

Mass Transfer Coefficient During Cathodic Protection of Low Carbon Steel in Seawater

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Abstract

The aim of this research is to calculate mass transfer coefficient, $k_d$, during cathodic protection of low carbon steel in neutral seawater (3.5% W/V NaCl in distilled water with pH = 7). Two types of cathodic protection were used: First: Sacrificial anode cathodic protection (SACP) were a pipeline of steel carrying seawater using zinc as a sacrificial anode and with variable temperatures ranged (0 – 45°C) and volumetric flow rate ranged (5 – 900 lit/hr). It was found that the $k_d$ increases with increasing temperature and volumetric flow rate of seawater, where $k_d$ ranged (0.24×10^-6 – 41.6×10^-6 m/s).

Second: Impressed current cathodic protection (ICCP) technique adopting a rotating vertical steel cylinder in seawater with variable temperatures ranged (0 – 45°C) and rotating velocity ranged (0 – 400 rpm). It was found that the $k_d$ increases with increasing temperature and rotating velocity, where $k_d$ ranged (7.25×10^-6 – 36.82×10^-6 m/s).

Keywords: Cathodic Protection, Momentum Transfer, Reynolds Number, Carbon Steel

1. Introduction

Corrosion is an electrochemical process in which a current leaves a structure at the anode site, passes through an electrolyte and reenters the structure at the cathode site. Current flows because of a potential difference between the anode and cathode that is the anode potential is more negative than the cathode potential, and the difference is the driving force for the corrosion current. The total system-anode, cathode, electrolyte and metallic connection between anode and cathode is termed a corrosion cell [Shrier(1), 1976 and George, 1985].

Cathodic protection involves the application of a direct current (DC) from an anode through the electrolyte to the surface to be protected. This is often through of as "overcoming" the corrosion currents that exist on the structure. There is no flow of electrical currents (electrons) through the electrolyte but flow of ionic current. Cathodic protection eliminates the potential differences between the anodes and cathodes on the corroding surface. There are two proved methods of applying cathodic protection: sacrificial anode (galvanic) and impressed current. Each method depends upon a number of economic and technical considerations and as certain advantages. For every structure, there is a special cathodic protection system dependent on the environment of the structure [Scully, 1975].

When an electrode is polarized, the surface concentration of species that is either being oxidized or reduced fall to zero. Additional material will then diffuse to the electrode surface towards this region of lower concentration. If the electrolysis experiment is carried out in an agitated solution, i.e. the solution is in motion with respect to the electrode or vise versa, then the resulting concentration-distance profile at the electrode surface can be represented as shown in figure (1) [Trethewey and Chamberlain, 1996 and Roberge, 2004].

In the figure (1) the electrode is represented by bold bar in the left side of figure. The x-axis is a scalar and represents distance away from the electrode. They-axis represents concentration. The maximum concentration is represented by $C_b$,
which is its concentration in the bulk solution. In figure (1) there are two regions of concentration. Because the solution is well mixed, in the bulk region the concentration is constant with respect to distance. This is represented by horizontal line where \( C = C_b \) (this is known as the convective region). There is then a region where the concentration drops, falling to zero at the electrode surface. The diffusion layer associated with this drop has thickness \( \delta_d \), the exact thickness of the diffusion layer depends upon the nature of the solution into which it extends. For stirred aqueous solution the thickness of the diffusion layer can between 0.001 to 0.01 mm Roberge, 2004].

For an unstirred solution it is about 0.5 mm thick [Uhlig, 1971]. In an important assumption of this mode is that when material reaches the surface of the electrode it is instantaneously oxidized or reduced thereby maintaining a zero concentration at the electrode surface. In practice, this is easy to achieve by selecting a suitable polarization voltage.

It is clear that the concentration gradient in the diffusion layer, we not that it both linear and constant. It is can be represented gradient mathematically as:

\[
\frac{dC}{dx} = \frac{C_b - C_s}{\delta_d}
\]  

\[\text{Equation 1}\]

Fick’s law of diffusion state that [Shreir (1), 1976, and Trethewey, 1996]:

\[
J = -D \frac{dC}{dx}
\]  

\[\text{Equation 2}\]

Where \( J \) is the flux of substance and \( D \) is a diffusion coefficient. It can be seen from Faraday’s law of electrolyte that:

\[
i = zFJ
\]  

\[\text{Equation 3}\]

