

EFFECT OF VELOCITY AND TEMPERATURE ON MASS TRANSFER OF OXYGEN IN CORROSION PROCESSES

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ABSTRACT

The present work investigated the corrosion behavior of carbon steel in 0.02 N NaCl solution.

Rotating Cylinder Electrode system was used in this investigation to measure the corrosion parameters by potentiostatic polarization technique under different conditions of temperatures (30, 40, 50 and 60 °C) and speed of rotation (600, 1000 and 1450 rpm).

The limiting diffusion currents of oxygen in air-saturated solutions under turbulent flow conditions has been correlated by the following equation with absolute average error = 1.915 % and correlation coefficient of 0.93.

$$Sh = 0.137 Re^{0.645} Sc^{0.362}$$

INTRODUCTION

In corrosion processes, which are under diffusion control, the corrosion rate equals the limiting current density, which can be represented by the following equation:

$$i_L = \frac{n F D C_b}{\delta_d} \quad (1)$$

Where D is the diffusivity of oxygen, C_b is the bulk concentration of oxygen, and δ_d is the diffusion layer.

For corrosion processes, which are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate, while if the corrosion process is under diffusion control (concentration polarization) as in aerated neutral solutions which are controlled by oxygen diffusion to the metal surface, the agitation and velocity increase the corrosion rate because they increase the mass transfer of oxygen to the metal surface (by influence on the thickness of the diffusion layer δ_d). The effect of flow velocity on corrosion was studied by many investigators⁽¹⁻³⁾. The results of some investigators showed that as the velocity increases the corrosion rate increases until it reaches a maximum value. Then the corrosion rate will decrease to a minimum value, after that there is another increase in the corrosion rate. Other investigators showed in their results that the corrosion rate increases with increase in velocity⁽³⁻⁴⁾.

Temperature increases the rate of almost all chemical reactions⁽⁵⁾. It influences the corrosion rate of a corrosion process that is under concentration polarization, but it has a higher effect on the corrosion process that is under activation polarization.

In general, if diffusion rate is doubled for certain increase in temperature, activation process may be increased by 10-100 times depending on the magnitude of activation energy of the reaction⁽⁶⁾.

The effect of temperature cannot be fully identified from other variables of the system, e.g. oxygen concentration or agitation.

The effect of temperature on corrosion reactions does not ordinarily satisfactorily fit the usual rate equations. The temperature effect is neither always exponential as it would be for most chemical reactions, nor it is linear as it would be if influenced by certain physical changes alone. Some experimental rate increases with temperature, while others show decreases. In some cases, maximums are observed⁽⁷⁾.

EXPERIMENTAL WORK

The material of the working electrodes used in this investigation was carbon steel with the following composition: C=0.226%, Mn=0.26%, Cr=0.04%, Cu=0.037%, S=0.029%, Ni=0.03%, Si=0.08%, P=0.002%, and Fe balance.

Distilled water and sodium chloride of 99.99 % purity were used. The pH of the solution was adjusted to 6.8 ± 0.1 .

Tests were carried out in a polarization glass cell with six-necks:

1. One for the working electrode,
2. Two for the counter electrodes.
3. One for water condenser.
4. One for immersing a thermometer in order to observe the test temperature.
5. One for the Luggin capillary probe.

Two graphite electrodes were used as the counter electrodes, each has dimensions of 3 x 1 x 1 cm.

Saturated Calomel Electrode was used throughout the experimental runs as the reference electrode.

The Rotating Cylinder Electrode (RCE) is shown in Fig. (1). The working electrode had a diameter of about 1.9 cm and length of about 1.2 cm.

Polarization was carried out using potentiostat (model-551) supplied by Amel (Italy). This potentiostat was connected to voltmeter and ammeter to read the voltage and current respectively.

After preparation of the working electrode, the corrosion cell parts were joined to each other, and then connected to the potentiostat. The polarization began after the corrosion potential variation with time as equal to about 1 mV/min. The polarization was done by changing the voltage 10 mV each step to the desired one and waiting for two minutes and then the current was read.

