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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 was. 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*

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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 corrosions are consider of 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 electrolytes 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-Moubaraki *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. Al 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/m^3. 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]

	Chemical Composition (%)						
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]

	Mechanical properties					
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	---	---

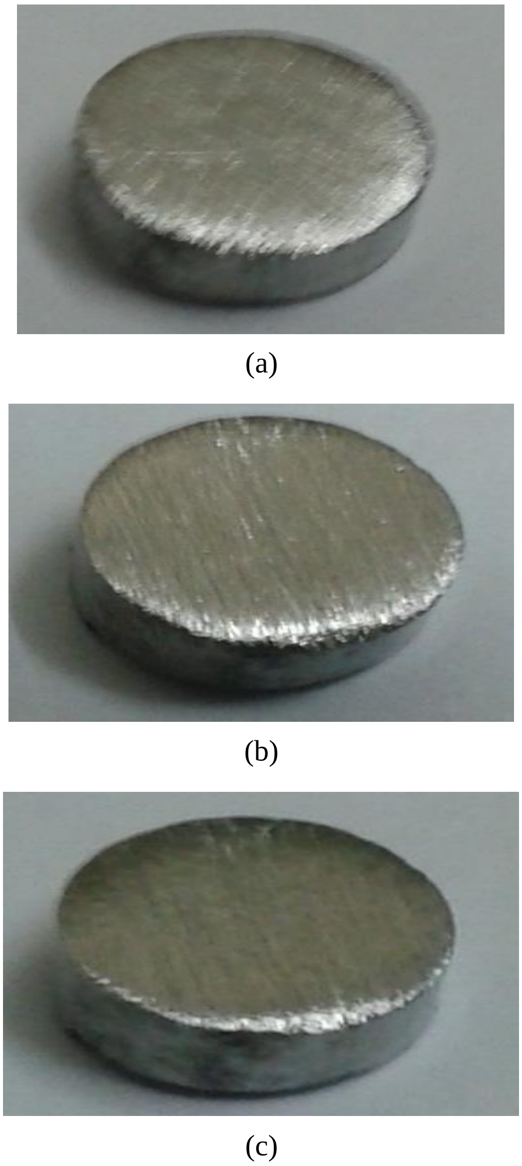

Figure 1: Specimens of the (a) model A steel (b) model B steel (c) model C steel used for Potentiostatic corrosion test.

III. Potentiostatic corrosion test method

Figures 2 and 3 show the M-Lap Potentiostatic apparatus and electrochemical flow cell. A glass cell has three-electrode was used. The working electrode represented the specimen for test. The counter electrode is Platonized Titanium (Pi-Ti) and silver/silver chloride (Ag/AgCl) reference electrode.

The glass cell is filled with 0.5L of sea water. The temperature of a test solution in the glass cell is controlled by a water bath heater containing water solution and maintained constant (within ±0.1°C). During a waiting time of (30 minutes) the specimen was under open circuit conditions and the potential was recorded at the end of the exposure period. Then the potential is applied at the working electrode at a scan rate of 5 mV/s starting from ±250 mV with respect to the open circuit potential according to ASTM methods [2]. A Potentiostatic technique is conducted for a period of 1hr. interval throughout the test.