Where \( i \) is the current density, \( \mu A/cm^2 \), \( z \) is the valancy number of electrons involved in reaction, eq/mol, and \( F \) is Farady’s constant (96496), c/mol. From equations 1, 2, and 3:

\[
i = -zFD \frac{(C_b - C_s)}{\delta_d}
\]  

\[\text{Equation 4}\]

The negative sign is conventional, it us the current is being carried away from the cathode (as hydroxyl ion). The magnitude of current is interesting only and since, \( C_s \) can never be negative, and the magnitude of the current is great when \( C_s = 0 \), again the maximum or limiting current density:

\[
i = -zFD \frac{C_b}{\delta_d}
\]  

\[\text{Equation 5}\]

Notice that when \( C_s > C_b \) , the implication is that the concentration of species in the region of electrode is increasing. The resulting sign from negative to positive tell us the current is reversed [Trethewey and Chamberlain, 1996, Hanson, 2000 and Cottis, 2002].

The present work considered two types of cathodic protection. In the sacrificial anode cathodic protection, the effect of temperature (0 – 45°C) and flow rate (5 – 900 lit/h) on the mass transfer coefficient, \( k_d \), are studied with constant \( \text{pH} = 7, \) duration time = 3 hrs and NaCl in distilled water = 3.5% W/V. In the impressed current cathodic protection, the effect studied were temperature (0 – 45°C), rotating velocity (0 – 400 rpm) on the \( k_d \) with constant \( \text{pH} = 7 \) and NaCl in distilled water = 3.5% W/V.

2. Experimental Work
I. Sacrificial Anode Cathodic Protection System:

Working electrode (cathode): working electrode was tube specimen of low carbon steel with dimensions of 13.50 cm length, 2.68 cm inside diameter and 0.23 cm thick. Anode
electrode: Anode electrode was zinc strip with dimensions of 12.50 cm length, 1.00 cm width and 0.6 cm thick.

The chemical composition of tube specimen of low carbon steel and zinc strip were analyzed by Specialized Institute of Engineering Industries were as shown in table (1) and (2) respectively.

The apparatus shown in figure (2) [Champion, 1964] was used to study the variables, temperature (0 – 45°C) and flow rate (5 – 900 lit/h] on corrosion rate or zinc consumption rate to compare with the mass transfer coefficient \( k_d \). After the container vessel was filled with seawater (3.5 % W/V NaCl solution) adjusting pH to 7 and temperature to the desired values. The zinc strip was weighted and fixed at the inlet of the steel tube by rubber stopper and was electrically connected by an insulated copper wire to the steel tube outlet as shown figure (2). The zinc strip is extended along the steel tube to ensure uniform current and potential distribution along the tube wall.

The seawater was pumped from the vessel by the pump through the rotameter to measure the desired flow rate, then the seawater inter from from the below the steel tube and out from upper the tube to return to the vessel again (i.e. the seawater is circulated between the vessel and steel tube). After each run the zinc strip was rinsed in distilled water and brush to remove the corrosion products, dried with clean tissue then immersed in the benzene and acetone, dried again and re-weighted to determine the weight loss and prepare for another experiment. The steel tube is also rinsed and dried by the same way above in order to re-use another time. After each run the vessel is emptied from the solution and washed with distilled water, then filled wit a new prepared solution for a new run.

**Table 1. Chemical Composition of Low Carbon Steel**

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.1648</td>
</tr>
<tr>
<td>Si</td>
<td>0.2540</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5101</td>
</tr>
<tr>
<td>S</td>
<td>0.0062</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0253</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0090</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1511</td>
</tr>
<tr>
<td>V</td>
<td>0.0034</td>
</tr>
<tr>
<td>Fe</td>
<td>Rem.</td>
</tr>
</tbody>
</table>

**Table 2. Chemical Composition of Zinc Strip**

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.12</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0034</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0017</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0033</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0032</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0023</td>
</tr>
<tr>
<td>Zn</td>
<td>Rem.</td>
</tr>
</tbody>
</table>

![Fig.2. Schematic Diagram of Apparatus Used in Sacrificial Anode Test System.](image-url)
II. Impressed Current System:

Working electrode (cathode): working electrode was cylinder specimen of low carbon steel with dimensions of 1.58 cm length, 2.33 cm outside diameter and 0.18 cm thick. The composition of steel is the same of that of low carbon steel which was illustrated in table (1).

Auxiliary electrode (anode): auxiliary electrode was a rod of high conductivity graphite, 4.5 cm length and 0.8 cm outside diameter.

Reference electrode: the cathode potential is determined with respect to saturated calomel electrode (SCE).

