

APPLICATION OF TWO THEORETICAL MODELS TO CORROSION OF MILD STEEL AND COPPER – NICKEL ALLOY IN HYDROCHLORIC ACID

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ABSTRACT:- The aim of present work is to apply Barnartt`s three point method (TPM) and McLaughlin method on the corrosion rate data of mild steel and Cu-Ni alloy in hydrochloric acid. The data of our previous work of corrosion of mild steel and copper – nickel alloy in hydrochloric acid were taken in order to apply these methods. The parameters of these methods, such as, corrosion currents and Tafel slopes were estimated using Levenberg-Marquardt estimation method. Both methods can be used to represent the corrosion rate data with high correlation coefficient. The results were more accurate with McLaughlin equation.

Keywords:- Corrosion, three point method, hydrochloric acid, metal alloys.

INTRODUCTION

It is well known that iron-based alloys, and copper – nickel alloys are used most widely in industry. Consequently, great attention has been paid to studies on the corrosion of iron and its alloys. Acid solutions are extensively used in industry, the most important of which are acid pickling, industrial acid cleaning, acid-descaling and oil well acidizing ^(1, 2). The commonly used acids are hydrochloric acid, sulfuric acid, nitric acid, etc. Since acids are aggressive, many researches were concentrated on corrosion by theses acids and how to determine the corrosion parameters, such as corrosion rates, corrosion currents, Tafel slopes ... etc. These parameters often determined by conventional techniques, such as, weight loss and Tafel extrapolation. Therefore, the aim of present study was to apply two methods from the literature. The first method was Barnartt`s three point method (TPM) ⁽³⁾, while the second one was McLaughlin method ⁽⁴⁾. These methods were applied on our previous works of the

corrosion rate data of mild steel in 3 M hydrochloric acid at 30 °C ⁽⁵⁾ and copper – nickel alloy in 5% hydrochloric acid at 35 °C ⁽⁶⁾.

THEORETICAL BASIS OF BARNARTT'S THREE POINT METHOD AND MCLAUGHLIN METHOD

Barnartt's three point method was used to calculate corrosion current and Tafel slopes from polarization curves. This method was based on the basis that a polarization curve can be represented by the equation:

$$I = I_{corr1} (10^{\frac{x}{ba1}} - 10^{\frac{-x}{bc1}}) \quad (1)$$

i is applied current density, I_{corr1} is the corrosion current, b_{a1} and b_{c1} are the Tafel slopes for the anodic and cathodic process respectively, and $x = E - E_{corr}$, where E_{corr} is the corrosion potential and ϕ is the electrode potential corresponding to the applied current. On the other hand, McLaughlin method was based on the following equation:

$$I = \frac{I_{lim,a} \cdot I_{corr2}}{I_{corr2} + (I_{lim,a} - I_{corr2}) 10^{\frac{-x}{ba2}}} - \frac{I_{lim,c} \cdot I_{corr2}}{I_{corr2} + (I_{lim,c} - I_{corr2}) 10^{\frac{x}{bc2}}} \quad (2)$$

$I_{lim,a}$ and $I_{lim,c}$ are diffusion currents for anodic and cathodic processes respectively. The symbols I_{corr2} , b_{a2} and b_{c2} have been used instead of I_{corr1} , b_{a1} , and b_{c1} in order to avoid confusion when comparing the results obtained by equation 1 (TPM) and equation 2. The total derivation of equation 1 and 2 were given in the literature ⁽⁴⁾.

RESULTS AND DISCUSSION

Two systems were taken from literature. Polarization behavior of mild steel corrosion in 3 M HCl at 30 °C ⁽⁵⁾, and corrosion of copper – nickel alloy in 5% HCl at 35 °C ⁽⁶⁾. In order to estimate the values of corrosion current density and Tafel slopes, potential against current density data can be used as input and output of equation 1 and 2. The variation of potential with current density was shown in Figure 1 for mild steel-HCl system and in Figure 2 for copper- nickel-HCl system. Nonlinear regression of equation 1 and 2 was used in order to obtain the parameters of these equations. The regression method based on *Levenberg-Marquardt* estimation method was used. The data input to equation 1 and 2 were shown in

Table 1, while the results of the two methods were shown in Table 2. Table 2 gives values of I_{corr} , b_a , and b_c corresponding to various values of x . For $x > 20$ mV, there is little variation in these parameters; for $x < 20$ mV there is large variation. This variation at low values of x may be attributed to the nonlinearity of potential – current curve near the corrosion potential. Khadom *et. al.* ⁽⁷⁾ discussed this behavior in detailed. He concluded that the shape of both anodic and cathodic curves, in turn, depends on the respective kinetic parameters of their reaction. The current-potential curve of corroding metal is rather complex non-linear equation; hence a general analytical solution is equally complex.