The polarization was carried out first cathodically to a voltage of -1200 mV. Then the cell was switched off until the corrosion potential returned approximately to its initial value. Then the anodic polarization began and continued to about 250 mV above the corrosion potential.

RESULTS AND DISCUSSION

Effect of Velocity

Limiting current density

Limiting current density of oxygen (i_L) is the most important characteristic of the cathodic region, because it represents the maximum rate of mass transfer of oxygen from the bulk to the metal

surface, and equals the corrosion rate. Figures (2-5) show the limiting current density values of oxygen as obtained from polarization curves.

The values of the limiting current density are plotted vs. Reynolds number at constant bulk temperature in Fig. (6). It can be seen that limiting current density of oxygen increases with increasing Reynolds number.

In neutral aerated solutions, oxygen reduction reaction is the main cathodic one. It is well known that diffusion of oxygen to the metal surface is the controlling step of the reduction of oxygen in corrosion processes (i.e. concentration polarization)^(5,8,9). Therefore, the limiting current density represents the maximum rate of oxygen mass transfer to the metal surface, and could be expressed by equation (1). Figure (6) shows that (i_L) increase with increasing velocity. This is due to decrease in the diffusion layer thickness (δ_d) with velocity^(5,8); i.e. the higher the velocity, the thinner the diffusion layer thickness the higher the limiting current density.

Corrosion potential

Table (1) shows the corrosion potentials at the various temperatures and velocities and indicates that increasing velocity at constant bulk temperature shifts the corrosion potential to a more positive value.

The relation between corrosion potential and $\log Re$ is found to be linear as shown in Fig. (7).

The cathodic reaction that is under mass transfer is increased by increasing velocity, i.e. the limiting current density is increased, while the anodic reaction, which is under activation, control is not affected by velocity^(5,9). Since E_{corr} is determined by the rate of the anodic and cathodic partial reactions, this leads to increase the corrosion potential with increasing velocity. The corrosion potential is given by Tafel equation as follows:

$$E_{corr} = E_a^0 + b_a \log \frac{i_{corr}}{i_{o,a}} \quad (2)$$

where E_{corr} and E_a^0 are the corrosion potential and equilibrium potential of the anodic partial process respectively, (i_{corr}) and ($i_{o,a}$) are the corrosion and exchange current densities, respectively, and b_a represents the anodic Tafel slopes. For iron corrosion in neutral aerated solutions, the corrosion current density is equal to the limiting

current density for the cathodic process, i.e.,

$$i_{\text{corr}} = i_L = n F \frac{D}{\delta_d} C_b \quad (1)$$

For Rotating Cylinder Electrode, the limiting current density can be calculated from the equation obtained by Eisenberg (equation 3).

$$i_L = 0.0791 n F C_b V (Re)^{-0.3} (Sc)^{-0.644} \quad (3)$$

Substituting the value of i_L from equation (2) into equation (3) gives:

$$E_{\text{corr}} = E_{\text{Fe}}^0 + b_a \log \frac{0.079 \ln F C_b V (Re)^{-0.3} (Sc)^{-0.644}}{i_{\text{o,Fe}}}$$

$$E_{\text{corr}} = E_{\text{Fe}}^0 + b_a \log 0.079 \ln F C_b V^{-0.3} \nu^{-0.344} D^{0.644} - b_a \log i_{\text{o,Fe}} + 0.7 b_a \log V$$

$$\therefore E_{\text{corr}} = a + 0.7 b_a \log V \quad (4)$$

where;

$$a = E_{\text{Fe}}^0 + b_a \log 0.079 \ln F C_b V^{-0.3} \nu^{-0.344} D^{0.644} - b_a \log i_{\text{o,Fe}}$$

= Constant at a constant temperature

Equation (4) shows that the value of the corrosion potential is a function of the thermodynamic properties (i.e. the equilibrium electrode potential) and the kinetic properties (i.e. the exchange current density and the anodic Tafel slope) and the physical properties of the solution. thus at a constant temperature, the corrosion potential changes linearly with the logarithm of the velocity.

The values of E_{corr} of the present work is plotted against the logarithm of Re number at constant temperatures (Fig. 7), a linear relationship is obtained which is in agreement with the theoretical behavior.

