A GALVANOSTATIC POLARIZATION INVESTIGATION OF STEEL CORROSION IN ALKALINE SOLUTIONS

Aprael S. Yaro

Chemical engineering department, college of engineering,Univeristy of Baghdad

ABSTRACT

The electrochemical behavior of iron and steel in alkaline media is complex,not well understood.It is difficult to determine corrosion rates of steel in high pH solutions by extrapolation of Tafel curves.Polarization resistance (R_p) must be determined in some other way.In this study an attempt was made to find (R_p) values of steel corroding in saturated $Ca(OH)_2$ by anodic currents impressed galvanostatically to the steel from a counter electrode placed together with a reference electrode(I.e. impressed anodic current densities were (10,20,40,and 100µA/Cm^2 and duration time was about 25 minutes). It was found that this rapid and non destructive polarization technique yields accepted and reasonable information on corrosion behavior.

الخلاصة

التصرف الكهروكيمياوي للحديد والفولاذ في الأوساط القاعدية معقد وليس واضحا بصورة جيدة.من الصعوبة ايجاد معدلات التآكل للحديد في المحاليل القاعدية بطريقة تافل لذلك لا يمكن ايجاد مقاومة الأستقطاب (R_p) ويجب البحث عن طريقة اخرى لأيجادها.في هذه الدراسة جرت محاولة لأيجاد قيم مقاومة الأستقطاب لحديد يتعرض للتآكل في وسط من هيدروكسيد الكالسيوم المشبع و الذي يشبه السمنت في أسه الهيدروجيني (pH>12.5) بتسليط تيارات كلفانية انودية ساكنة على الحديد من القطب المساعد (counter electrode) يرافقه قطب المرجع (reference electrode).(سلطت تيارات بقيم 10,20,40,100 مايكروامبير/سم^2)خلال زمن يقارب 25 دقيقة.لوحظ من الدراسة ان استعمال هذه الطريقة افضت الى نتائج مقبولة و معقولة على تصرف تلآكل الحديد.

KEYWORDS

Alkaline solutions, solution resistance , polarization resistance , corrosion current , capacitance , Galvanostatic method.

INTRODUCTION:

The best known technique of evaluation of the instantaneous corrosion rate in the laboratory and in the field is the polarization resistance method (linear polarization),developed by Stern et al **[1-3].** The corrosion rate is calculated from the formula:

$$I_{corr.} = [\beta a\beta c/2.3(\beta a+\beta c)] \ \mathrm{x} \ (\Delta I / \Delta E) = B/R_p \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Many studies **[4-6]** showed and investigate the limits of application and accuracy of Stern and Geary development.The results of these studies led to state that in many systems the correct determination of corrosion intensity is limited by many factors,namely (i) The Tafel slopes are unknown or vary with time; (ii) The corrosion potential varies during the measurement; (iii) The system being polarized requires a given time to achieve a steady state…….etc.

Steel immersed in the strongly alkaline solutions will not normally corrode due to the formation of a protective iron oxide film which passivates the steel.This passivity can be destroyed by corrosive species (i.e. Cl^-).Corrosion is then initiated leading to establishment of corroding and passive sites on the metal surface in which both anode and cathode reactions are taken place.The anode reaction are **:** **Fe $\rightarrow$ Fe^{++} + 2e ………………(2) (metal dissolution,active corrosion)**

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 8H^+ + 8e\ldots\ldots\ldots(3)\text{(formation of passive layer)}$$

The released electrons travell through the steel to the local cathode on which they are used in the oxygen reduction reaction:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

These reactions lead to the development of regions of different electrochemical potentials and result in current flow within alkaline solution.The galvanostatic pulse technique has been introduced for field application in 1988 to overcome problems with the interpretation of corrosion risk of reinforcement occurring when half cell potential readings are applied in wet ,dense, or polymer-modified concrete,when access of oxygen is limited.since introduction of this technique the development work is conducted in order to allow the quantitative evaluation of the ongoing reinforcement corrosion **[7,8]** .The principle of galvanostatic pulse corrosion rate estimation is based on inducing a short duration anodic current pulse into the reinforcement galvanostatically from a counter electrode placed on the concrete surface together with the reference electrode. The applied current is normally in the range of 5-400 µA and the typical pulse duration is up to 10 seconds **[9]**.Accordingly , the technique which is gradually gaining acceptance by engineers is the transient galvanostatic pulse technique.This method applies a small constatnt-current perturbation $I_{app.}$ To the steel reinforcemet in a similar manner to a galvanostatic linear polarization resistance(LPR)measurement.This resulting potential transient response,is analyzed according to electronic theory **[8]** were for asimple resistance and capacitor in parallel :

$$E_t = I_{app.} R_\Omega + I_{app.} R_p [1-\exp(-t/R_pC_d)]\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

