SURFACE TREATMENT EFFECTS ON THE CORROSION OF REINFORCED STEEL IN CONCRETE EXPOSED TO DRY CONDITION

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ABSTRACT

The destroying of Tafel region in many cases is not due to complication with mass transfer , but due to IR – drop effect specially in dilute solutions (i.e., of high resistivity) . Accordingly, the corrosion behavior of reinforcement in reinforced concrete was investigated using electro – chemical measurements. The work was carried out with small steel rods: cleaned and previously oxidized embedded in resistance Portland cement concrete cylinders exposed to dry conditions. In this investigation a theoretical model equation has been adopted including IR- drop term:

$$\Delta E = \Delta EA + R\Delta i = -bc\log icorr. + bc\log/\Delta i/ + R/\Delta i/$$

In order to determine corrosion parameters of system investigated (i.e., icorr., bc, and Rc. A) equation above was based on the analysis of cathodic Polarization curve free from mass transfer effect .It has been found that the corrosion current of pre- oxidized steel is higher than the cleaned one , and this corrosion rate is concrete contaminant & time of exposure dependant, because of the importance of electrical resistance of concrete & its relationship to the corrosion rate of reinforcing steel. An attempt was made to find this resistance from the IR-drop term in the above mentioned equation.

الخلاصة

ان اختفاء او عدم ظهور مناطق "تافل" في منحنيات الاستقطاب التي تربط فرق الجهد بالتيار في كثير من الحالات ليست بسبب التداخل مع انتقال المادة عند حدوث عملية التآكل ولكن بسبب التداخل مع مقاومة المحلول او الوسط الناقل للتيار خاصة في المحاليل المخففة (ذات المقاومة العالية). استناداً لهذا تم دراسة عملية تاكل الحديد المسلح في الخرسانة المقاومة وباستعمال الطرق الكهروكيميائية. تم العمل باستعمال نماذج من الحديد المسلح قسم منها منظف والقسم الاخر متاكسد اصلاً تم وضعها في السمنت المقاوم بعد صبها في قوالب اسطوانية الشكل وتم عرضها للظروف الجوية الجافة. اعتمدت المعادلة التالية:

$$\Delta E = -bc\log icorr. + bc\log \Delta i + R\Delta i$$

لايجاد متغيرات التاكل. ان النتائج التي تم الحصول عليها تثبت ان معدلات التاكل للنماذج المتاكسدة سابقاً اعلى من معدلات التاكل للنماذج النظيفة بالاضافة الى ان معدلات التاكل تعتمد على محتويات السمنت والزمن. جرت محاولة لايجاد مقاومة السمنت كوسط ناقل من المعادلة المعتمدة وتحليلها احصائياً.

KEY WORDS

Total and activation overpotential, corrosion rate, Ohmic resistance, oxidized and cleaned steel, electric resistance.

INTRODUCTION

Under most operating conditions concrete offers a high resistance to the passage of current to or from embedded steel due to controlling effects which are electrochemical rather than physical. The resistance of the concrete is, by ohms law, equal to the slope of the voltage – current curve, that is R= E/I.

It is a fundamental concept of electrochemistry that the transfer of electricity between an electrolyte and metal electrode occurs through chemical reactions at the electrode surface. At an electrode from which current discharges (the anode) the chemical reactions which occur release electrons. Conversely, at a current- collecting electrode (the cathode), electrons are used up. An earlier study of the literature revealed that the most widely accepted method for detecting corrosion in concrete is "stratfulls technique" of mapping the half cell potential of steel from the surface of the concrete (Stratfull, 1957) .This approach , does not reveal information on the rate of deterioration . Other useful techniques were used in measuring the rate of corrosion of steel in solutions of high pH and concrete slurries, in a laboratory setting, but data evaluation becomes difficult when applied to steel in concrete {Dawson, 1978}. The observed current necessary to change the corrosion potential of a metal which is directly related to the rate of corrosion of the metal in the electrolyte, is the basis of determination of corrosion rate from recorded polarization curves and data .Many techniques of polarization have been used previously, they differ only in how this change in potential is achieved.

