrosion rate, ABS DQ47 steel has larger values and AB/FH32 marine steel plates has moderate values.

Keywords - corrosion Potentiostatic, Tafel extrapolation, sea water, flow velocity, salinity

1. Introduction

Most navy hull ship structures are built from different types of steel metals. This is due to have a good mechanical strength, easy fabricability, formability and weldability, abundance and low cost. These different types of steel when exposed to sea water they will appear different types of corrosion rates. The general and pitting corrosion are considered the most common and frequent occur in the hulls of ships as a result of exposure to sea water. Sea water is considered one of the most electrolys that cause corrosion of steel used in shipbuilding structures because of the sea water has heterogeneous compositions of salts and dissolved gases [1].

Potentiostatic corrosion test is considering one of the best methods used in corrosion testing at short time. It basically involves applying a fixed potential of ±250 mV to the specimen immersed in a solution for fixed period and then obtained potential – log current density curve. Analysis of curve using Tafel extrapolation method can yield corrosion current density [2].

Panayotova et al. [3] listed and studied the factors governing marine corrosion phenomena on the structural steel component and identification of the key parameters of corrosion of the ballast, oil tanks and cargo ships. Ajeel et al. [4] used both immersion and Potentiostatic corrosion test methods to study the gray and ductile cast irons in different NaCl salt concentrations. They found that the corrosion resistance of grey iron is less than that of ductile iron in different NaCl salt concentrations. Kim et al. [5] studied the effects of various chloride concentrations on the material used for ship ballast water tanks using Potentiostatic test methods. They found that the current density for Potentiostatic experiments subjected to seawater with an applied potential at various chloride concentrations have similar effects. Boirs [6] demonstrated by the measuring the concentration changes of ions of sea water near the surface of corrosive metals that the maximum corrosion rate is depending on dissolved oxygen, sea water temperature and speed of water motion. Paul [7] studied the corrosion problems of mild steel in sea water solution. The author show that the major parameters that influencing on the rate of corrosion are: salinity, sulphate, dissolved oxygen, pH and temperature. Sekunowo et al. [8] used Potentiostatic corrosion test method to study the corrosion of mild steel in sea water and acid solutions. It was concluded that corrosion mitigation of mild steel in seawater and hydrochloric acid entails either an entire deterrence of accumulation of corrosion product or an efficient neutralization of the nature of acidic.

Jakubowski [9] studied pitting corrosion types in marine environment. He described the mechanisms of a short and long-term pitting corrosion in marine environment containing pit nucleation and growth phases. Al-Moubarak et al. [10] studied the corrosion of C-steel in red sea water using chemical and electrochemical techniques. Their results indicated that the corrosion of C-steel occurs under mixed control of charge transfer and diffusion processes. AI Shikshak et al. [11] studied
and discussed the corrosion rate of low carbon steel in saline environment. They showed that the variety of conditions that represent the actual conditions such as the flow velocity and sea water solution composition has the major effects on corrosion of low carbon steel. Aromaa et al. [12] determined the corrosion rates of steel tested in the Baltic sea water. Their test results showed that the water temperature effect directly on values of corrosion rates and the corrosion rate values in summer is higher that found in winter.

The current research studies the corrosion behavior of three different types of steel used in building hull ship structure in the Arabian Gulf sea water. The effects of temperature, flow velocity and sea water composition on corrosion rate were studied in detail using Potentiostatic electrochemical corrosion test method in the case under static and flow conditions. Tafel method was used for analyzing data obtained from Potentiostatic test.

2. Experimental methods

I. Types of steel used for testing

Three different types of steel alloys were utilized in the experimental work. A NV/EH40 ship steel plate, AB/FH32 marine steel plates and ABS DQ47 steel shipbuilding steel plate manufactures by Henan Bebon iron and steel International Co. Ltd., China. Tables 1 and 2 lists the percentage of element chemical compositions and mechanical properties of the three types of steel. All grade steels are standard carbon steels have a density of 7800 kg/m³. The three types of steel materials during testing and analysis were referred as NV/EH40 ship steel plate is model A, AB/FH32marine steel plates is model B, while, the ABS DQ47 shipbuilding steel plate is model C.