This may be converted to:

$$\mathbf{Log\ (E_{max}\text{-}\ E_t) = log\ (I_{app.}\ .\ R_p) – t/R_pC_d}\ldots\ldots\ldots\ldots(6)$$

It is believed that the present investigation of the corrosion behavior of steel in alkaline $Ca(OH)_2$ is similar in many respects to the aqueous phase of cement, so it will contribute to better understanding of the behavior of embedded reinforcement. The duration period in this investigation is relatively long compared with the mentioned technique but the induced applied currents cause polarization of immersed steel In the " anodic direction" compared to its free corrosion potential.

EXPERIMENTAL PROCEDURE:

A single Compartment cell containing sodium hydroxide test solution was used for the galvanostatic measurements.The counter electrode was a platinum foil.The potential of the working electrode was measured V's a saturated calomel electrode(SCE),supplied with a fine luggin capillary which was placed within 0.1 Cm of the electrode surface.The working electrode was a rod measuring 6.35 mm in diameter and 10mm in length with a total exposure area of $31.7mm^{2.}$ Befor being used,the electrode was abraded with emery papers of 320,400,and 600 grades,degreased with aceton(CH_3COCH_3) and finally washed with distilled water(which was also used in preparing the test solution),then pickled in 50%wt. Hcl for 5 minutes[10].The chemical composition(Wt.%) of the working electrode was:P=.006;C=.124;Mn=.494;S=.oo7;and the remainder Fe.

Galvanostatic polarization curves were traced under constant current densities(I,e;10,20,40 and $100\mu A/Cm^2$).The variation of electrode potential with the quantity of electricity was followed as function of time(see figure 2).The anodic experiments were started after a steady potential was attained using the same current density.When the potential of working electrode reaches the final steady state potential value,the current was swiched off[11].The experiments were carried out at (25+1)C. The circuit diagram is shown in details in figure(1) .

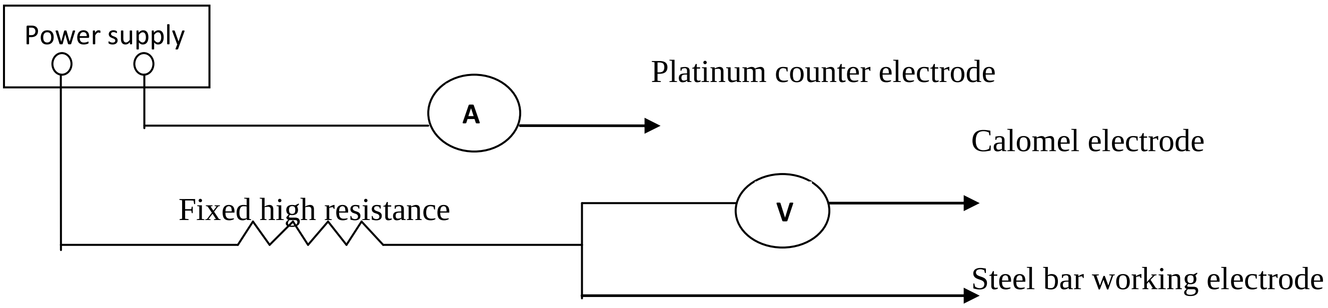


FIG.(1) Circuit diagram for galvanostatic polarization measurement

RESULTS AND DISCUSSION:

Four potential time curves at fout different current densities (i.e.,10,20,40 & $100\mu A/Cm^2$) shown in fig.(2)were obtained immediately after immersion in the aerated saturated $Ca(OH)_2$ solution. It is clear that the four curves have the same characteristic form , and the potential shows a rapidly rise until it reaches the final steady state potential valume(i.e.,0.6-0.7V(SCE)).Also it is quite clear that the time required to reach the final steady state potential value decreases with increase in current density.Fig(2) also shows the anodic potential increases with increase applied current density from 10 to 100 $\mu A/Cm^2$,but this increase was less pronounced at high current density 40 and 100µA/Cm^2.In order to obtain values of R_p & C_{dl} separate from the omic resistance (Rohm) , equation(5) can be transferred to linear form as in equation (6) (Appendix A shows the linearization of equation(5)).