1- For small values of overpotential, Stern and Geary {Stern, 1957} consider the slope of the overpotential , ΔE, versus applied current , I, is related to the corrosion current, Icorr., by their relation :

$$(dE/dI)_{E\Rightarrow 0} = \frac{babc}{2.303(ba+bc)Icorr.} \qquad (1)$$

where ba & bc are the anodic and cathodic tafel slopes respectively .

2- Schwerdtfegers empirical {Schwerdtfegr, 1952} determination of the corrosion current, Icorr; the technique requires that the polarization curve cover an overpotential of ± 100mv, so that the change (i.e., breaks) in polarization curve may be observed. The corrosion current is then calculated from the following equation:

$$Icorr. = \frac{Ip.Iq}{Ip+Iq} \qquad (2)$$

where Ip and Iq are the cathodic and anodic corrosion currents found at the breaks points.

3- Barnartt three points methode {Barnartt, 1970} , in this technique three overvoltage/current data points are measured along the polarization curve , and from this , ba,bc and Icorr . are calculated (i.e,for first overpotential ΔE ,the 2nd and 3rd are 2ΔE &-2ΔE respectively) .The resulting currents at each potential are substituted into the ratios:

$$r1=I(2\Delta E)/I(-2\Delta E);\ r2=I(2\Delta E)/I(\Delta E) \qquad (3)$$

which in turn , r1and r2 related to each other leading to a quadratic equation in which its solution yielding the relations that allow to solve ba , bc &Icorr.

4- A computer analysis of polarization data developed by Mansfeld {Mansfeld, 1973}, is another technique in which the computer makes a best fit analysis to theoretical curves generated for different values of Tafel slopes and in this way ba, bc and Icorr. are found .

The aim of the present investigation is to find the corrosion rate , cathodic Tafel slope (bc) and the ohmic resistance , through analysis of the cathodic polarization curve representing the cathodic reaction of reinforced steel in concrete which is thought to be complicated with IR – drop and according to equation proposed.

EXPERIMENTAL WORK

Materials and Procedure

Steel specimens for this study were made from 1.2 cm outside diameter carbon steel rods, 10 cm long (The chemical analysis of steel is given in **Table (1)**. Two types of different surface treated rods , were used in this investigation(i.e.,cleaned and previously oxidized) . **Fig. (1)** illustrates the concrete sample of cylindrical geometry and the placement of a single specimen within the casting. The composition ratio of the concrete was:

1 part cement ,0.5 parts water , 1.5 parts sand, 3 parts gravel , max. 5 mm diameter. The chemical analysis of portland cement used in this study is given in **Table (2)**. After casting, the concrete samples were cured for 28 days , keeping in mind that the concrete surface from which the steel specimen exits from the concrete was coated with silicone base rubber to reduce the corrosion effects at that interface . After curing the samples were exposed to atmosphere in laboratory air for 6 months (i.e., from July to December) **Fig.(2)** shows a simplified form of the circuit used for polarization studies in concrete. The polarization technique employs a three electrode system having one electrode as the steel specimen under study , a second electrode serving as a voltage reference , and a third electrode from which current is impressed on the specimen(i.e., the counter electrode in this case was stainless steel container holding the concrete sample). The type of reference electrode used in this study is saturated standard calomel electrode, contact is made to the concrete cylinder through a small wetted sponge located at the concrete surface directly above the steel specimen being polarized, the sponge is wet with a tap water.