The values obtained for E_{corr} (-387 to -478 mV) in the present work are in a reasonable agreement with those of Einas⁽¹⁰⁾ (-300 to -400 mV) for 600 ppm NaCl solutions at temperature range of 30-50 °C, Jaralla⁽¹¹⁾ (-320 to -400 mV) for 0.01 NaCl solutions at 25 °C.

Effect of Temperature

Limiting current density

The limiting current densities of oxygen, which are given in Table (2), are plotted versus temperature at constant Reynolds number as shown in Fig. (8). It is seen that the oxygen limiting current density decreases with increasing temperature.

Al-Mashta⁽¹²⁾ studied the effect of temperature on i_L under cross flow conditions. He found that the limiting current density decreases with increasing temperature. Sameh⁽¹³⁾ had investigated the effect of temperature on limiting current density at 600 ppm NaCl under 0-500 rpm and 30-50 °C. Her results showed a decrease in limiting current density when plotted versus Reynolds number rather than rpm. Butler and Ison⁽¹⁴⁾ and Mahato *et al.*⁽¹⁵⁾ found a decrease in corrosion rate with increasing temperature.

The temperature is an important factor affecting the rate of any reaction. In corrosion process, temperature has an influence on:

1. activation process.
2. solubility of the reactants in the solution.
3. diffusivity of the reactants on the metal surface.
4. thickness of the diffusion layer (δ_d).

In aqueous solutions where the cathodic reaction is the reduction of oxygen, the reaction is under diffusion control. The activation energy of the reaction is small compared with that of hydrogen reduction reaction in acid solutions. The effect of diffusion parameters (solubility, diffusivity and thickness of the diffusion layer) is greater than that of activation energy change.

It is well known that increasing temperature will decrease the solubility of oxygen in the test solution and increase the thickness of the diffusion layer (δ_d), this will lead to decrease oxygen mass transfer to the metal surface, i.e. decreasing limiting current density and corrosion rate. On the other hand, increasing temperature increases the diffusivity of oxygen and corrosion rate. These three parameters are related to each other by equation (1).

To show the effect of these parameters on the limiting current density with increasing temperature, it is found that when temperature increases from 30 to 40 °C, diffusivity of oxygen increases by 15.9 % oxygen solubility decreases by 13.6 % and the diffusion layer thickness (δ_d)

calculated by equation (5) which derived from equations (1) and (3) increases by 12.2 %.

$$\delta_d = 12.642 (\text{Re})^{-0.7} (\text{Sc})^{-0.356} \quad (5)$$

Many investigators show an increase in the limiting current density with temperature. This may be due to the high Schmidt number of test solution used, see Table (3), which means a small value of diffusion layer thickness (δ_d) compared with its value for solution of low Schmidt number, i.e. increasing temperature will not change (δ_d) significantly for solutions of high Schmidt number. The value of Schmidt number of the test solutions of the present investigation ranged from 89 to 308.

Corrosion potential

The effect of temperatures on corrosion potentials is reported in Table (1). It indicates that corrosion potential shifts to more negative value as the temperature increases.

It is well known that corrosion potential is affected by both the anodic and cathodic partial reactions. The anodic region is activation controlled^(5,9), therefore at constant velocity, increasing temperature will stimulate this reaction. This will lead to shifts the E_{corr} value to more negative value.

The behavior of E_{corr} of the present investigation with temperature is in agreement with the previous investigations^(10,12,16,17).

Estimation of Mass Transfer Correlation

The general form of the mass transfer relationship is:

$$\text{Sh} = a \text{Re}^b \text{Sc}^c$$

Table (4) shows the value of K_m , Sc and Sh at different run conditions. This table shows that increasing velocity at constant bulk temperature causes the mass transfer coefficient (K_m) and (Sh) to increase. At constant velocity, Table (4) indicates that the mass transfer coefficient increases as bulk temperature increases. This increment in mass transfer coefficient is countered by an increase in diffusion coefficient (see Table

5), which will cause the decrease in Sherwood number. Increasing bulk temperature is accompanied by a decrease in Schmidt number.