A luggin capillary bridge leading to the reference electrode is mounted near the center of cathode to within one millimeter from the side of the cathode. The opening of the capillary tube near the cathode is equal to one millimeter in diameter

The apparatus shown in figure (3) was used in the polarization technique. [Cornet and Kappser, 1969 and Harvey and Robert, 1988]. After preparing the seawater (3.5% W/V NaCl solution), and construct the electrochemical cell with desired variable of temperature and velocity, the circuit is switched on and the voltage of power supply is stabilized on 3.0 V. Changing the current by altering the resistance of the circuit, where at each setting of the resistance, two parameters are recorded (potential and cathodic current) by voltmeter and ammeter respectively, i.e. to measure the cathodic portion of the polarization curve. Two minutes at least were are allowed in order to record the steady state values of the polarization process. After reaching E\textsubscript{corr} (steady state corrosion potential) of the steel specimen used, the run was ended by switched off the circuit and electrochemical cell is emptied from used seawater. The system is then washed with distilled water to ensure that there is no electrolyte left in the system. the above procedure is repeated exactly for other conditions of temperature and velocity. Each test was made twice and if reproducibility was in doubt a third was carried out.

Fig.3. Schematic Diagram of Apparatus Used in Impressed Current Test System.
3. Results and Discussion

I. Sacrificial Anode Cathodic Protection System:

**Zinc consumption rate:** Before calculation of mass transfer coefficient, $k_d$, it must measure the zinc consumption rate in order to show variables effect on corrosion, where $k_d$ is an indication to reaction rate (corrosion rate). It can be seen from the figure (4) that the zinc consumption rate increases with increasing temperature and flow rate of seawater. It can explain that as follows:

(i) **Temperature effect**

(1) A temperature increases usually increases the reaction rate which is the corrosion rate and according to the Freundlich equation [Shrier (2), 2000]:

$$\text{Corrosion rate} = k C_{O_2}^n \quad \ldots (6)$$

Where $k$ is the rate constant of reaction, $C_{O_2}$ is concentration of oxygen and $n$ is order of reaction. The rate constant, $k$, varying with temperature according to Arrhenius equation [Shrier (2), 2000]:

$$k = k_o e^{-E/RT} \quad \ldots (7)$$

Where $k_o$ is constant, $E$ is activation energy, $R$ is universal constant and $T$ is temperature. Then from equation (7) indicates that the $k$ is increased with increasing temperature and then the corrosion rate which is lead to increasing the of zinc dissolution.

(2) Increasing seawater temperature leads to decreasing seawater viscosity with a consequent increase in oxygen diffusivity according to Stockes-Einstein equation [Cussler, 1984 and Konsowa and El-Shazly, 2002]:

$$\frac{\mu D}{T} = \text{constant} \quad \ldots (8)$$

Where $\mu$ is seawater viscosity and $D$ is the diffusivity of the dissolved oxygen. As a result of increasing the diffusivity of dissolved oxygen, the rate of mass transfer of dissolved oxygen to the cathodic surface increases according to the following equation [Konsowa and El-Shazly, 2002]:

$$J = k_d C_{O_2} = \frac{D}{\delta_d} C_{O_2} \quad \ldots (9)$$

With a consequence increase in the rate of zinc dissolution. Where $J$ is mole flux of oxygen.

(3) The decrease in the seawater viscosity with increasing temperature improve the seawater conductivity with a consequent increase in corrosion current and the rate of corrosion.

(4) On the other hand, increase of temperature reduce the solubility of dissolved oxygen with a subsequent decrease in the rate of oxygen diffusion to the cathode surface and the rate of corrosion.

It seems that within the present range of temperature effects 1, 2, and 3 are predominating.

(ii) **Flow rate effect:** Increase zinc consumption rate with increasing flow rate is attributed to the decrease in the thickness of hydrodynamic boundary layer and diffusion layer across which dissolved oxygen diffuses to the tube wall of steel with consequent increase in the rate of oxygen diffusion which is given by equation (9). Then the surface film resistance almost vanishes, oxygen depolarization, the products of corrosion and protective film are continuously swept away and continuous corrosion occurs. The flow rate of seawater may also used erosion which combined with electrochemical attack.