Results and Discussion

Typical corrosion potential measurements from different samples containing pre- oxidize and cleaned electrodes are shown in **Fig . (3)**, as a function of time .As can be seen , the potential data showed a pronounced fluctuation during the first (12) weeks of exposure to dry conditions for the cleaned electrode ,followed by a regular variation toward the less negative values , until the steady value was practically attained . Results from previously oxidized electrode, showed a different behavior. It is clear from the curve, a trend of increasing, through a regular and very small fluctuation, generally toward positive potentials could be observed through out the experimental period. This is an indication of better stability of pre- oxidized electrode compared with the behavior of the cleaned electrode especially during the first three months, which is attributed to the anodic dissolution of the embedded clean steel surface, leading to pitting and / or general corrosion. **Figs.(4and 5)** gives the anodic and cathodic potentiostatic polarization curves for the portland cement concrete samples containing pre- oxidized and cleaned electrodes which had been exposed to dry conditions (after removed from curing water) for 180 days respectively.

The anodic and cathodic polarization curves for pre- oxidized steel shown in **Fig. (4)** indicate that the cathodic and anodic current density are time of exposure dependant . Also it can be seen that the current decreased as the time of exposure increases. This can be explained by retardation of the corrosion reaction by the oxide passive film presence previously. **Fig.(5)** shows the relationship between the potential & the current density for a cleaned specimen embedded in the concrete; the results of this leads to the following:

1- The anodic & cathdic current density after 4 weeks is the lowest and its increased with increasing time of exposure generally.

2- The corrosion potential shifts to more negative values (i.e., active direction) during the first 3 months , then return back to its initial value within the remaining experimental period . This can be explained and indicated that the clean steel corrodes sharply during the first half of the experimental period by the preferential adsorption of chloride ions and other effects in its environment.

3- The anodic polarization curves indicated to some extend that the clean steel passivates in the concrete sample and the passivity of steel was maintained at least during the experimental period.

The unknown parameters, Icorr , bc & R were obtained using a least square fit . For all cases the correlation coefficient was>0.98 , indicating a good fitting of equation proposed to the experimental data . It was assumed that the applied ΔE (E- Ecorr) included, in addition to activation polarization , an IR drop term :

$$\Delta E = - bc \log icorr . + bc \log ic + R\, ic$$

The following procedure was used : The cathodic polarization curves of figures (4 & 5) were assumed to be complicated with IR drop,neglecting the reverse anodic current (i.e., Δi = ic) . (15) data points were extracted from the cathodic polarization curve for fitting by the method of least square with ΔE values spaced equally at 10 mv starting from ΔE = 50 mv from the Ecorr. .The corrosion parameters determined by the above procedure are shown in **Table (3).**

The corrosion currents varied with time.**Fig. (6)** shows a graphic presentation of results from 2 weeks –up for preoxidized and cleaned rods. In the case of cleaned speciemen at the beginning some fluctuation can be observed compared with the preoxidized one. Generally, corrosion current from preoxidized material were higher than attained for cleaned bars.

Costa,et.al{Costa, 1990} in their study of the effect of fly ash on the corrosion of steel in concrete concluded that the corrosion of preoxidized steel in concrete is higher than that of non- oxidized one & is concrete composition dependent.

These differences in corrosion rate of the preoxidized & cleaned rods were initially more important, but they diminish with time after about 10 weeks, it was found that for both types the corrosion rate increases steadily with time,but generally the corrosion rate of cleaned specimen was in a trend of less corrosion rate. Its clear from the results of this investigation that neither preoxidation inhibited attack,nor no preoxidized exhibit excessive corrosion,but the results suggest that in both cases the regime of protection was achieved for at least the experimental period . [Lato, 1989 and Christopher, 1989]. Rodriguez et. al. [Mark, 2002] in 1995 report that rates less than 0.2μA/cm^2 indicate reinforcement in the passive condition, values up to 0.5μA/cm^2 indicate low to moderate rates; values in the range of 0.5μA/cm^2 to 1.0μA/cm^2 indicate moderate to high rates. Values greater than these are indicative high corrosion rates. Its important to mention here that the approach used to find corrosion parameters included IR-drop term designated by R(ohm.cm2)is not valid for polarization curves affected by diffusion or specific adsorption processes which is in excellent agreement with the conditions of this study {Kajimoto, 1985}.**Table(3)** shows the values of electric resistance of concrete reinforced with both pre-oxidized & clean steels(i.e.,IR drop term in ohm.cm2 found by the method of least square was divided by the surface area of reinforced steel embedded in the concrete,$A=\pi dl=1.2*3.14*8=30.15$Cm2).The relationship that was found between the concrete electrical resistance & time of exposure in dry conditions is shown in **Fig.(7)**.According to this figure,the distribution of electric resistance of pre-oxidized & cleaned air exposure test specimens with a coverage of 1.9 Cm had irregular peaks & valleys,but this irregularity is more pronounced in cleaned specimen than in the pre-oxidized one. The cause of such irregularity can be attributed to the initial non-uniformity of the steel surface which causes a difference in the permeation of the concrete contained corrosive ions or moisture from the outside & then an irregularity in the distribution in the electric resistance to produce a concentration cell of ions etc.on the surface of reinforced steel {Mori, 1975}. The fact that all the results were not exactly the same should come as no surprise.Small differences that can