The values of Sh as related to Re and Sc are fed to a multivariable least square program and the following correlation is obtained:

$$\text{Sh} = 0.137 \text{Re}^{0.043} \text{Sc}^{0.302}$$

With absolute average error = 1.915 % and correlation coefficient = 0.93.

Many correlations of such type are available in the literature, which are satisfactorily applied to electrochemical processes under turbulent flow conditions. Samples of such results for isothermal conditions are shown in Table (6).

Table (6) shows that the range of exponent "b" is between 0.61-1. The value of the exponent "b" obtained in the present work is 0.645, this is in excellent agreement with those reported by Cornet and Kappesser⁽¹⁸⁾ and it is also with the range of results of many investigators. The agreement of the results with the equation of Cornet and Kappesser may be due to the low Schmidt number used by the investigators which is 450. The Schmidt number used in the investigation has a range of 89-308.

Table (6) shows that the exponent "c" was found to have a range of 0.33-0.4 with the majority of 0.356, which is obtained by many investigators. The value of "c" obtained in this work is equal to 0.362, which is in good agreement with those of the previous investigations.

The constant "a" depends on the physical properties of the solution such as diffusivity, kinematic viscosity and mass transfer coefficient. There is no fixed value of this constant found in the literature.

The most reliable correlation for turbulent mass transfer, established by Eisenberg *et al.*⁽¹⁹⁾ (equation 3).

The maximum error estimated between the experimental and theoretical values of limiting current densities is 11 %. The error may be due to surface roughness of the metal and the assumption that the concentration of oxygen at the solution-metal interface is zero.

CONCLUSIONS

1. The limiting current density of oxygen increases with increasing Reynolds number.
2. The limiting current density of oxygen decreases with increasing temperature.
3. The effect of temperature on corrosion potential is more significant than that of velocity.
4. The limiting current density of oxygen reduction for RCE can be represented by $(Sh = 0.137 Re^{0.645} Sc^{0.362})$ with absolute average error = 1.915 % and correlation coefficient = 0.93.

ACKNOWLEDGMENTS

We would like to thank Al-basil Company and the Department of Chemical Engineering-College of Engineering-University of Baghdad for providing the research facilities.

REFERENCES

1. Butler, G. and Ison, H.C.K., "Corrosion and its Prevention in Waters", Leonard Hill-Leonard, 1st Edition (1966).
2. Roetheli, B.E. and Brown, R.H., Ind. Eng. Chem., 23, 1010 (1931).
3. Speller, F.N. and Kendall, V.V., Ind. Eng. Chem., 15, 134 (1923).
4. Whitman, W.G., Chem. Rev., 2, 419 (1925).
5. Fontana, M.G. and Green, N.D., "Corrosion Engineering", McGraw-Hill, 2nd Edition (1978).
6. Shrier, L.L., "Corrosion", News Butterwrths, 2nd Edition, Vol. 1, P. 1:85-1:90 (1976).
7. Hackerman, N., Ind. Eng. Chem., 44, 1752 (1952).
8. Uhlig, H.H., "Corrosion and Corrosion Control", John Wiely & Sons, 2nd Edition (1971).
9. West, J.M., "Electrodeposition and Corrosion Processes", V.N.R. Co. (1971).
10. Einas A., M.Sc. Thesis, U.O.T. (1998).
11. Jaralla, A.A., M.Sc. Thesis, University of Baghdad (1978).
12. Al-Mashta, E.S., M.Sc. Thesis, Saddam University (1996).
13. Sameh, S.A., Ph.D. Thesis, U.O.T. (1994).