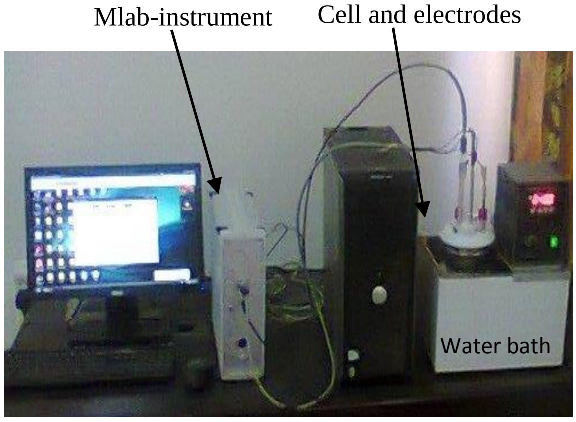

Figure 2: M-Lap Potentiostatic test collection

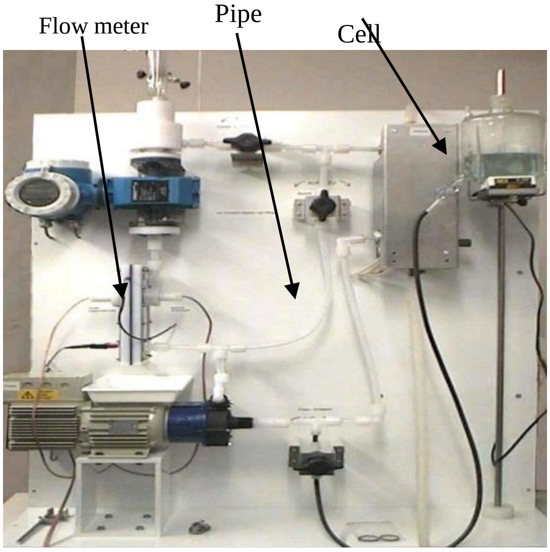

Figure 3: Electrochemical flow cell

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]:

$$C_r = 3.27 * 10^{-3} * \frac{i_{cor.}}{\rho_m} E_w \qquad (1)$$

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

$$i_{cor.} = \frac{I_{cor.}}{A_s} \qquad (2)$$

Where,

A_s: Surface area of specimen (cm^2).

ρ_m : Density of metal (g/cm^3).

$I_{cor.}$: Corrosion current obtained from Tafel plot in mA.

The equivalent weight (E_w) is given by the relation [17]:

$$E_w = \frac{1}{\sum \frac{n_i * F_i}{A_i}} \tag{3}$$

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 the 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.

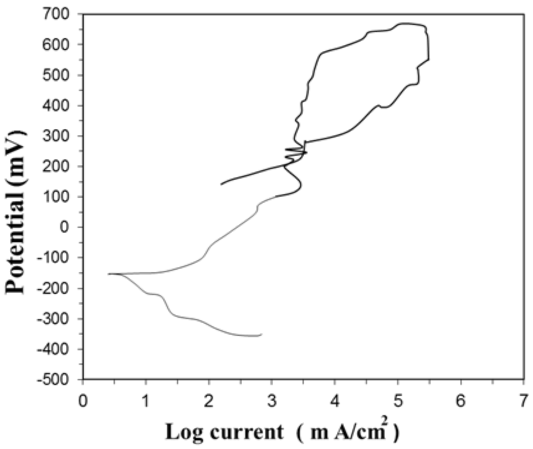

Figure 4: Cyclic polarizations curve for model A at 25℃

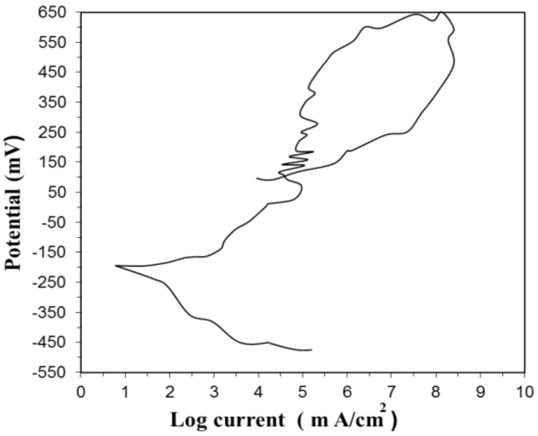

Figure 5: Cyclic polarization curve for model B at 25℃

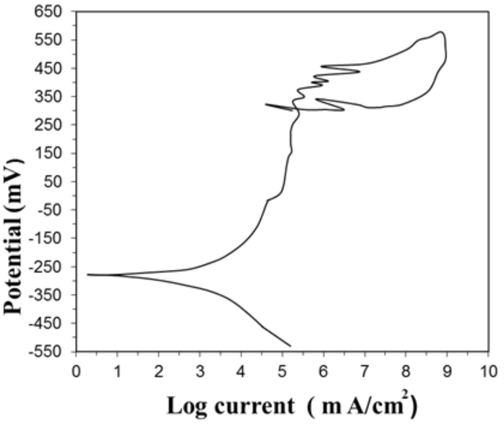

Figure 6: Cyclic polarizations curve for model C at 25℃

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/cm²)), 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℃ 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.