Also he concluded ⁽⁷⁾ that the deviation from linearity may be attributed to effect of mass transfer or concentration polarization on activation process. Therefore, the accurate values of corrosion parameters will be above 20 mV. The average values above 20 mV (i.e. at 30, 40, 50 mV) of corrosion kinetic parameters were shown in Table 2.

For application of equation 2, values of $I_{lim,a}$ and $I_{lim,c}$ were set as large as enough for figure 1 since there is no indication of concentration polarization. Value of $I_{lim,a} = 10000$ mA.cm⁻², and $I_{lim,c} = -1000$ mA.cm⁻². For figure 2, value of $I_{lim,a} = 10000$ mA.cm⁻², and $I_{lim,c} = -100$ mA.cm⁻².

As shown in figure 2, $I_{lim,c}$ was taken as a small value because of concentration polarization with cathodic reaction. For figure 1, both equation 1 and 2 gives comparable results.

The results are more accurate with figure 2; the corrosion parameters are closer than data of figure 2. This may be attributed to that equation 2 applicable with systems contains concentration polarization more than the system with activation process only. The behavior of equation 1 and 2 was shown in figures 3 and 4. Equation 2, not only handles polarization curves with diffusion limited currents but also, when there is no indication of concentration polarization.

McLaughlin ⁽⁴⁾ stated that equation 2, always gives results, while equation 1 is not. Equation 2 yields essentially the same results of equation 1.

CONCLUSIONS

Barnart's three point method (TPM) and McLaughlin method can be applied to determine the corrosion kinetic parameters with high correlation coefficients. Barnart's three point method (TPM) better than McLaughlin method in activation control systems. While McLaughlin method can be applied successfully with system contains mass transfer effects.

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Table (1): Polarization data input to equation 1 and 2.

x (mV) potential increment	Figure 1				Figure 2			
	i_x (mA.cm ⁻²) applied current at +x	i_{-x} (mA.cm ⁻²) applied current at -x	i_{2x} (mA.cm ⁻²) applied current at +2x	i_{-2x} (mA.cm ⁻²) applied current at -2x	i_x (mA.cm ⁻²) applied current at +x	i_{-x} (mA.cm ⁻²) applied current at -x	i_{2x} (mA.cm ⁻²) applied current at +2x	i_{-2x} (mA.cm ⁻²) applied current at -2x
	5	199.5	-211.9	469.2	442.1	24.2	-18.4	41.1
10	200.7	-220.2	477.1	467.9	44	-33.5	74.6	-78.3
20	210.3	-233.8	485.4	471.6	58.3	-44.5	98.9	-103.8
30	225.8	-244.2	500.5	482.3	71.8	-54.8	121.8	-127.9
40	233.1	-250.1	505.3	501.8	89.5	-68.3	151.8	-159.4
50	243.7	-256.8	510.5	522.9	100.4	-76.5	170.2	-178.7

Table(2): Corrosion parameters obtained by equation 1 and 2.

x (mV)	Fig. 1						Fig. 2					
	Eq. 1			Eq. 2			Eq. 1			Eq. 2		
	I_{corr1}	b_{a1}	b_{c1}	I_{corr1}	b_{a1}	b_{c1}	I_{corr1}	b_{a1}	b_{c1}	I_{corr2}	b_{a2}	b_{c2}
5	195.3	25	34	130.6	21	29	25.5	66	300	29.2	72	339
10	220.2	33	41	196.4	26	37	33.4	78	340	37.1	85	343
20	270.6	42	50	200.3	39	49	40.2	101	390	44	111	428
30	310.4	55	60	288.7	47	54	50.1	140	439	55.1	156	482
40	312.3	56	62	289.5	47	55	51.3	144	440	56.3	158	483
50	315.7	56	63	290.3	48	55	51.6	145	450	56.7	159	494
Average above 20 mV	312	55	61	289	47	54	51	143	443	56	157	486