14. Butler, G. and Ison, H.C.K., J. Appl. Chem., 10, 80 (1960).
15. Mahato, B.K., Steward, F.R. and Shemilt, L.W., Corrosion Science, 8, 737 (1968).
16. Abdul-Masih, N.S., Ph.D. Thesis, University of Baghdad (1990).
17. Chin, R.J., and Nobe, K., Corrosion, 33, 364 (1977).
18. Cornet, I. and Kappesser, R., Trans. Inst. Chem. Eng., 47, 222 (1969).
19. Eisenberg, M., Tobisa, C.W., and Wilke, C.R., J. Electrochem. Soc., 101, 306 (1954).
20. Hubbard, D.W. and Lightfoot, E.N., I&EC Fund., 5, 370 (1966).
21. Misushina, T., Ogino, F., Oka, Y. and Fukuda, H., Int. Heat Mass Transfer, 14, 1705 (1971).
22. Pickett, D.J. and Ong, K.L., Electrochimica Acta, 19, 875 (1974).
23. Ross, T.K. and Wrang, A.A., Electrochimica Acta, 10, 1093 (1965).
24. Shaw, D.A. and Hanratty, T.J., AIChE J., 23, 28 (1977).
25. Kappesser, R. and Cornet, I., J. Electrochem. Soc., 118, 189 (1957).
26. Vilambi, N.R. and Chin, D.T., J. Electrochem. Soc., 134, 2501 (1987).
27. Gabe, D.R. and Robinson, D., Electrochimica Acta, 17, 1121 (1972).

Table (1) Corrosion potential values at different conditions

Run NO	Temperature (°C)	rpm	E _{corr} (mV)
1	30	600	-404.4
2	30	1000	-395.0
3	30	1450	-387.5
4	40	600	-423.0
5	40	1000	-419.5
6	40	1450	-411.5
7	50	600	-443.0
8	50	1000	-427.0
9	50	1450	-417.5
10	60	600	-475.0
11	60	1000	-457.0
12	60	1450	-443.5

Table (2) Experimental limiting current densities ($\mu\text{A}/\text{cm}^2$)

Temperature ($^{\circ}\text{C}$)	Rpm	Re No.	i_L (exp.) ($\mu\text{A}/\text{cm}^2$)
30	600	14454	678
30	1000	22909	936
30	1450	33884	1127
40	600	17783	692
40	1000	281184	941
40	1450	40738	1176
50	600	20893	740
50	1000	33113	945
50	1450	48978	1288
60	600	23714	792
60	1000	38019	964
60	1450	56234	1369

Table (3) Schmidt number values for different investigations

Ref. No.	Sc No.	Temperature ($^{\circ}\text{C}$)
20	1700-30000	1-25
21	800-15000	25
22	2500-5410	25
23	2450	18
24	1730-37200	25

Table (4) K_m , Sc, and Sh values for different conditions

Run NO.	Temperature ($^{\circ}\text{C}$)	rpm	$K_m \times 10^5$ (m/s)	Sc	Sh
1	30	600	7.49	308.11	533.4
2	30	1000	10.35	308.11	747.2
3	30	1450	12.46	308.11	903.3
4	40	600	8.69	212.99	519.5
5	40	1000	11.82	212.99	716.9
6	40	1450	14.77	212.99	899.4
7	50	600	10.95	142.03	516.4
8	50	1000	13.99	142.03	668.2
9	50	1450	18.02	142.03	872.1
10	60	600	13.68	89.72	472.1
11	60	1000	16.65	89.72	582.7
12	60	1450	23.63	89.72	832.7

Table (5) Diffusion coefficient of Oxygen

Temperature ($^{\circ}\text{C}$)	Diffusivities $\times 10^9$ (m^2/s)
30	2.610
40	3.104
50	3.915
60	5.314

Table (6) Mass transfer correlations for RCE

Ref. No.	Correlation	Temp (K)	Experimental Condition
19	$Sh = 0.079 Re^{0.7} Sc^{0.356}$	298	Fern-Ferro-Cyanide in alkaline solution. For $10^3 < Re < 10^5$ and $835 < Sc < 11490$
18	$Sh = 0.973 Re^{0.64}$	296	4 % NaCl aqueous solution ($Sc = 450$).
25	$Sh = \left[1.25 + 5.79 \log \left(\frac{d}{\epsilon} \right) \right]^{-2} Re Sc^{0.61}$	296	$3.2 \times 10^3 < Re < 5.2 \times 10^5$
26	$Sh = 0.2 Re^{0.61}$	296	Fern-Ferro-Cyanide in alkaline solution. For $800 < Re < 8000$ and $Sc = 1900$
27	$Sh = 0.079 Re^{0.69} Sc^{0.4}$		$2900 < Re < 338800$ and $830 < Sc < 2210$