II. Preparation of the specimens for Potentiostatic test

The test specimens for Potentiostatic corrosion test were cut in the form of a small circular species have 1 cm diameter and 5 mm thickness. The specimens have been polished with different types of emery papers (160, 180, and 200 grades), then washed by the distilled water and dried by hot air at atmospheric pressure and temperature. The test specimens of the three models are shown in Figure 1. A total of 75 specimens of the three types will be used for Potentiostatic testing.

| Table 1: Chemical composition steel grades NV/EH40, AB/FH32 and ABS DQ47 tested [13, 14, 15] |
|-------------------------------|---|---|---|---|---|---|---|---|
| Steel grade | C | Si | Mn | P | S | Al | N |
| NV/EH40 | 0.18 | 0.1-0.50 | 0.9-1.6 | 0.035 | 0.035 | 0.015-0.08 | 0.009 |
| AB/FH32 | 0.16 | 0.1-0.50 | 0.9-1.6 | 0.025 | 0.025 | 0.015 | 0.009 |
| ABS DQ47 | 0.21 | 1.7 | > 0.55 | 0.035 | 0.035 | 0.015 | 0.009 |

| Table 2: Mechanical properties of steel grades NV/EH40, AB/FH32 and ABS DQ47 tested [13, 14, 15] |
|-------------------------------|---|---|---|---|---|---|
| Steel grade | Thickness mm | Yield Strength MPa | Tensile strength MPa | Elongation % | Transverse impact test J | Longitudinal impact test J |
| NV/EH40 | 5 | 390 | 510-650 | 20 | 27 | 42 |
| AB/FH32 | 5 | 315 | 440-590 | 22 | 22 | 31 |
| ABS DQ47 | 5 | 570-720 | 460 | 17-19 | --- | --- |
III. Potentiostatic corrosion test method

A Potentiostatic technique is conducted for a period of 1hr. interval throughout the test.

![M-Lap Potentiostatic test collection](image)

![Electrochemical flow cell](image)

A computer was used for operating and controlling the M-Lap Potentiostatic test, recording of data (currents, voltage and time of test) and also data processing. The M-Lap science bank-electronics program version 5.1.exe software is used. A graphical output of the experiment is a plot of log current versus potential. An analysis of the curve using Tafel linearization method can yield the corrosion potential and corrosion current. The corrosion rate \( C_r \) is calculated as a penetration rate per unit time (mm/year) at a test temperature using the following equation [16]:

\[
C_r = 3.27 \times 10^{-3} \frac{I_{cor}}{\rho_m} E_w
\]  

(1)

The value of corrosion current is given by [7]:

\[
I_{cor} = \frac{I_{cor}}{A_s}
\]  

(2)

Where,

- \( A_s \): Surface area of specimen (cm\(^2\)).
- \( \rho_m \): Density of metal (g/cm\(^3\)).
I_{corr}: Corrosion current obtained from Tafel plot in mA. 
The equivalent weight (E_w) is given by the relation [17]:
\[ E_w = \frac{1}{\Sigma \frac{n_i F_i}{A_i}} \]  (3)
Where,
A_i: Atomic mass (g/mol) of the element i.
n_i: Valiancy of element i.
F_i: Mass fraction of the any i element in alloy.

IV. Arabian Gulf sea water test solution
The sea water is an extremely complex, heterogeneous solution. It contains a large amount and diversity of dissolved solid material, dissolved gas and various species of biological matter [18]. The sea water was collected directly from the Arabian Gulf at distance of 10 km from the south sea Iraq boundaries. The compositions of the sea water in mg/L are analysis by using the Spectrophotometer apparatus and the values of composition analysis are shown in Table 3. The pH of the sea water was determine using the pH-meter and has an average value of 8.1, while the total dissolved solids, i.e., the TDS value was determine experimentally and has a value of 41.5 ppm.

3. Results and Discussion
In order to measure the resistance of the three steel models to pitting corrosion, used the cyclic Potentiostatic anodic polarization method for testing. Figures 4-6 show the cyclic polarization curves for the three models of steels tested. It’s noted from the Figures 4-6, the cyclic polarization curves of these models, it’s shown that it’s positioned longitudinally and then transversely to the reference electrode. The shape of the curve indicates that the steel types tested is in the active range and will corrode at a comparatively different rate.