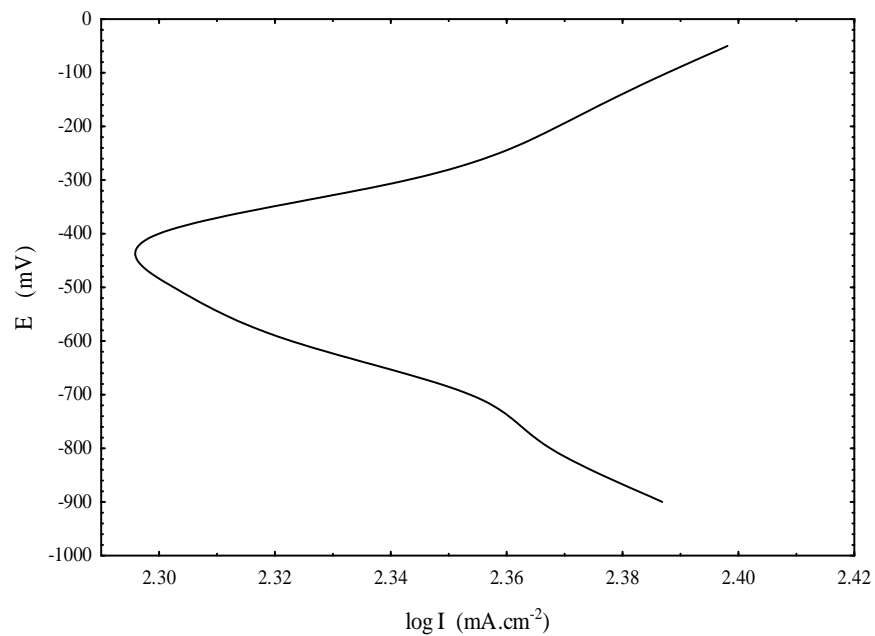


Fig.(1):Mild steel-3 HCl system.

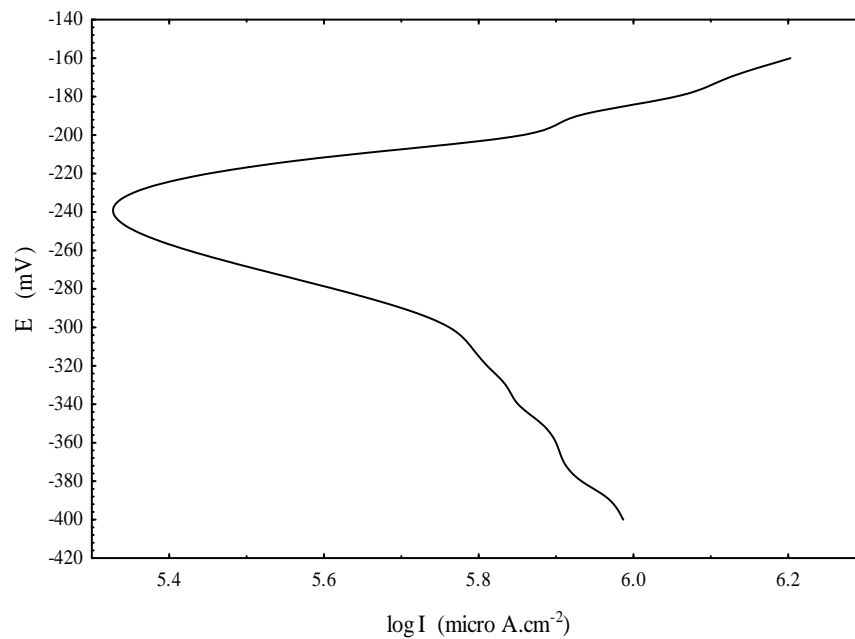


Fig.(2): Cu-Ni-5% HCl system.