not be controlled,such as small variation in metal composition or location of the sample in the container besides the actual surface treatment of steel samples used , cause the individual results to differ.Compairing the two-series of electrical resistance observations of concrete was a problem occurs in this study.From statistical point of view it was decided to state whether there is any significant difference between them.This problem was solved using the t-test to establish a confidence interval for the difference between two means.The appendix shows the best estimate of the intervals in which 95% of the time the population mean of the electrical resistance of concrete embedded by both steels are :
For cleaned steel: 7800.3 ± 3171.8 Ohms
For pre- oxidised steel: 3177 ± 1339 Ohms
And with 95% confidence, the difference in the two means falls between
2408.9 and 6837.8 Ohms.

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APPENDIX

Columns A & B represent the concrete electric resistance data in (ohms) obtained by equation adopted for cleaned & pre-oxidized steel surface respectively. The best estimate of the true population mean for each type is required, besides establishing a 95% confidence interval for the difference between the two means [Bennett, 1989].

Cleaned steel, A	Pre-oxidized steel, B
825	907
9410	2434
11312	1479
5822	2679
6600	1921
9514	7882
6954	3357
16814	2824
7761	404
2991	5004
	5153
	4074

$nA=10$ $\qquad$ $nB=12$

$\bar{X}A=7800.3$ $\qquad$ $\bar{X}B=3177$

$S^2_A=19662555$ $\qquad$ $S^2_B=4404033.6$

$n_A-1=9$ $\qquad$ $n_B-1=11$

$tc=2.262$ $\qquad$ $tc=2.210$

$$95\%\ c.l=7800.3 \pm 2.262\sqrt{\frac{19662555}{10}} = 7800.3 \pm 3171.8$$

$$95\%\ c.l= 3177 \pm 2.21\sqrt{\frac{4404033.6}{12}} = 3177 \pm 1339$$

∴ 95% of the time the population mean, μ is inside the interval

7800.3 ± 3171.8 for concrete embedded by cleaned steel & 3177 ± 1339 for concrete by pre-oxidized steel.

The best estimate of difference is calculated from[Nennett, 1989]

$$(\bar{X}_A - \bar{X}_B) \pm t_c\sqrt{\frac{(nA+nB)}{nA*nB} * S_p^{\ 2}}$$

where s2p,the pooled variance ,is calculated from weighted average of the individual variance:

$$S^2{}_p = \frac{(nA-1)S^2{}_A + (nB-1)S^2{}_B)}{(nA+nB-2)}$$

∴ for tc (n_A-n_B-2) at the 95% level is 2.086.the 95% confidence interval [Bennett, 1989].

for the difference between the two means is :

$$(7800.3-3177) \pm 2.086\sqrt{\frac{22}{220}*11270300}$$

$$= 4623.3 \pm 2214.5$$

∴ It can be stated with 95% confidence that the difference in the two means falls between 2408.9 & 6837.8

Table (1) chemical analysis of reinforced steel used in present study .