Table 3: Ion compositions of Arabian Gulf Sea water in mg/L.

| Ions     | (Cl\(^{-}\)) | (Na\(^{+}\)) | (SO\(_{4}\)^{2-}) | (Mg\(^{2+}\)) | (Ca\(^{2+}\)) | (K\(^{+}\)) | (HCO\(_{3}^{-}\)) | (Br\(^{-}\)) | (SiO\(_{3}\)^{2-}) |
|----------|-------------|-------------|----------------|-------------|-------------|-------------|----------------|-------------|-------------|
| Value mg/L | 23          | 15.85       | 3.20           | 1.765       | 500         | 460         | 142           | 80          | 1.5         |

The passive current density (i_{pass} (mA/cm\(^2\)), protection potential (E_{pro.} (mV)) and pitting potential (E_{pit} (mV)) for model A are 600, 3.6 and 235. These values for model B are 530, 4.8 and
240, while the values for model C are 438, 5.3 and 300 respectively. These values were obtained from the curves in Figures 4-6. Following observations can be made on the basis of these data, model A shows a lower passive current density and high pitting potential, compared to both the other models. This means that model A which has lower currents in the passive region and this indicate a higher degree of passivation. Model C need small voltage to pits began to initiates. By comparing the difference between the corrosion potential and the pitting potential of the three types of steel tested, the protection potential is less than pitting potential and this lead to suppose that pitting can initiates and prepare in surface of steel tested.

Figure 7 show the polarization curves for the three steel types obtained from the Potentiostatic test of the steel specimens in the seawater solutions at a temperature of 25°C for a period of 30 min. The shape and behaviors of the curves varied with various types of steel material tested. The anodic and cathodic parts of the polarization curves indicate some fluctuating points. The shape of the polarization curves is brought about by the nature of the electrochemical anodic and cathodic reactions which can take place at a particular potential and by the rate at which these reaction can occur proceed at the specimen’s surface. From the anodic and cathodic polarization curve, as the potential increases in negative side, the current density also generally increases.

The potential corrosion \( E_{\text{corr}} \) (mV) and log corrosion current \( \log I_{\text{corr}} \) (mA/cm\(^2\)) obtained from polarization curve using Tafel plots for model A under static conditions are 96.2 and 2.54. The corresponding values for model B are 184.3, and 2.66, while for model C are 293.64 and 2.70 respectively. The equivalent weight for model A, B and C are 0.20116, 0.19081 and 0.36012 respectively calculated using Eq. (3). Then using \( I_{\text{corr}} \) values and equivalent weights to obtain the corrosion rate in mm/y using Eq. (1). The values of corrosion rates are 0.029, 0.037 and 0.075 for models A, B and C respectively.

As indicated from these values, the model C has large values of corrosion rate 0.075 mm/y, the model A has smallest value 0.029 mm/y while, the model B has moderates value 0.037 mm/y. This difference in corrosion resistance due to the difference in the chemical composition and mechanical properties of each type of metal tested as given in the Tables 1 and 2. As given in Tables 1 and 2 the model A has the large mechanical properties compared to the other types.

Figure 8 show comparisons of the corrosion rate obtained from a Potentiostatic test of steel models at a test periods of 30 min. as functions of temperature.

Temperature change affects the rate of reaction occurs at poles the cathode and the anode and this in turn affects the corrosion rate of the steel metal. As it is clear from the shape increasing temperature, increase of the corrosion rate. High temperature leads to the refraction of bounded between atoms and thus increase the loss of electrons and increase the corrosion rate. Whereas at the low temperature, the sea water salt solubility decreases, this causes seawater to exhibit higher electrolyte resistivity and lower conductivity. Temperature effects on chemical composition of sea water, increase temperature will cause to dissolve salts which release different ions in the sea water solutions. One of the most significant ions in sea water resulting from degradation of salts is the chloride ion. This is attributed to its being present in larger quantities and to its ability to penetrate corrosion products iron films to continue its activity in the corrosion process. As given in Table 3, the total salts as 41.5 mg/L and Cl\(^-\) are 23 mg/L which has large values. Chloride
ion can react with iron oxide film to create ferrous chloride according to reaction:

$$2 \text{Fe (s)} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 \quad (4)$$

These ferrous chloride products can react with dissolved oxygen to produce $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_4$ or can reduction to $(\text{FeCl}_2)$ which consider oxidation agents and enhanced general and pitting corrosion on metal surface. In addition, the chloride ions increases the conductivity of sea water and this faster the electrochemical reactions at anode and cathode part of cell through test which faster corrosion.

Bicarbonate originally present in seawaters. As given in Table 3, Bicarbonate value is 142 mg/L. Bicarbonate ions (HCO$_3^-$) can analyses in sea water following the equation:

$$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^- \quad (5)$$

The result is increasing the hydrogen concentrations which increase acidity of sea water, i.e. pH of sea water which reflects increase the corrosion rates. On the other hand ions CO$_3^-$ react with Ca$^+$ to produce CaCO$_3$ which patricides as film and can reduce the values of corrosion.