Figures (3,4,5,and 6) show the transformation for calculation of the ln($I_{app.}R_p$) and ($1/R_pC_{dl}$) values for 10,20,40 & 100 µA/Cm^2 respectively. Extrapolation of the straight line to T=0 using least square linear regression analysis produced an intercept corresponding to ln($I_{app.}R_p$) and a slope of the line of ($1/R_pC_{dl}$).for each applied current density.The remaining over potential correspondes to $I_{app.}R_p$ the omic voltage drop after the polarization resistance R_p is determined by means of this analysis, the corrosion current $I_{corr.}$ Can be calculated from the Stern-geary equation[1]:

$$I_{corr.} = B/R_p \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where B is an empirical constant determined to be 0.026 V for actively corroding steel and 0.052V for passive steel [12,13].Table(1) shows the corrosion parameter determination using galvanostatic method according to above explanation & in the light of electronic theory with a sample of calculation in appendix(B).

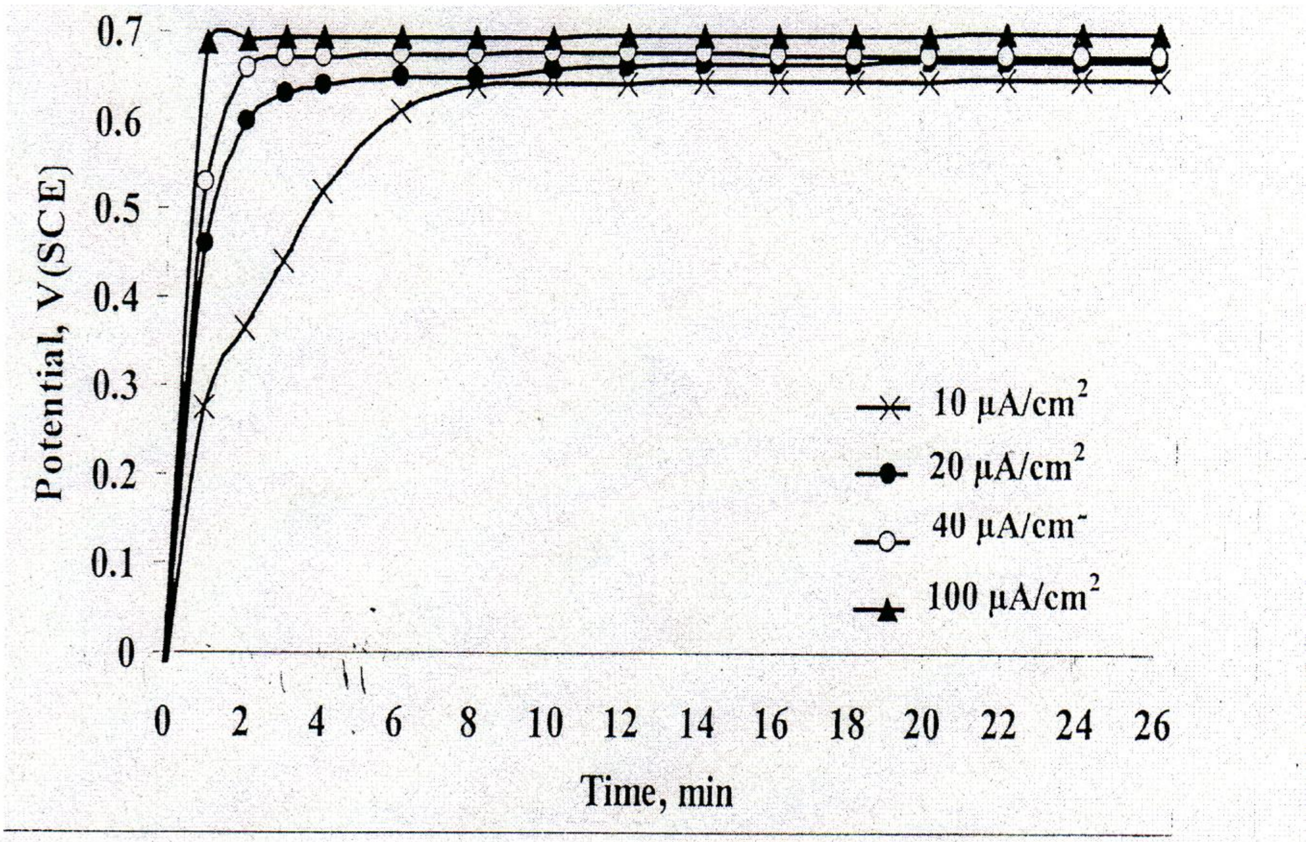


Fig. (2) Anodic polarization of steel in calcium hydroxide solution at different current densities.