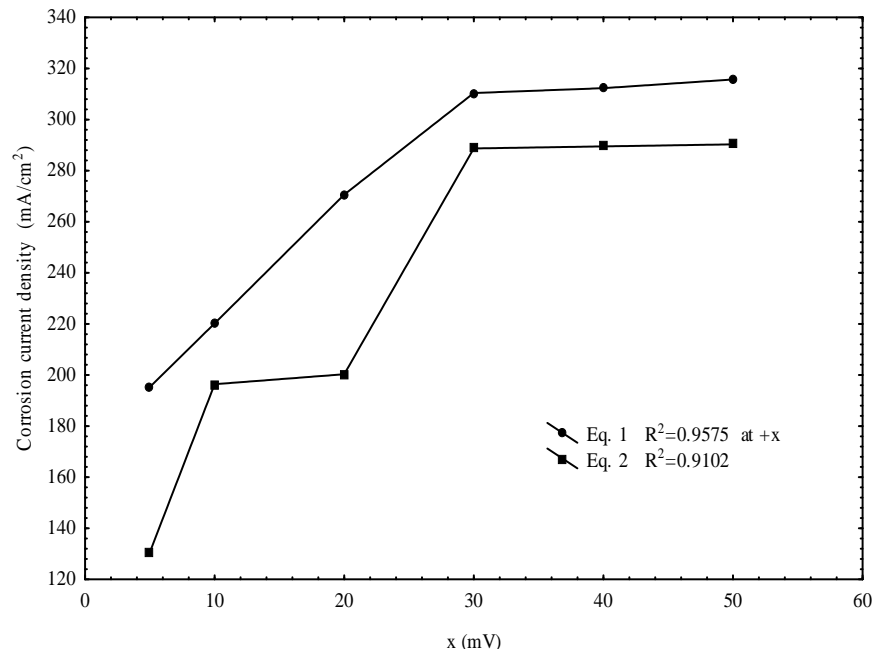


Fig.(3):Application of equation 1 and equation 2 to mild steel -3 M HCL.

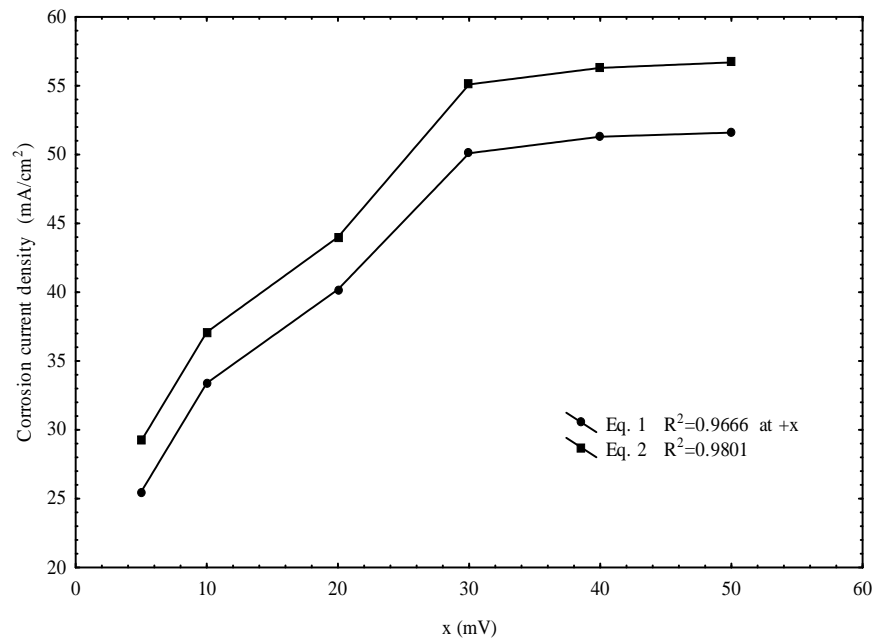


Fig.(4): Application of equation 1 and equation 2 to Cu-Ni alloy-5% HCL.

تطبيق موديلان نظريان على عملية تآكل الحديد المطاوع وسبيكة النحاس - نيكل في حامض الهيدروكلوريك

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الخلاصة

يهدف البحث الى تطبيق موديل (TPM) Barnart's three point method و McLaughlin method على عملية تآكل الحديد المطاوع وسبيكة النحاس نيكل في حامض الهيدروكلوريك. حيث تم الاستعانة ببيانات سابقة للباحث لغرض تطبيق هذه الموديلات الرياضية. تم ايجاد ثوابت عملية التآكل مثل تيار التآكل والميل الانودي والكاثودي باستخدام برنامج حاسوبي يستند على طريقة *Levenberg-Marquardt* لايجاد الثوابت. وجد انه كلا الطريقتين من الممكن استخدامهما بمعامل ارتباط عالي. الا ان طريقة McLaughlin اعطت نتائج اكثر دقة.