INSTANTANEOUS AND TOTAL CORROSION LOSSES BY L.P.R. DATA: MILD STEEL IN OXYGEN SATURATED SODIUM BENZOATE SOLUTIONS

G. N. Mehta and T. P. Sastry

S. V. Regional College of Engineering and Technology, Surat-395 007

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Mild steel when exposed to oxygen-saturated sodium benzoate solutions exhibits tendency for passivation. A semi-logarithmic plot of corrosion potentials (Ek) measured at different intervals of time of exposures υ_s corresponding values of Linear Polarisation Resistance (L.P.R.) gives a straight line with a positive slope equal in magnitude to Cathodic Tafel Constant (β). In this passivating system corrosion rates are very low. L.P.R. Data are used to evaluate such small corrosion rates. It has been found that the plot of (L.P.R.) R υ_s (t) time of exposure both on logarithmic scale, yields a straight line. This obseyvation is used to determine the corrosion rate at any desired instant and also to calculate the lotal corrosion loss suffered by the metal over specific period of exposure to the environment.

Sodium benzoate is very widely used as an antifreeze, preservative and anticorrosive. The role of benzoate as inhibitor of corrosion of iron is extensively studied by many investigators[1—8]. It exhibits the tendency for passivation of mild steel in presence of oxygen. This has been established because a straight line obtained in the plot of Ek Vs log R (L.P.R.) gives a characteristics positive slope, the magnitude of which is equal to β_c and the anodic tafel constant (β_a) is infinity[9—11].

Scold and Larson[12] used the polarisation data for measurement of the instantaneous corrosion rates, while Stern[13] has developed L.P.R. technique using an equation derived by Stern and Geary[14] to monitor the very low corrosion currents. This technique offers many advantages when compared to conventional weight-loss method. It is quick and reliable and can be used for 'in situ' and 'in vivo' measurements. A more convenient method known as "Transient L.P.R." technique evolved by Jones and Greene[15] is adopted in this work for calculation of instantaneous and total corrosion losses of mild steel in oxygen saturated benzoate solutions.

EXPERIMENTAL

a) **Working Electrode:** The mild steel sample was obtained through kind Courtesy of National Metallurgical Laboratories, Jamshedpur who reported the analysis as C = 0.130%, Mn = 0.50%, P = 0.065%, S = 0.03% and Si = 0.05%. A cylindrical electrode was carefully cut, machined and thoroughly polished. The area was measured and the electrode mounted on the glass electrode holder as was done by Stern and Makrides[16]. The electrode was cleaned with a lukewarm mild detergent solution under agitation, repeatedly washed with double distilled water and then immediately placed in the polarisation cell containing benzoate solution.

b) **Electrolyte:** The 0.1M sodium benzoate solution was prepared by dissolving 14.4 gms. of AR grade sample in double distilled water and then diluting to one litre. The sample (Sarabhai Merck Ltd., Baroda) is 99.00% pure and 5.8 PPM of chloride ions as well as 23.0 PPM of sulphate ions are reported to be present as impurities. This solution when transferred to polarisation cell was saturated with pure oxygen gas through a gas dispersion tube. The pH of the solution was 7.3 in the beginning and remained constant almost throughout the entire investigation.

c) **Experimental Set-up:** Two cylindrical Platinum Electrodes (Auxiliary) are placed on eitherside of the mild steel (Working) electrode in order to provide an uniform current flux. The polarisation cell is assembled as described by Green[17]. The experimental Set up is essentially similar to the one described by Sastry[9].

i) **Application of Currents:** The conventional Battery—High Resistance combination as source of constant current is substituted by a Constant Potential Source unit built with operational amplifier circuit in the Electronics Laboratory of this college. This in combination with variable precision decade resistance box provided the constant direct currents required for the investigations. The Constant Potential Source unit is capable of delivering constant potentials up to a maximum of 2.7 Volts.

ii) **Measurement of Potentials:** To measure the potentials of working electrode, an electrometer-potentiometer circuit is used. As a substitute for electrometer a pH-meter with input impedance of 10^9 ohms is used in the present work. The potentiometer

is connected in series opposition to the working cell and is so adjusted to null the deflection of the pH-meter. The potentiometer is wire wound unit (0 to 1.8 V range) with terminals for a 2 V battery, for galvanometer, for Weston Standard Cell and for experimental cell. A storage battery fully charged and then slightly discharged is used as a stable power supply for the potentiometer and only occasional calibration against Weston Cell is needed. Saturated Calomel Electrode is used as a reference electrode.

iii) **Procedural:** As corrosion currents investigated in this passivating system are very low, it takes little more time to attain steady state of the potential when D.C. current is applied to working electrode. Hence, to make the method quick, the transient linear polarisation technique described by Jones and Greene[15] is adopted to measure the values of L.P.R.