Table (1) Experimental results for determination of R_p, Rohm, i_{corr} & conductance using galvanostatic pulse technique.

Corrosion Parameter	**Current Density, µA/cm^2**			
	Applied current 10 µA/cm^2	I_{app} 20 µA/cm^2	I_{app} 40 µA/cm^2	I_{app} 100 µA/cm^2
Solution Resistance R_Ω, ohm	412	31505	16420	6761
Polarization Resistance R_p, ohm.cm^2	23728	1994	580	239
Corrosion Current, i_{corr}.µA/cm^2	1.095	13.14	44.8	108.9
Conductance, µF/cm^2	150	153	11045	30092

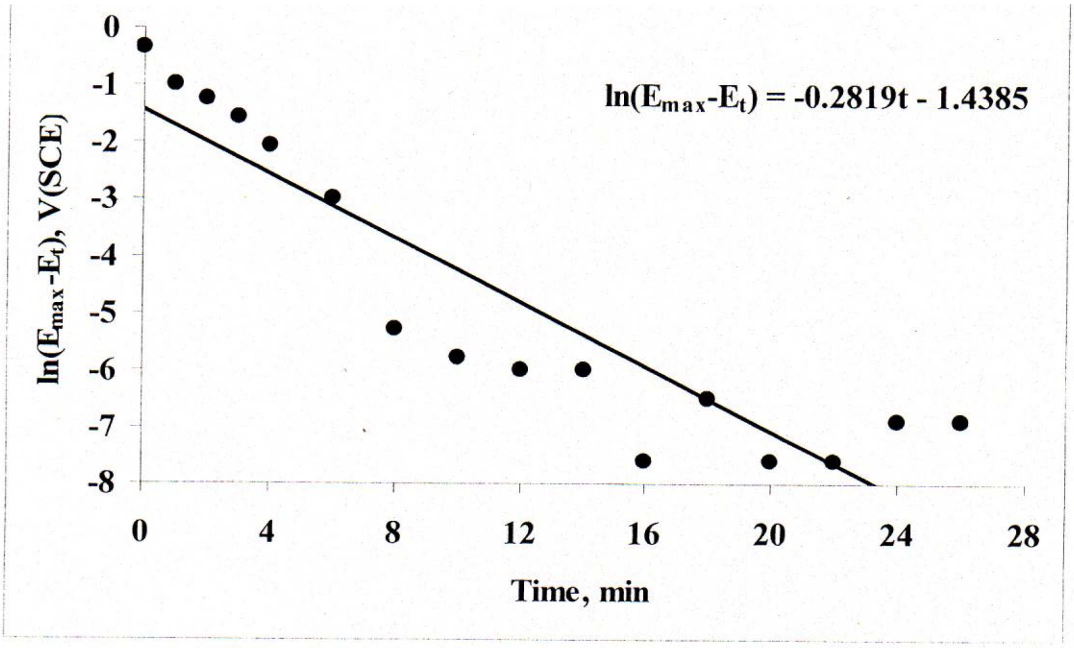


Fig.(3) Galvanostatic pulse transient from active steel in $Ca(OH)_2$ solution. E_{max} = 0.65 V(SCE), $I_{app.}$ = 10 μA/Cm^2.