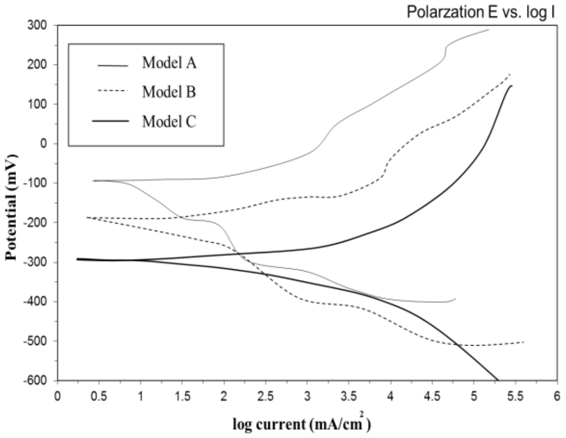

Figure 7: Polarizations curves of different steels at 25℃ tested in sea water under static condition

The potential corrosion $E_{cor.}$ (mV) and log corrosion current (Log $I_{cor.}$ (mA/cm²)) 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 $I_{cor.}$ 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.

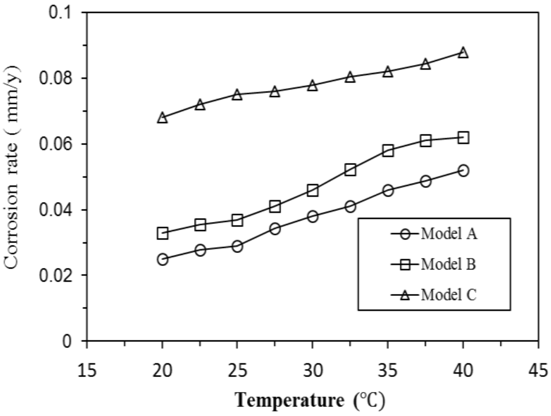

Figure 8: Comparison of corrosion rates of model steels at various temperature and static condition

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:

$$2\,Fe\,(s) + 3Cl_2 \longrightarrow 2FeCl_3 \qquad (4)$$

These ferrous chloride products can reaction with dissolved oxygen to produces Fe_2O_3 and Fe_2O_4 or can reduction to ($FeCl_2$) 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 corrosions.

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:

$$HCO_3^- \longrightarrow H^+ + CO_3^- \qquad (5)$$

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℃ 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.

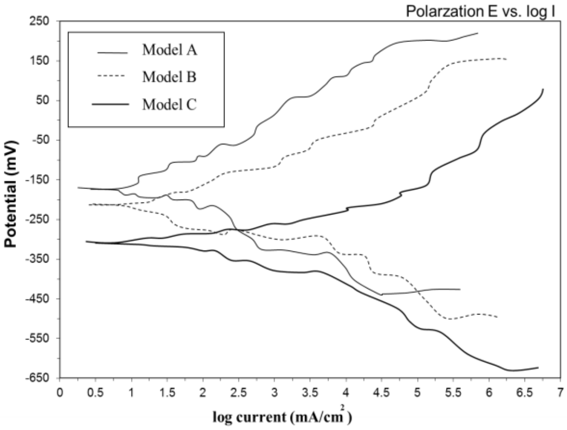

Figure 9: Polarizations curves of the three types of steel test in sea water under flow condition at 25℃

The Tafel constants Ecor. (mV) and Log Icor. (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℃ for flow conditions are 0.041, 0.058 and 0.102 respectively.