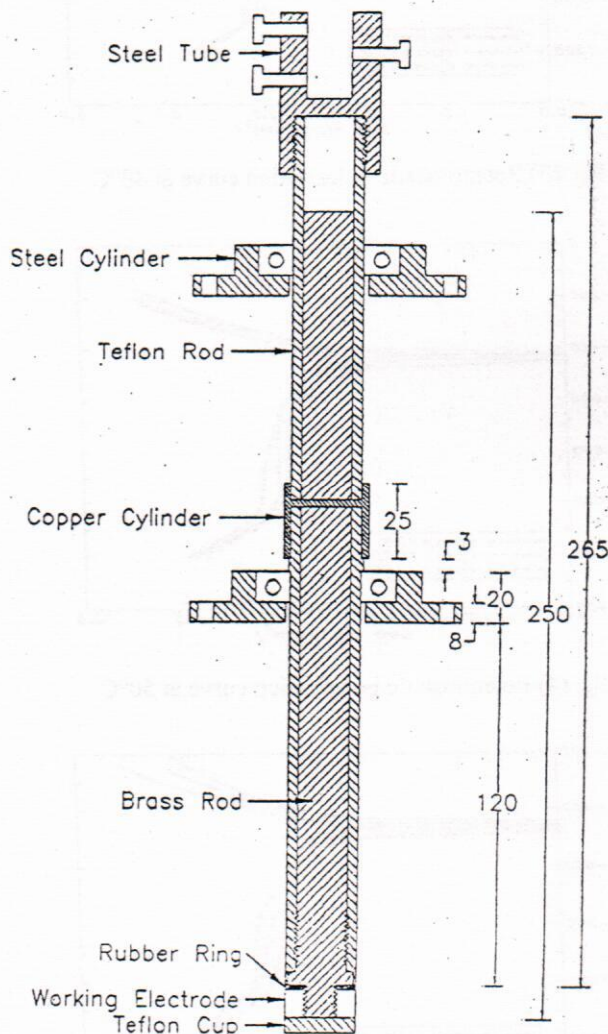


Fig. (1) Rotating cylinder electrode

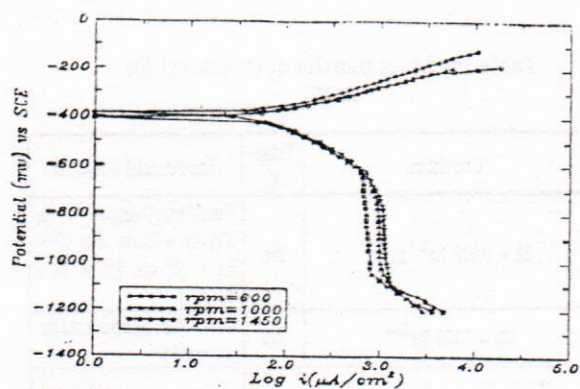


Fig. (2) Potentiostatic polarization curve at 30°C

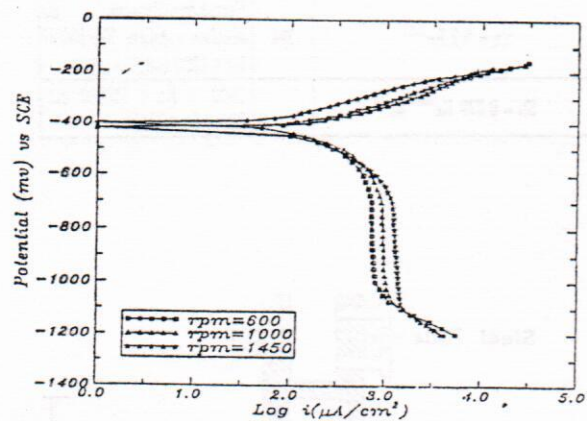


Fig. (3) Potentiostatic polarization curve at 40°C

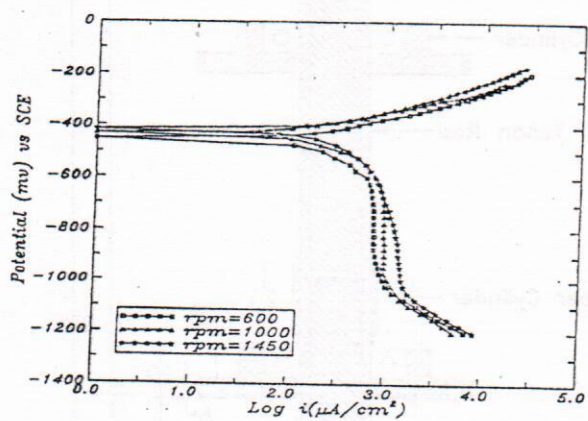


Fig. (4) Potentiostatic polarization curve at 50°C