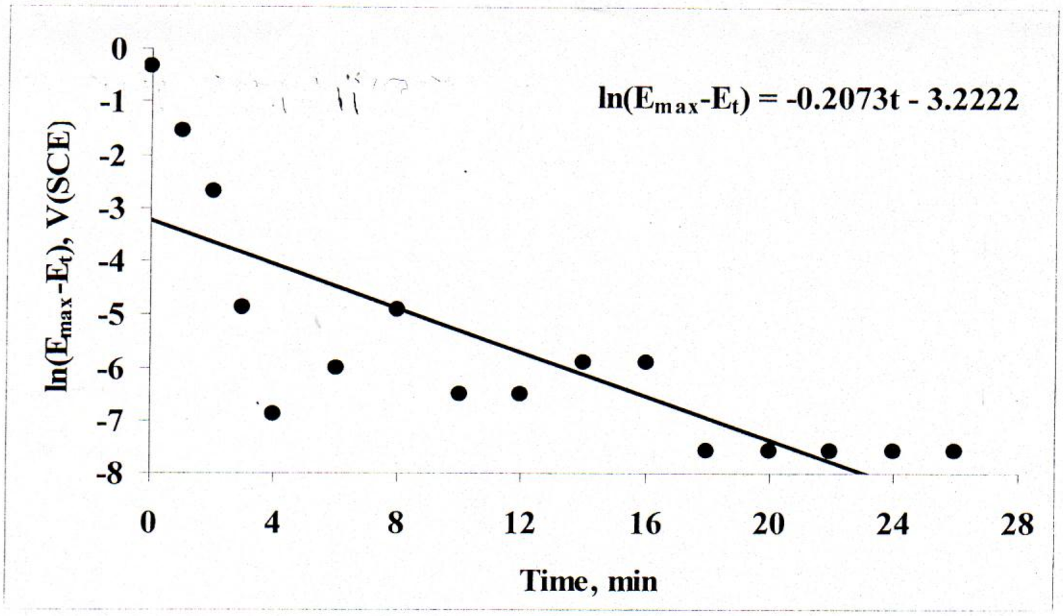


Fig.(4) Galvanostatic pulse transient from active steel in $Ca(OH)_2$ solution. E_{max} = 0.67 V(SCE), $I_{app.}$ = 20 μA/Cm^2.

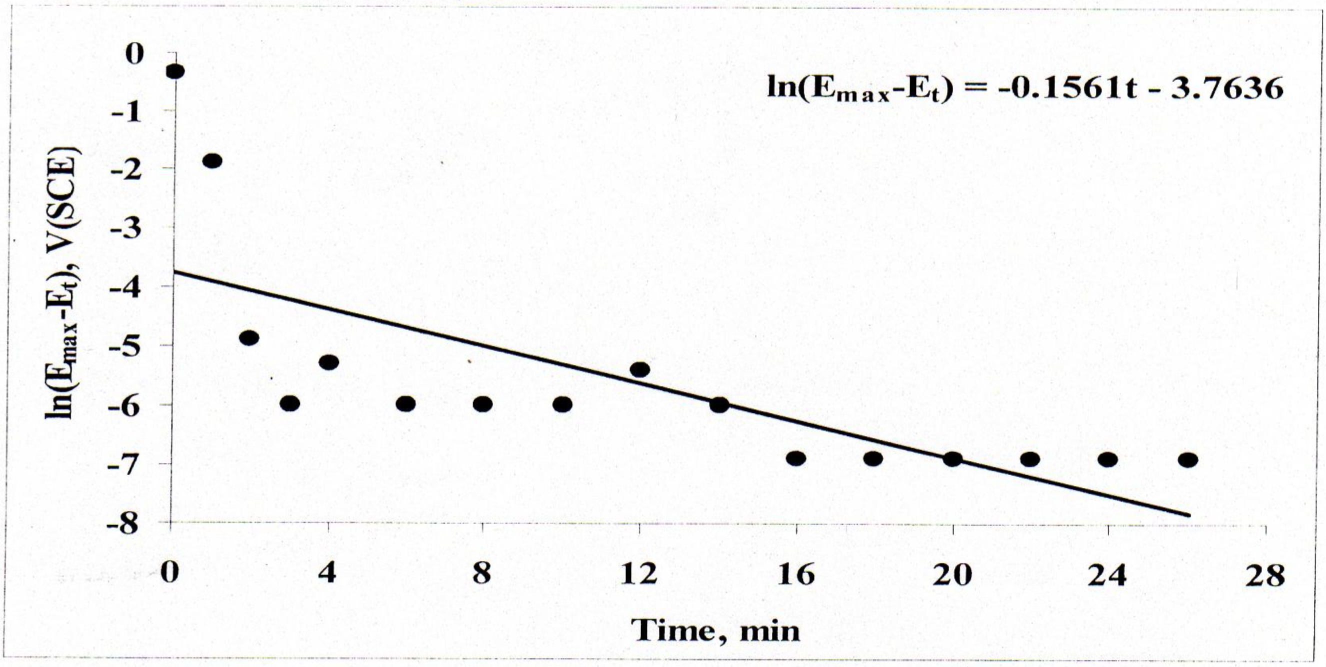


Fig.(5) Galvanostatic pulse transient from active steel in $Ca(OH)_2$ solution. E_{max} = 0.68 V(SCE), $I_{app.}$ = 40 μA/Cm^2.