Component	C	Si	Mn	PO_4	Cr	Ni	Al	Cu	Fe
% Wt.	.1	1.5	.8	3.7	.06	.1	.01	.34	remainder

Table (2) The chemical analysis of resistance portland cement used

Compound	L.O.S.	SiO_2	R_2O_3	CaO	MgO	SO_3
% Wt.	1.29	19.99	9.55	63.51	3.61	1.95

Table (3) Corrosion parameters of the surface treated reinforced steel in concrete exposed to a dry condition at different times of exposure .

Time of exposure	Corrosion parameters							
	Pre-oxidized				Cleaned			
	Icorr	*bc*	*R*	*ER*	*Icorr*	*bc*	*R*	*ER*
Weeks	*µA/cm²*	*mv*	*Ohm.cm²*	*ohm*	*µA/cm²*	*mv*	*Ohm.cm²*	*ohm*
2	$1.73*10^{-1}$	220	27356	907	$2.29*10^{-2}$	148	24877	825
4	$7.3*10^{-2}$	135	73421	2434	$7.09*10^{-2}$	252	283828	9410
6	$6.64*10^{-2}$	139	44618	1479	$2.89*10^{-2}$	386	341180	11312
8	$6.96*10^{-2}$	158	80785	2679	$5.84*10^{-2}$	424	*	*
10	$3.99*10^{-2}$	135	57930	1921	$2.37*10^{-2}$	202	175594	5822
12	$4.28*10^{-2}$	68	237708	7882	$3.26*10^{-2}$	248	199050	6599
14	$6.02*10^{-2}$	88	101234	3357	$4.16*10^{-2}$	227	286940	9516
16	$9.62*10^{-2}$	112	85160	2824	$4.66*10^{-2}$	476	209737	6954
18	$1.23*10^{-1}$	152	12173	403.6	$7.47*10^{-2}$	400	507116	16814
20	$1.35*10^{-1}$	49	150920	5004	$7.82*10^{-2}$	383	234068	7761
22	$7.96*10^{-2}$	527	155399	5153	$5.08*10^{-2}$	738	*	*
24	$1.65*10^{-1}$	155	122860	4074	$1.02*10^{-1}$	389	910210	2991

ER: Electrical resistance(ohm)