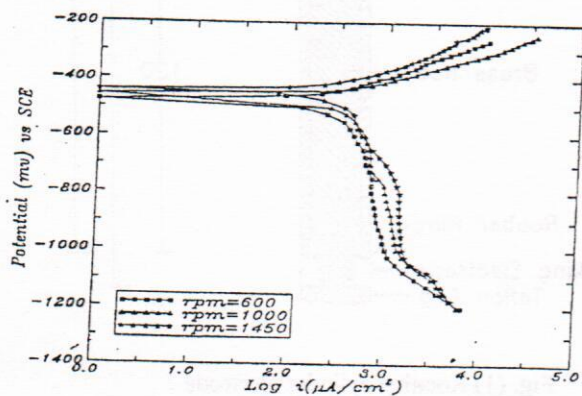


Fig. (5) Potentiostatic polarization curve at 60°C

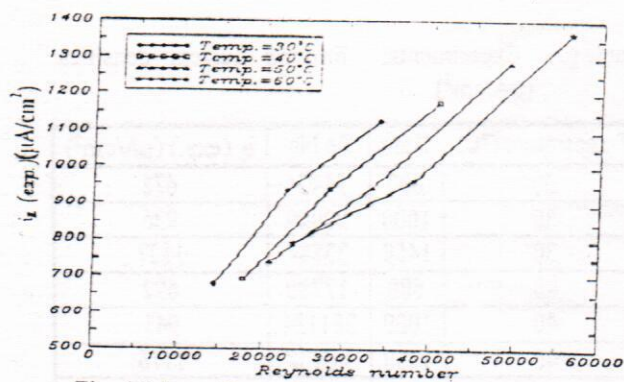


Fig. (6) i_L vs. Re at constant bulk temperatures

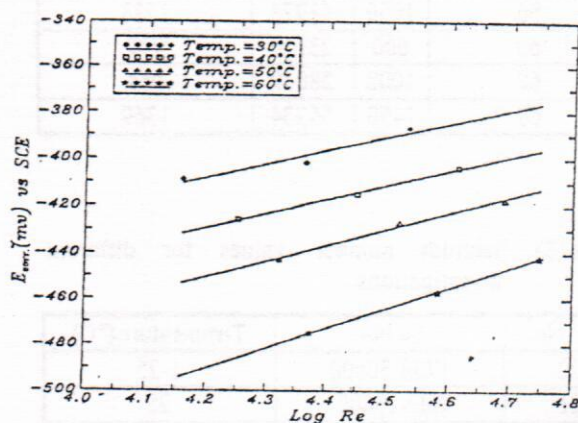


Fig. (7) $\log Re$ vs. $E_{corr.}$ For different bulk temperatures

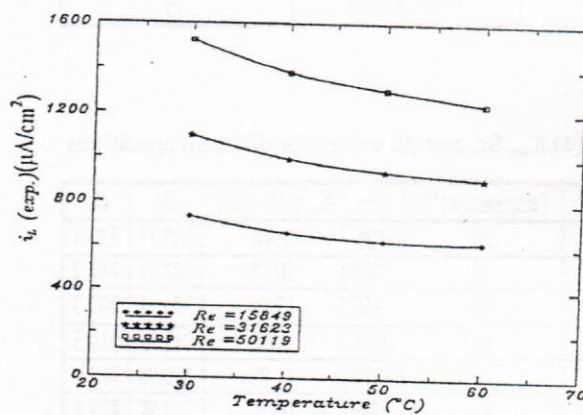


Fig. (8) Effect of temperatures on i_L