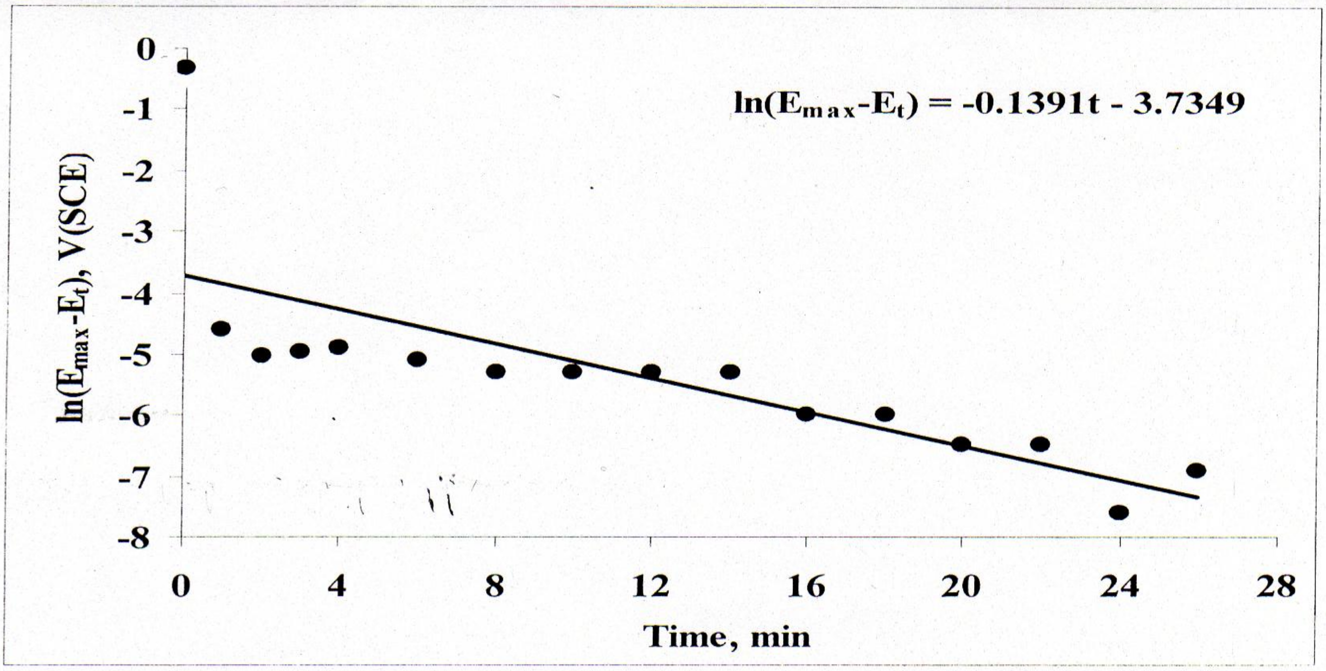


Fig.(6) Galvanostatic pulse transient from active steel in $Ca(OH)_2$ solution. E_{max} = 0.70 V(SCE), $I_{app.}$ = 100 μA/Cm^2.

CONCLUSIONS:

- By means of this polarization technique,the effective polarization resistance can be calculated which can be used for calculation of corrosion rate.

- The radical changes in the exposure conditions,especially the temperature and concentrations of corrosive species will alter the corrosion current by a certain factor

- Based on the results obtained in this study an equivalent circuit construction is recommended to check the validity of this attempt as simulation to corrosion behavior of steel in concrete.

References:

* Stern,M. and Geary,A.L.(1957),J.electrochem.Soc.,Vol.104,56.

* Stern,M. (1958) , Corrosion Vol.14,329.

* Ibid(1958) Corrosion Vo;.14,440.

* Mansfeild,F.(1976) Advance in corrosion science & technology,Vol.6,p.163-262,plenum press,New York.

* Callow,L.M.,Richardson ,J.A. & Dawson,J.L.(1976) corrosion ,J.,11,132.

* Mansfeild,F. & Oldham , K.B.(1971),corros.sci.11,787.

* Gonzalez,J.A.,Molina,A.,Escudero,M.L. and Andrade,C.(1985),J.corros.sci.,Vol.25,No.10.

* Newton,C.J.& Sykes,J.M.(1988) j.corros.sci.Vol.28,No.11.

* Elesener,B.,Wojtas,H.,Bohni,H.(1994),galvanostatic pulse measurement rapid on site corrosion monitoring"proceeding of international conference held in the Univ. of Sheffield ,24-28 July .