The sea water have more gases but especially are nitrogen (because of its overwhelming percentage), with oxygen and carbon dioxide because of their importance in corrosion. An increase in temperature leads to increases seawater conductivity and decreases oxygen concentration. The solubility of CO$_2$ and O$_2$ decreases with an increase in temperature and this effects corrosion rates. As mentioned in Table 3, the value of pH of Arabian Gulf sea water is 8.1 and this in alkaline range and has small effects on corrosion rate at room temperature.

Figure 9 shows the polarization curves of the studied three types of steels at 25°C under flow conditions of sea water for a period 30 min. The velocity of sea water was taken as 1 m/s at 25°C. As it can be seen, flow sea water test as compared to static solution case, changes the corrosion potential of steels, but also changes the initiation potential of pitting. The main reason of these variations is due to the extra reactions of ions which exist in sea water with specimen surface.

The Tafel constants $E_{cor.}$ (mV) and Log $I_{cor.}$ (mA/cm$^2$) of model A are 175.6 and 2.69 respectively. The corresponding values of model B are 215.4 and 2.86 respectively, while of model C are 311.7 and 2.91 respectively. The corrosion rate in mm/y for three models at 25°C for flow conditions are 0.041, 0.058 and 0.102 respectively.

It’s clear that by comparison results of corrosion rate for all types of steel tested the corrosion rate under flow is larger than under static case. Since the flow of sea water remove the formation of a passive layer oxide in surface of specimen tested.

Figure 10 shows variation of corrosion rate as a function of temperature at 1 m/s flow velocity. As clear, there are instable increase in corrosion rate with increasing temperature and the nonlinear relation between corrosion rate and temperature. Raising temperature, also affects corrosion kinetics, oxygen concentration, diffusion, the degree of movement of the water, and very considerably by the amount of biological activity which is taking place. As shown in Figure 10, the rate of corrosion increases with temperature increases at a constant sea water flow velocity.

Figures 11-13 show the effect of increasing velocity on behavior of polarization curve for
models A, B and C. As indicated increasing velocity, more shaft of open circuit potential to negative side and increasing the corrosion current results in increase of corrosion rates. Also it can be seen that as flow velocity increase the difference in open circuit potential and corrosion current become less compared to low speed case.

The sea water flow velocity affects the corrosion rate of steel in several ways. Increase the sea water velocity lead to increased oxygen that reaches to the sample surface and increases specimen metal surface interacts with corrosive agent’s ions of sea water and causing festering the corrosion problems. Also high velocity cause mechanical effects which in most cases are forms bubbles, when these bubbles are bombing may cause pitting at the specimen surface.

The increase in corrosion rate with increased velocity is attributed to the force of the water eroding the existing protective oxide films thereby exposing new of specimen surface to the corrosive environment. As shown in Figures 11-13 at flow velocities from 1 to 4 m/s both potential and corrosion current increase but after that at 5 m/s the potential and corrosion current will begin to decrease. Increasing sea water velocity lead to decrease reactions at the anode and cathodic parts because high velocity generate turbulent in fluid and reduces diffusion layer thickness formed on steel surface. This subsequently leads to decrease and limits in the corrosion current density at the oxidation part and also reduces the corrosion penitential between poles. This is because of increasing velocity leads to reduce the thickness of the diffusion boundary layer for dissolved oxygen and other contents of sea water on the metal surface and decreasing the migration of deleterious ions of sea water to metal surface.

4. Conclusions
Investigation of corrosion behavior of three different steels in Arabian gulf sea water with different values of temperature and flow velocity shows that:
1-An increase in the free corrosion potential ($E_{cor}$) and current density ($I_{cor}$) of the three different steel materials were observed with flow condition of seawater.
2-Steel corrodes at greater rates with case of flow compared to static case.
3-Increasing velocity of flow of sea water after 5 m/s will reduce corrosion rate
4-ABS DQ47 steel shipbuilding steel plate has larger values of corrosion rate, NV/EH40 ship steel plate has lower values and AB/FH32 marine steel plates has moderate values.
5-The sea water compositions significantly influenced by temperature; higher temperatures can increase degradation of sea water and enhanced the corrosion rates.