RESULTS

Mild steel (working) electrode is exposed to oxygen-saturated benzoate solutions for 102 hours. During these exposures, Ek and corresponding L.P.R. values are measured at different intervals of time of exposures and are recorded in Table-1.

TABLE-I. Corrosion potentials and Linear polarisation Resistance at different Time of Exposure. (Mild Steel in 0.1 M Sodium Benzoate Solution - Oxygen Saturated, pH - 7.3)

Exposure t (hours)	Corrosion Potentials Ek (V Vs S.C.E.)	L.P.R. Values R (Ohms)
3	— 0.125	7.2×10^4
12	— 0.005	2.0×10^5
20	+ 0.020	2.5×10^5
28	+ 0.065	4.4×10^5
45	+ 0.118	1.0×10^6
87	+ 0.170	1.4×10^6
102	+ 0.202	1.6×10^6

Finally, at the end of 102 hours of exposure, the mild steel electrode is polarised galvanostatically, first, in the cathodic and subsequently in the anodic direction in order to measure β_c and β_a. The values of β_c and β_a found from these experiments are — 0.220 volts/decade and infinity respectively.

DISCUSSION

Fig. I. shows a plot of Ek v_s log R (L.P.R.). The slope of this straight line is + 0.225 V/decade, the magnitude of which is close to the measured value (0.220 volts per decade) of β_c. This observation that the slope of Ek Vs log R plot is equal in magnitude but opposite in sign to that of β_c is an indication of passivity of the metal by the environment as shown earlier by Sastry[9,10] and by Mehta and Sastry[11]. This conclusion is further confirmed by the fact that the measured value of β_a is infinity.

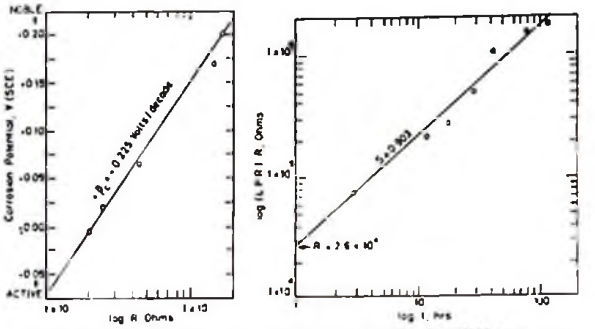


Fig 1 CHANGE OF L P R WITH CORROSION POTENTIALS (MILD STEEL IN OXYGEN SATURATED 0 1 M SODIUM BENZOATE SOLUTION pH = 7 3)

Fig 2 CHANGE OF LINEAR POLARISATION RESISTANCES (L P R) WITH TIME OF EXPOSURE (t). (MILD STEEL IN OXYGEN SATURATED 0 1 M SODIUM BENZOATE SOLUTION, pH = 7 3)

Fig. II. is a plot of log R v_s log t (time of exposure). The slope (S) of the straight line found is 0.903 and the intercept (R') on log R axis when t = 1 hour is 2.6×10^4 ohms.

(A) **Instantaneous Corrosion Loss:** Table II shows the values of instantaneous corrosion current densities (Ik) and respective weight losses calculated with the help of Stern-Geary equation given below.

$$Ik = \frac{\beta_a \times \beta_c}{2.303 \times R \times A(\beta_a + \beta_c)} \quad - - - (1)$$

Ik values, thus, calculated are converted into weight-losses (W) using Faraday's law. These are recorded in Table-II.

TABLE-II. Instantaneous Corrosion Current Density and Weight-Loss calculated from L.P.R. data. β_c = —0.220 V/decade, β_a = Infinity, A = 3.36 cms². (Mild Steel in 0.1 M Sodium Benzoate Solutions-Oxygen Saturated, pH = 7.3)

Exposure t (hours)	L.P.R. Values R (Ohms)	Corrosion Current Density. Ik (n Amps/cms²).	Weight -Loss W (mdd)
3	7.2×10^4	407	1.017
12	2.0×10^5	164	0.410
20	2.5×10^5	114	0.285
28	4.4×10^5	65	0.162
45	1.0×10^6	28	0.070
87	1.4×10^6	20	0.050
102	1.6×10^6	18	0.045

As the corrosion currents are very low, it was not possible to check the data by comparison with the conventional weight-loss measurements. For example, for a specimen corroding at 407 mA/cm² i.e. at 1.017 mdd., one has to immerse the specimen in the environment for a period of 417 days, as calculated from the empirical formula[18] $t = \frac{2000}{M}$, where t is time of exposure in hours and M is corrosion rate in (m p y) which is 0.20 corresponding to 1.017 mdd. Hence, the data obtained from our experiments were varified by running full cathodic polarisation curves and extrapolating them to Ek to figure out Ik.