* Believed to be spurious result

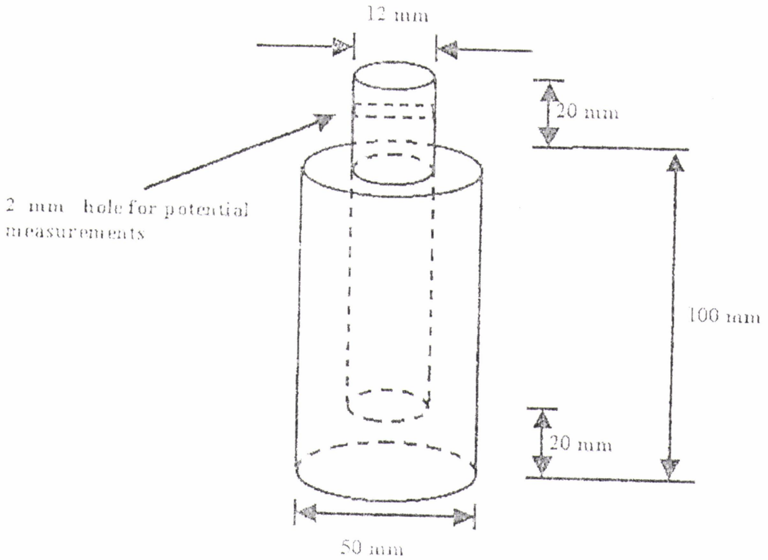

Figure (1) Concrete cylinder with single specimen reinforced steel

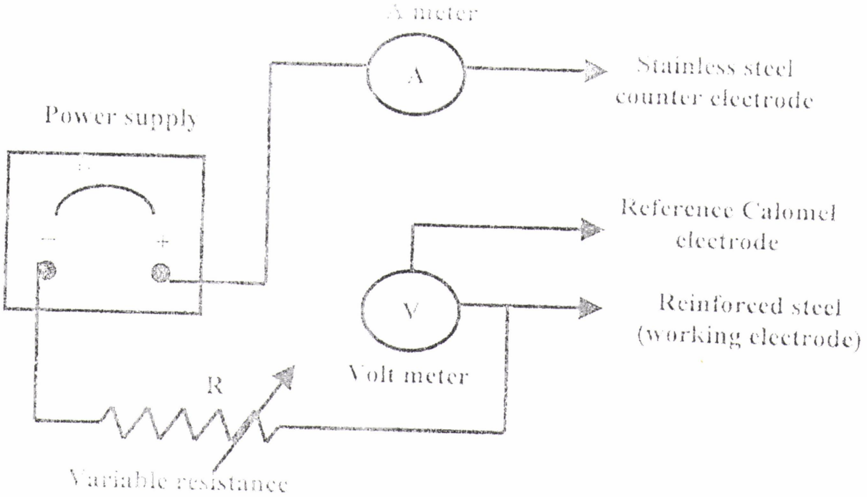

Figure (2) A simplified form of the circuit used for polarization studies in concrete.

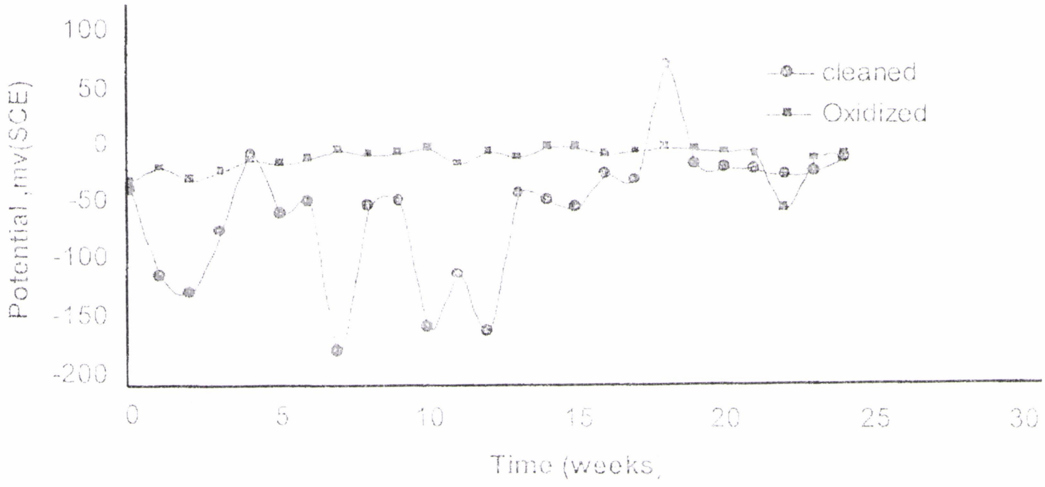

Figure (3) Variation of corrosion potential with time for oxidized and cleaned steel in concrete exposed to dry condition.