Acknowledgements
The authors express all thanks to staff chemical engineering department of Basrah University for his helps and supported during achieve test. Also the author expresses all thanks to Dr. Mohamed Toosi from college of engineering, Shahid Beheshti University, Iran for useful notes.

References
[1] S. A. Al-Fozan and A. U. Malik, “effect of sweater level on corrosion behavior of different alloys”, Desalination, Issues 1, Vol. 228, pp.61-67, 2008.
[2] ASTM G5–87, Standard reference test method for making Potentiostatic and Potentiodynamic anodic polarization measurements, Report of The American Society for Testing and Materials, 1987.
[3] M. Panayotova, Garbatov, Y. and S. C. Guedes, “Factor influencing corrosion of steel structural elements immersed in seawater”, Proceedings of the International Conference on Marine Science and Technology, National kaohsiung Marine University, Taiwan, pp.280–286, 2004.
[4] S. A. Ajeel and M. H. Safaa, “Ductile and gray cast irons deterioration with time in various NaCl salt concentrations”, Eng. & Tech., Vol.26, No.1, 2008.
[5] S. Jong Kim and S. Ki Jang, “Corrosion characteristics of steel in seawater containing various chloride concentrations generated by electrochemical method”, Trans. Nonfereeous Met. Soc. China, Vol.19, pp.50-55, 2009.
[6] Boirs B. Chernov, “Corrosion and metal protection in sea water”, Asia Pacific Journal of marine science and education, Vol.1, No.1, pp.81-87, 2011.
[7] S. Paul, “Modeling to study the effect of environmental parameters on corrosion of mild steel in sea water using neural network”, International Scholarly Research Network (ISRN Metallurgy), Vol. 2012, pp.1-6, 2012.
[8] O. I. Sekunowo, S. O. Adeosun, G. I. Lawal, “Potentiostatic Polarisation responses of mild steel in seawater and acid environments”, International Journal of Sciences and Technology research, Vol.2, No.10, pp.139-145, 2013.
[9] M. Jakubowski, “Influence of pitting corrosion on fatigue and corrosion fatigue of ship structures, Part I, Pitting corrosion of ship structures”, Polish Maritime Research, Vol.21, pp.62-69, 2014.
[10] A. H. Al-Moubaraki, A. Al-Judaibi and M. Asiri, “Corrosion of C-steel in the red sea: effect of immersion time and inhibitor concentration”, Int. J. Elect. Sci., Vol.10, pp.4252–4278, 2015.
[11] A. A. Al Shikshak, Mansour A. A. and Taher A., “Effect of flow velocity of sea water on corrosion rate of low carbon steel”, Applied Mechanics & Materials, Vol.799, pp.232-236, 2015.
[12] J. Aromaa and O. Forsen, “Factors affecting corrosion in Gulf of Finland Brackish water”, International Journal of Electrochemistry, Vol.2, pp.1-9, 2016.
[13] DNV EH40 steel plate specification data sheet, Report of Henan Bebon gang iron and steel International Co. Ltd., China, 2014.
[14] ABS Grade FH32 Shipbuilding steel plat data sheet, Report of Henan HZZ Iron and Steel Co. Ltd., China, 2015.
[15] ABS grade B steel plate specification data sheet, Report of Henan HZZ Iron and Steel Co. Ltd., China, 2015.
[16] M. Scendo, J. Trela, Antoszewski B and Kargul T., “Corrosion resistance of the joint of stainless steels in aggressive Solution”, Innovations in Corrosion and Materials, pp.118-126, 2014.
[17] ASTM G102-89, Standard practice for calculation of corrosion rates and related information from electrochemical measurements, Report of American Society for Testing and Materials, USA, 1999.
[18] R. E. Melchers and R. Jeffrey, “Early corrosion of mild steel in seawater”, Corrosion Science, Vol.47, No.7, pp.1678-1693, 2005.

Author's biography
Haider Hadi Jasim, Ph.D. in corrosion engineering, mechanical engineering department, Basrah University, Basrah, Iraq. His research interests includes epoxy coating, the corrosion problems, fracture mechanics and polymer material. Assist. Prof. Haider Hadi Jasim currently teacher in chemical engineering department, Basrah university, Basrah, Iraq.

Raed Abedul Hussain, MSc in laser science, the physical science department, Basrah University, Basrah, Iraq. His research interests includes, corrosion, laser equipment design and polymer material. Assist. Mr. Raid currently teacher in chemical engineering department, Basrah university, Basrah, Iraq.