![Fig.4. Temperature Effect on Zinc Consumption Rate with Variable Flow Rate.](image-url)
Mass transfer coefficient: The mass transfer coefficient can be expressed in terms of the dimensionless Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers. These numbers are defined by [Coulson and Richardson, Vol. 1 & 2, 2002]:

\[
Re = \frac{\rho ud_e}{\mu} \quad \text{...(10)}
\]

\[
Sc = \frac{\mu}{\rho D} \quad \text{...(11)}
\]

\[
Sh = \frac{k_d d_e}{D} \quad \text{...(12)}
\]

Where \( \rho \) is density, \( u \) is velocity \( d_e \) is equivalent inner tube (based on cross section area of zinc exist in the inner tube), \( \mu \) is dynamic viscosity \( D \) is diffusivity and \( k_d \) is mass transfer coefficient. For single phase flow in a straight pipe, the correlation of Berger and Hau (1997) and Anederko et al. (2001) can be used:

\[
Sh = 0.0165 Re^{0.86} Sc^{0.33} \quad \text{...(13)}
\]

The physical properties of seawater at \( pH = 7 \) are explained in table (3).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (kg/m³)</td>
<td>0 1005.5 1003.9 999.7 995.8</td>
</tr>
<tr>
<td>( \mu ) (Pa.s)</td>
<td>2×10⁻³ 1.3×10⁻³ 0.91×10⁻³ 0.72×10⁻³</td>
</tr>
<tr>
<td>( D ) (cm²/s)</td>
<td>1.67×10⁻⁵ 1.8×10⁻⁵ 1.95×10⁻⁵ 2.1×10⁻⁵</td>
</tr>
</tbody>
</table>

Where \( \rho \) is practically measured \( \mu \) is from Coast (1999) and \( D \) is from Harvey and Robert, (1988).

To estimate \( k_d \) e.g. at 15°C, 300 lit/hr flow rate and \( d_e = 2.533 \) cm the velocity \( u \) is 16.5 cm/s. Equation (10) gives that Re is 3227, from equation (11) Sc is 719, from equation (13) Sh is 151 and then from equation (12) \( k_d \) is 10.73×10⁻⁶ m/s. Figure (5) shows that the effect of flow rate (i.e. velocity or Re) on \( k_d \) with different temperature, where \( k_d \) increases with increasing flow rate and temperature according to figure (4).

II. Impressed Current System:

Polarization: The characteristic of cathodic polarization curves with variation of temperature and angular velocity have been illustrated in figures (7) to (26). These polarization curves provide information about effects of changes in potential on the corrosion of the cathode as current density (current per unit area). Since the electrolyte is seawater (saltwater), the concentration polarization type is predominant [Ailor, 1971 and Fontana and Green, 1984].

From polarization curves, it can be determined practically the free corrosion potential, \( E_{corr} \) and limiting current density, \( i_L \). Where \( E_{corr} \) is determined when the potential becomes approximately constant with decreasing current. The limiting current plateau is not well defined, thus the method given by Gabe and Makanjoula (1986) will be adopted to find \( i_L \) values:

\[
i_L = \frac{i_1 + i_2}{2} \quad \text{...(14)}
\]

Where \( i_1 \) and \( i_2 \) are the current associated with \( E_1 \) and \( E_2 \) respectively as shown in figure (6). From figure (7) to (26) one can see that \( E_{corr} \) is more negative with increasing temperature and with decreasing velocity. While \( i_L \) increases with increasing temperature and velocity. \( i_L = i_{corr} \) is indication for corrosion rate, where the high value
of \( i_L \) means the high corrosion and vice versa. So the interpretation of increasing \( i_L \) with increasing temperature and velocity are as mentioned in sacrificial anode system.

For more explicit and simplicity \( i_L \) were calculated from figures (7 – 26) using equation (14) and figure (6) and plotting the results in figure (27) with variables.
Fig. 11. Cathodic polarization curve at 0°C and 100 rpm.

Fig. 12. Cathodic Polarization Curve at 15°C and 100 rpm.

Fig. 13. Cathodic Polarization Curve at 30°C and 100 rpm.

Fig. 14. Cathodic Polarization Curve at 45°C and 100 rpm.

Fig. 15. Cathodic Polarization Curve at 0°C and 200 rpm.

Fig. 16. Cathodic Polarization Curve at 15°C and 200 rpm.
Fig. 17. Cathodic Polarization Curve at 30°C and 200 rpm.

Fig. 18. Cathodic Polarization Curve at 45°C and 200 rpm.

Fig. 19. Cathodic Polarization Curve at 0°C and 300 rpm.

Fig. 20. Cathodic polarization curve at 15°C and 300 rpm.

Fig. 21. Cathodic Polarization Curve at 30°C and 300 rpm.

Fig. 22. Cathodic Polarization Curve at 45°C and 300 rpm.
Fig. 23. Cathodic polarization curve at 0°C and 400 rpm.