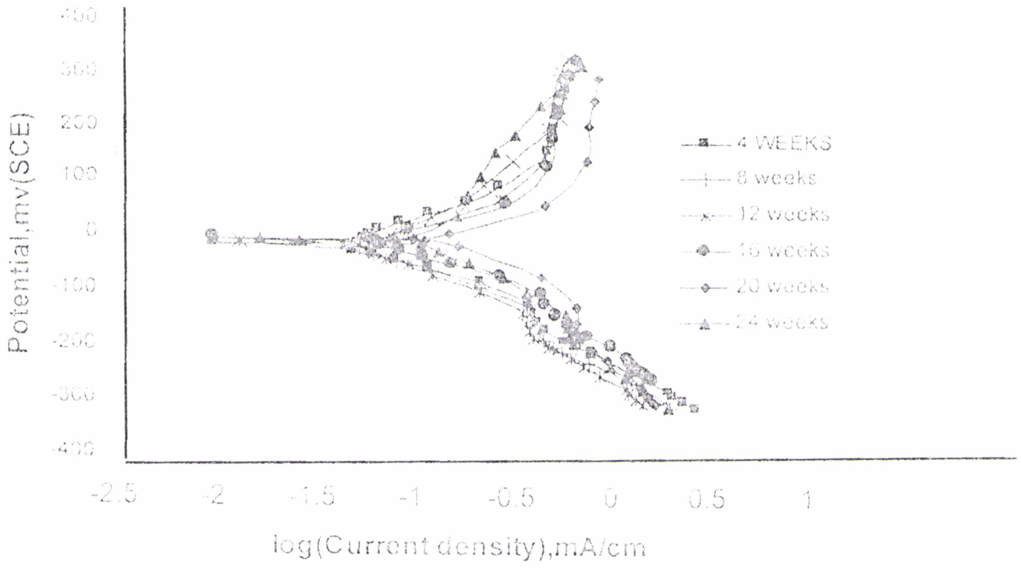

Figure (4) Anodic and cathodic polarization curves of oxidized steel in concrete sample exposed to dry condition of laboratory for 180 days.

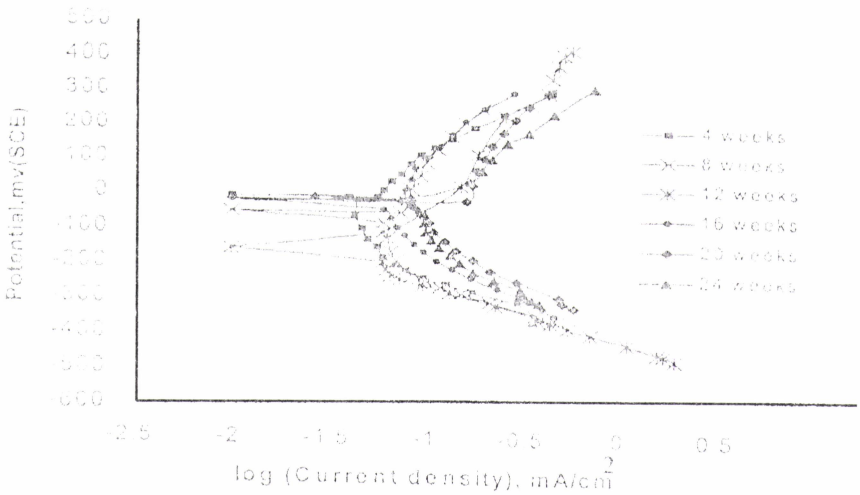

Figure (5) Anodic and cathodic polarization curves of cleaned steel in concrete sample exposed to dry condition of laboratory for 180 days.