* Gouda,V.K.,(1970) , Br.corros.J.,Vol.5,P.198.

* Abd-El-Haleem, S.M. and Abd-Aal,E.E.(2006) electrochemical behavior of copper in alkaline sulfide solutions,corrosion,Vol.62,NO.2,P.121-128.

* Andrade,C.,Castillo V.,Alonso C., and Gonzalez J.A(1984) The determination of corrosion rate of steel embedded in concrete by polarization resistance and AC impedence methods,American society for testing and materials Philadelphia,P.43-63.

* Moosavi A.N.,John G.,and Gedge J. (1994) assessment of corrosion of refrigerant tubes in reinforced concrete eyes ring using corrosion mapping,Sheffield academic press,Sheffield ,Vol.1,p.116-127.

Appendix A

When the constant current I_{app} is applied to the system, the polarized potential of the steel rod E_t, at given time t, can be expressed as:

$$E_t = I_{app}\left[\ R_p\left\{\ 1-\left(\exp(-t/R_pC_{dl}\right)\right\}+R_\Omega\right] \qquad \text{.....(5)}$$

where: R_p is the polarization resistance
C_{dL} is the double layer capacitance
R_Ω is the ohmic resistance

When t »»»» ∞, $1/\left(\exp(\quad t/R_pC_{dl}\right)$»»»»0, E_t »»»E_{max}

∴ equation (5) reduces to:

$$E_{max} = I_{app}\left[R_p(1-0)+R_\Omega\right]$$

$$E_{max} = I_{app}\,R_p + I_{app}\,R_\Omega \qquad \text{.....(7)}$$

Subtracting (5) from (7) leads to:

$$E_{max}-E_t = \cancel{I_{app}.R_p} + \cancel{I_{app}.R_\Omega} - \cancel{I_{app}.R_p} + I_{app}.R_p\,e^{\left(-t/R_pC_{dL}\right)} - \cancel{I_{app}.R_\Omega}$$

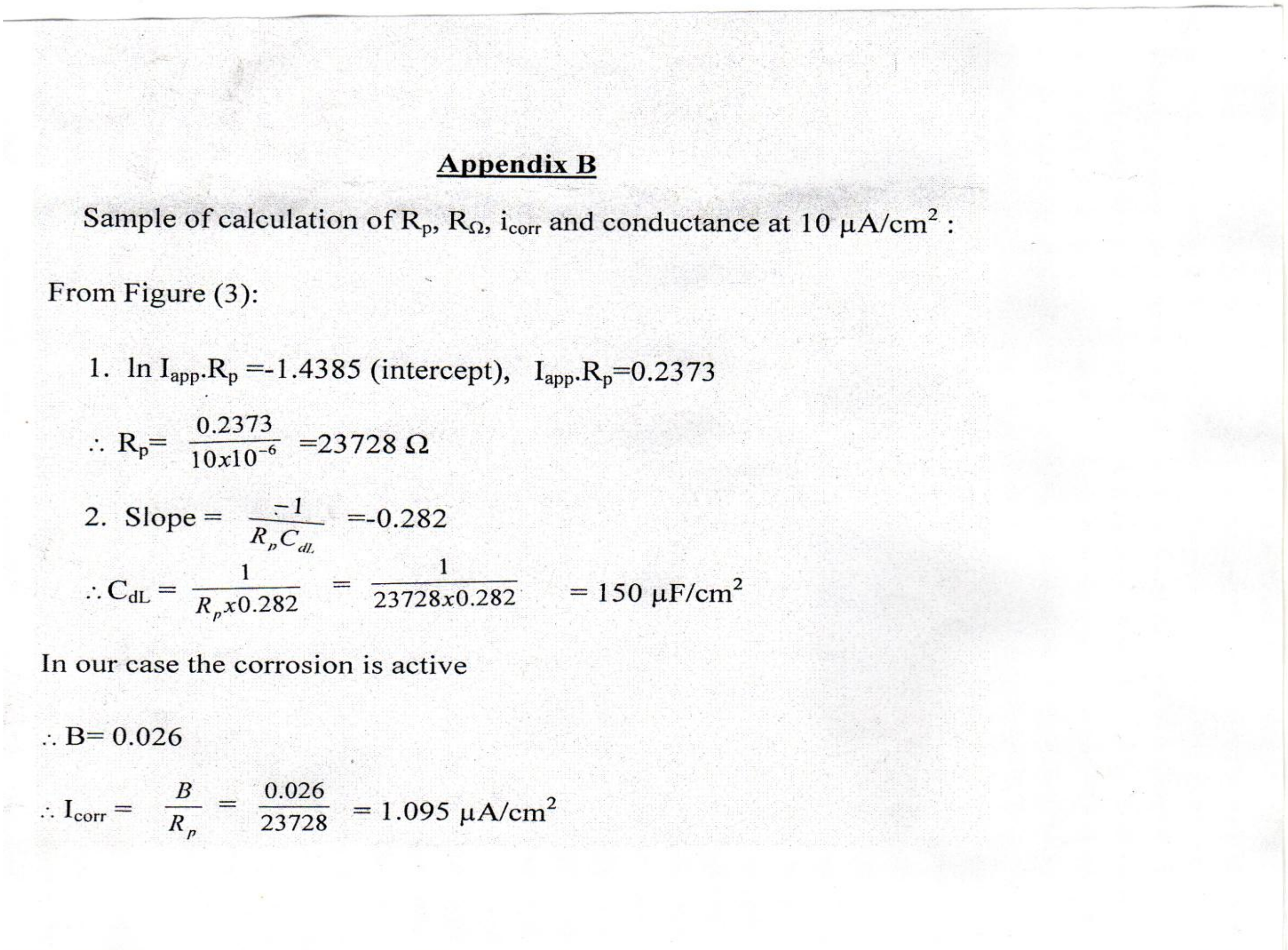
$$\therefore E_{max}-E_t = I_{app}.R_p\,e^{\left(-t/R_pC_{dL}\right)} \qquad \text{.....(8)}$$