(B) **Total Corrosion Loss:** (W_t). The straight line obtained in Fig. II of the plot of log R vs log t can be expressed mathematically by the following equation.

$$\log R = S \log t + \log R'$$

where S is a slope of Fig. II and R' is the Intercept on log R axis when t = 1 hour. On simplification, we get. .

$$R = R' (t)^S \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad [2]$$

As β_a is infinity, Equation [1] can be written as :

$$Ik = \beta_c / (2.303 \times A \times R) \quad \ldots \quad \ldots \quad [3]$$

Total Corrosion Current Density (Ikt) over any time (t hours) can be obtained by integration of Ik with respect to t as follows.

$$Ikt = (\beta_c / 2.303\ A) \int_{\varepsilon}^{t} dt/R \quad \ldots \quad \ldots \quad [4]$$

where 'ε' is a small number tending to zero.

Substituting the value of R as derived in eq. 2 into eq. 4, we get. .

$$Ikt = (\beta_c / 2.303 \times A \times R') \int_{\varepsilon}^{t} dt/t^S$$

$$= \frac{\beta_c \times t^{(1-S)}}{2.303 \times A \times R' (1-S)} \quad \ldots \quad \ldots \quad [5]$$

Using eq. 5 Ikt for any length of exposure can be calculated and that can be converted to total corrosion loss (Wt) in mg/dm².

For different values of t in hours, 'Wt' values are calculated and recorded in Table - III.

TABLE - III. Total Corrosion losses calculated for Different Time of Exposure. (Mild Steel in 0.1 M Sodium Benzoate Solutions - Oxygen Saturated, pH = 7.3)

Exposure t (hours)	Exposure Days	Total Corrosion Losses Wt (mg/dm²)
24	1	1.629
48	2	1.742
72	3	1.812
96	4	1.863
240	10	2.036
2400	100	2.546
3600	150	2.650
8760	365	2.887

CONCLUSION : L.P.R. Technique can be used with advantage to calculate instantaneous and Total Corrosion Loss of metals corroding at very low rates. Usefulnes of this technique is demonstrated by studying the corrosion of mild steel in 0.1 M Sodium benzoate solutions saturated with oxygen.

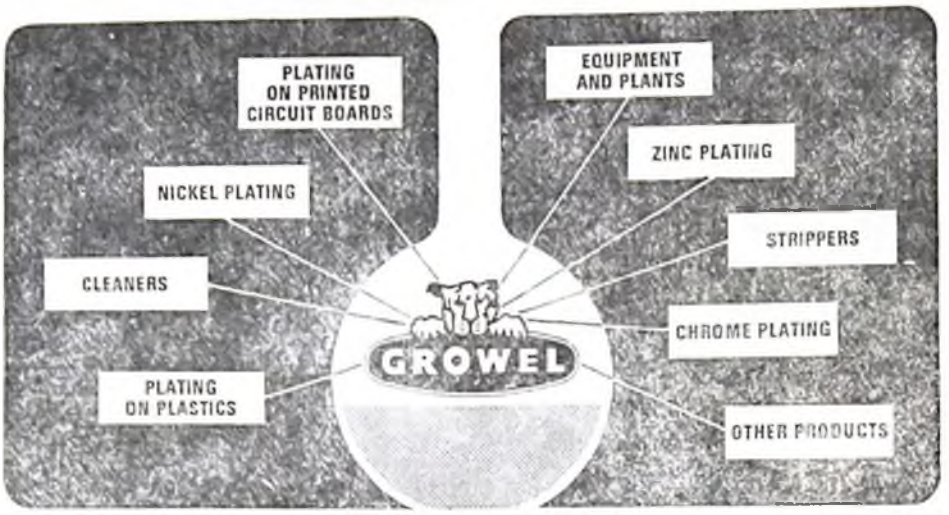
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