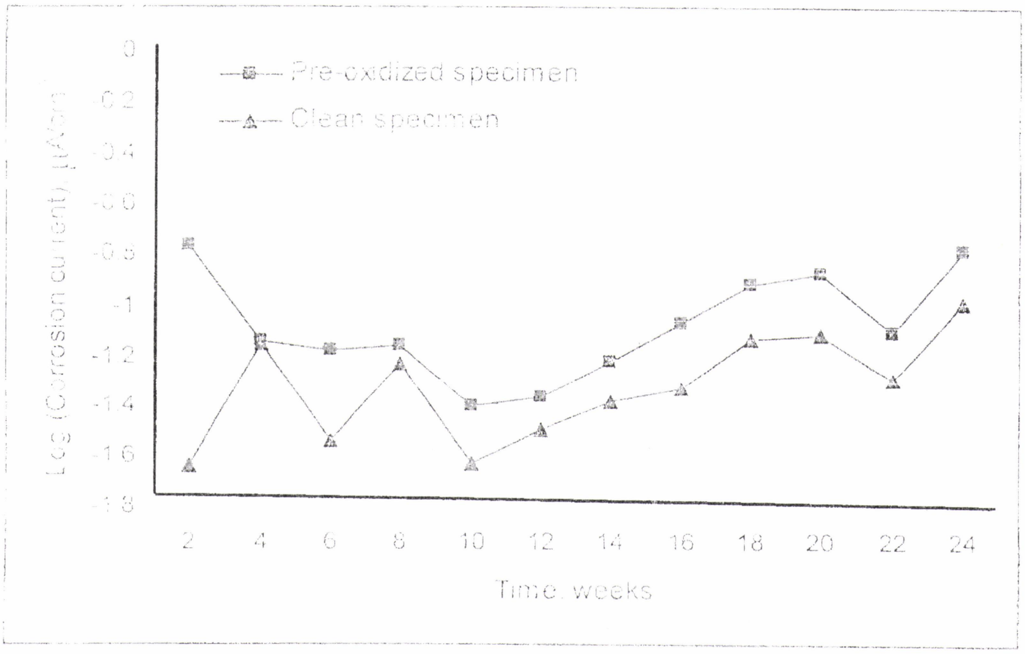

Figure (6), Corrosion current as function of time for pre-oxidized and cleaned steel embedded in concrete exposed to dry condition

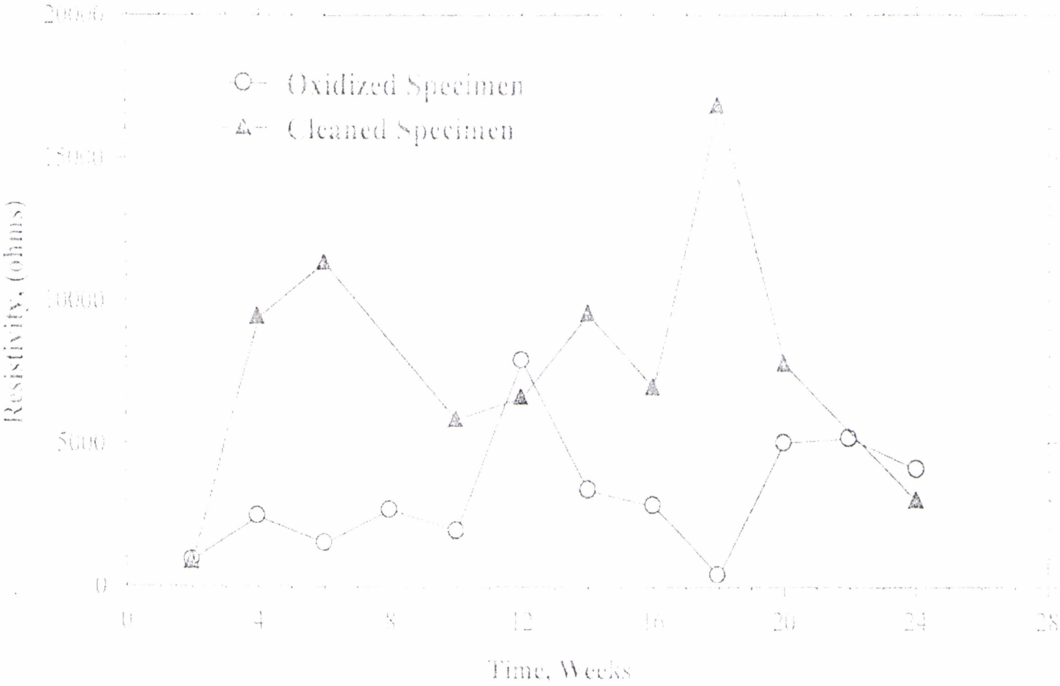

Figure (7) The relationship between the concrete electric resistance and the time of exposure at dry condition for the oxidized and cleaned reinforced steel in concrete. Working electrode area=31.15 (cm^2)