linearization eq$^{\underline{n.}}$ (8) by taking ln of both sides:

$$\ln(E_{max}-E_t) = \ln.\ I_{app}.R_p - \frac{t}{R_pC_{dl}} \qquad \text{......(9)}$$

Plotting ln(E_{max}-E_t) vs' t will lead to:

Intercept= ln $I_{app}.R_p$ and Slope= $\frac{1}{R_pC_{dL}}$



Appendix B

Sample of calculation of R_p, R_Ω, i_{corr} and conductance at 10 $\mu A/cm^2$:

From Figure (3):

1. $\ln I_{app}.R_p$ =-1.4385 (intercept), $I_{app}.R_p$=0.2373

$\therefore R_p= \dfrac{0.2373}{10x10^{-6}}$ =23728 Ω

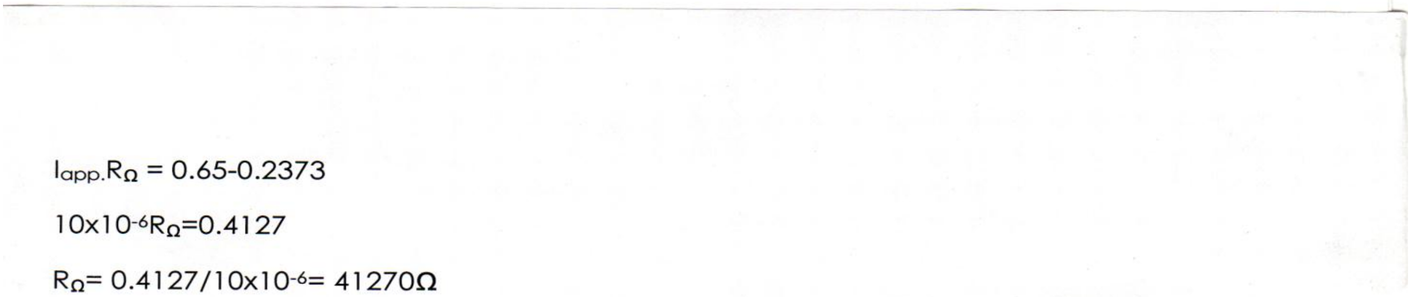
2. Slope = $\dfrac{-1}{R_p C_{dL}}$ =-0.282

$\therefore C_{dL} = \dfrac{1}{R_p x0.282} = \dfrac{1}{23728x0.282} = 150\ \mu F/cm^2$

In our case the corrosion is active

$\therefore$ B= 0.026

$\therefore I_{corr} = \dfrac{B}{R_p} = \dfrac{0.026}{23728} = 1.095\ \mu A/cm^2$



$I_{app}.R_\Omega$ = 0.65-0.2373

$10x10^{-6}R_\Omega$=0.4127

R_Ω= 0.4127/10x10^{-6}= 41270Ω