Fig. 24. Cathodic polarization curve at 15°C and 400 rpm.

Fig. 25. Cathodic polarization curve at 30°C and 400 rpm.

Fig. 26. Cathodic polarization curve at 45°C and 400 rpm.

Fig. 27. Variation of practical limiting current density with flow rate at different temperature.
**Mass transfer coefficient:** when cathodic current is limited by oxygen reduction reaction (as in equation 15) and when oxygen diffusion through a fluid boundary layer limits the supply of oxygen at the specimen surface for a rotating cylinder, equation (16) is applied to calculate mass transfer coefficient, $k_d$ [Shrier (1), 2000 and Silverman, 2004].

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad \cdots (15)$$

$$k_d = \frac{i_L}{zFC_b} \quad \cdots (16)$$

It can be seen from equation (16) that that the parameters which can be influence on $k_d$ are $i_L$ and $C_b$. $i_L$ was estimated from figures (7 – 26) by using the method in figure (6) and equation (14). Figure (28) shows that the variation of $k_d$ with flow rate or Reynolds number at different temperature.

Limiting current density, $i_L$, can be estimated theoretically from the following equation [Eisenberg et al., 1954 and Harvey and Robert, 1988]:

$$i_L = 0.0791zFC_bURe^{-0.3}Sc^{-0.644} \quad \cdots (17)$$

So from equations (16) and (17) the $k_d$ is estimated as:

$$k_d = 0.0791URe^{-0.3}Sc^{-0.664} \quad \cdots (18)$$

Where $U$ is the tangential velocity of specimen surface ($\pi \times d \times rpm/60$), $d$ is the diameter of specimen cylinder (2.33 cm), $z$ is the number of electrons in reduction reaction of oxygen (equation (15)) which is equal to 4 eq/mol, $C_b$ is the concentration of oxygen in bulk [Shrier, 1, 2000] and $F$ is Faraday’s number (96494 c/eq). Reynolds and Schmidt numbers are estimated as in equations (10) and (11), respectively. Figure (29) shows mass transfer coefficient, $k_d$, which was estimated theoretically versus Reynolds number at different temperature. It can be noted that $k_d$ increases with $Re$ (or rotation velocity, $\omega$) and with increasing $T$, that s mean increasing corrosion rate with increasing $\omega$ and $T$. 
4. Conclusions

1. In the sacrificial anode cathodic protection (SACP) method the mass transfer coefficient $k_d$ increases with increasing volumetric flow rate or Reynolds number and with increasing temperature that's mean the corrosion rate increases with two variables above.

2. In the impressed current cathodic protection (ICCP) method, $k_d$ increases with increasing rotation velocity or Reynolds number and with temperature.

3. There is some a difference between the practical results and theoretical results of the $k_d$ in the ICCP.

5. References


معامل انتقال المادة خلال الحماية الكاثودية لحديد واطئ الكاربون في مياه البحر

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الخلاصة

الهدف من البحث هو حساب معامل انتقال المادة، $k_r$، خلال الحماية الكاثودية لحديد واطئ الكاربون في مياه البحر المتعادل (3.5% NaCl وزن/حجم في الماء المقترب) ودالة حامضية = 7). تم استخدام طريقة مسح الحماية الكاثودية بطريقة أنبوب التضحية لأنبوب الحديد حاملاً مياه البحر باستخدام قطب الخارصين كأنبوب تضحية عند المتغيرات الالتباسية: درجة الحرارة (0 – 45 °C) والجريان الحمضي (5 – 900 لتر/ساعة). لقد وجد أن $k_r$ يزيد بزيادة درجة الحرارة وزيادة معدل الجريان الحمضي أو رم رينولدز، حيث تراوحت قيمة $k_r$ (0.24×10^6 – 41.6×10^6 m/s) (0.24×10^6 – 41.6×10^6 m/s).

الخليفة الثانية: الحماية الكاثودية بطريقة التيار المرسل لأسطوانة حديدية مدورة عمودياً في مياه البحر المتعادل عند المتغيرات الالتباسية: درجة الحرارة (0 – 45 °C) وسرعة تدوير (0 – 400 دوراً/دقيقة). لقد وجد أن $k_r$ يزيد بزيادة درجة الحرارة وزيادة سرعة تدوير الأسطوانة أو رم رينولدز، حيث تراوحت قيمة $k_r$ (7.25×10^6 – 36.62×10^6 m/s) (7.25×10^6 – 36.62×10^6 m/s).