The shape of the polarization curves for the anode and cathode electrode of the state of flow contain a lot of fluctuations and instability compared with the static situation. This is because of the sea water flow that directly effect on the speed and nature of interactions occurring at the electrodes. Also the form of curves varies depending on the types of tested metals. Each types of steel models tested have percent of element compositions differ from the others. This effected in conductivity, ion release and resistance to corrosion. The surface contacting the sea water solution corrodes more severely because the oxygen originally present is consumed and cannot be supplemented quickly enough.

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.

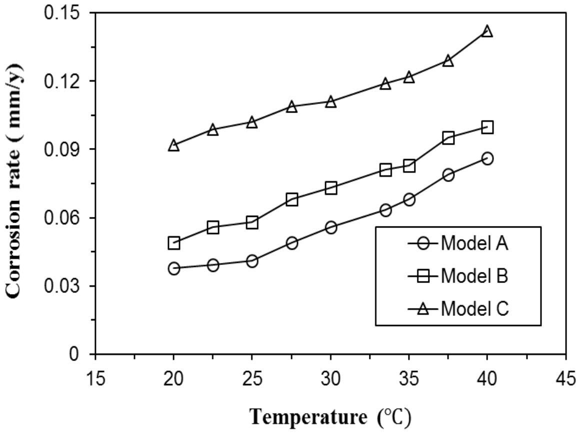

Figure 10: Comparison of corrosion rate of steel models at various temperature and flow condition

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 reducee 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.

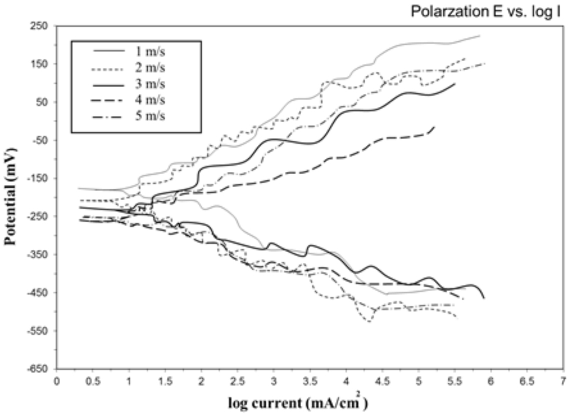

Figure 11: Polarization curves for model A of steel at 25℃ tested in sea water under flow condition

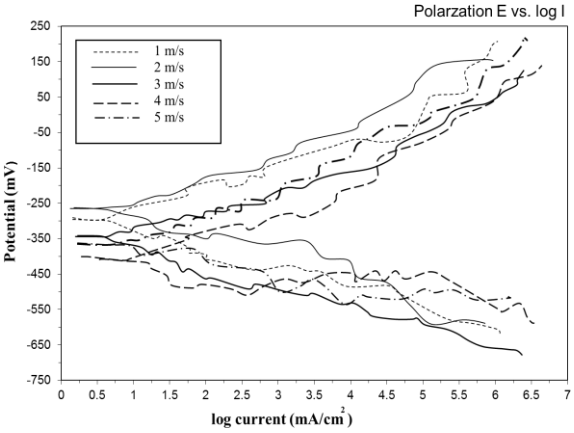

Figure 12: Polarization curves for model B of steel at 25℃ tested in sea water under flow condition

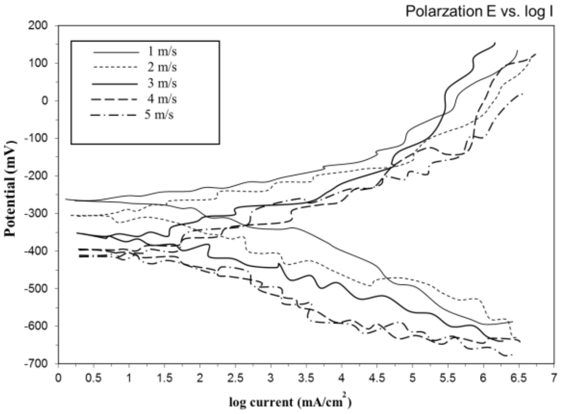

Figure 13: Polarization curves for model C of steel at 25℃ tested in sea water under flow condition

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.

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