Corrosion rate measurements by polarization resistance on hindered surfaces exhibiting pseudo-capacitance

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Polarization resistance (R_p) measurements are of widespread use in corrosion testing. Some difficulties usually arise in studying hindered surfaces: the R_p response is markedly slowed down and affected by spurious contributions. In this work the overvoltage response to a galvanostatic step in a neutral solution was analysed. A model based on an equivalent circuit accounting for both R_p and noise is proposed and checked experimentally.

1. Introduction

The application of electrochemical methods to the study of corrosion phenomena has extended metallographic observation and enabled mechanisms to be clarified and the phenomena to be quantified. From a practical point of view, however, electrochemistry has not been fully exploited in field service as a tool to detect and follow corrosion rates in plants and installations. Many efforts have been devoted to the application of the polarization resistance method [1] which could give a direct measure of actual corrosion currents. A comprehensive review of theory and applications, together with practical difficulties, has been published recently by Pražák [2].

As the corrosion system is never in static equilibrium conditions, an outstanding difficulty encountered in polarization resistance methods arises from the corrosion potential shift during the time interval necessary to perform the measurement [2, 3]. In this work a model based on an equivalent circuit is proposed, which allows the determination of the polarization resistance from a galvanostatic pulse even in the presence of a noticeable corrosion potential shift.

2. Theory

The polarization resistance method is based on the well-known Stern and Geary equation [1], relating the slope of the $E-i$ curve, at the point of zero current, to the corrosion current:

$$\left(\frac{dE}{di}\right)_{i \to 0} = R_p = \frac{1}{2,3} \cdot \frac{b_a \cdot b_c}{(b_a + b_c)} \cdot \frac{1}{i_{corr}} \quad (1)$$

where E is the electrode potential of the corroding metal, i is the external applied current density, R_p is the polarization resistance, b_a and b_c are the anodic and cathodic Tafel slopes, and i_{corr} is the corrosion current. To determine the derivative $(dE/di)_{i \to 0}$, a galvanostatic step can be applied to the metal electrode, and the corresponding potential variation can be measured with reference to another electrode of the same metal by means of a high impedance voltmeter. The current density chosen is small enough to avoid potential variations larger than 10 mV.

In the theoretical derivation of Equation 1, it is assumed that the only anodic current present in the corrosion system corresponds to the passage of metal ions, with fixed valency, into solution. Through Faraday's equation it is thus possible to relate the measured corrosion current to the corrosion rate expressed as weight loss. In a number of corrosion systems, however, this assumption is not verified because other oxidation reactions are possible at the electrode: a common case is the coexistence of ions of the dissolving metal at two valency levels (i.e., a redox couple as Cu^+/Cu^{++} or Fe^{2+}/Fe^{3+}). The passage of an externally applied current then results in a modification of the concentration ratios of the redox couple which in turn determines the variation of the mixed potential.

When the electrolyte is not definitely acidic,

the dissolving metal surface is soon covered by corrosion product layers or films and the electrode capacity becomes very large; the time necessary for the attainment of steady state in galvanostatic step measurement increases correspondingly [4] and in the meanwhile the corrosion potential shift increases, introducing a large error in the measured ΔE.

In analysing the potential response to a galvanostatic step, the electrode-solution interfacial impedance is generally simulated by a $C-R$ parallel circuit [4] (Fig. 1a).
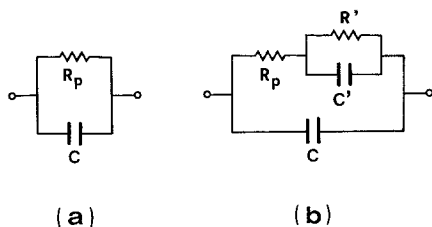

(a)   (b)

Fig. 1. Equivalent circuits of a metal/electrolyte interface.

To describe variations in potential other than that determined by the charge transfer overpotential, (η) [5], a double $C-R$ circuit can be used, as sketched in Fig. 1b, where C' is defined by:

$$\frac{1}{C'} = \frac{1}{i} \cdot \frac{dE_{corr}}{dt}. \qquad (2)$$

The potential response can be described analytically by:

$$\Delta E(t) = \eta(t) = I \cdot R_p \left[1 - \exp\left(-t/R_p C\right)\right] \qquad (3)$$

when the electrode impedance is represented by circuit a (i.e. only charge transfer overpotential η occurs) and by:

$$\Delta E(t) = \eta(t) + \Delta E_{corr}(t) = IR_p$$
$$\left[1 - \exp(-t/R_p C)\right] + IR'\left[1 - \exp(-t/R'C')\right] \qquad (4)$$

when the electrode impedance is represented by circuit b (approximate solution). The separation of η from ΔE_{corr} is possible with numerical computation when $R_p C \neq R'C'$. By means of a computer a least squares interpolation for non-linear models [6] can be applied to experimental data in order to obtain R_p from Equation 4.

A special case arises when $R_p C \ll R'C'$, so that the variation of E_{corr} with time is much slower than the variation of η. Thus, at $t \ll R'C'$, $\Delta E(t) \simeq \eta(t)$, and Equation 3 can be used. In this case it is worthwhile to obtain R_p from the graphical extrapolation [7] of experimental data plotted as $\eta(t_j + \Delta)$ versus $\eta(t_j)$, where Δ is a small time increment.

3. Experimental

Specimens of Armco iron and of an experimental steel (C 0·03, Si 0·33, Mn 2·47, Al 0·94, Mo 0·48) were allowed to corrode in a 0·5 M NaCl + 0·1 M NaHCO$_3$ + 0·03 M Na$_2$SO$_4$ freely-aerated solution at $25 \pm 3°$ C in electrolytic cells. An exposed surface of 5 cm^2 was obtained by a flat Viton gasket designed to avoid crevice corrosion.

Prior to exposure, specimens were polished down to 1 μm with diamond paste, degreased with alcohol-ether mixture, dried and weighed.

The corrosion potentials (E_{corr}) were measured and the potential responses to a galvanostatic anodic step were recorded by using a model 561 AMEL Corrograph. The applied current density was small enough to keep potential variations within 10 mV.

After 24, 72, 144, 337 and 674 h, one specimen for each steel was pickled in inhibited HCl, washed in alcohol-ether, dried and weighed again.

The consistency and validity of the R_p values obtained either from computer analysis or, under suitable conditions (i.e., for $t \ll R'C'$ when $R_p C \ll R'C'$), from the graphical extrapolation of experimental data can be tested by correlating weight losses ΔP with polarization resistance R_p by means of the relationship:

$$\int_0^t \frac{1}{R_p} \, dt = K \cdot \frac{nF}{M} \cdot \Delta P \qquad (5)$$

where M is the atomic weight, F the Faraday, n the valency of the dissolving ions and:

$$K = \frac{2,3(b_a + b_c)}{b_a \cdot b_c}. \qquad (6)$$

4. Results

Figs. 2 and 3 show two typical potential-time curves obtained in response to a galvanostatic step
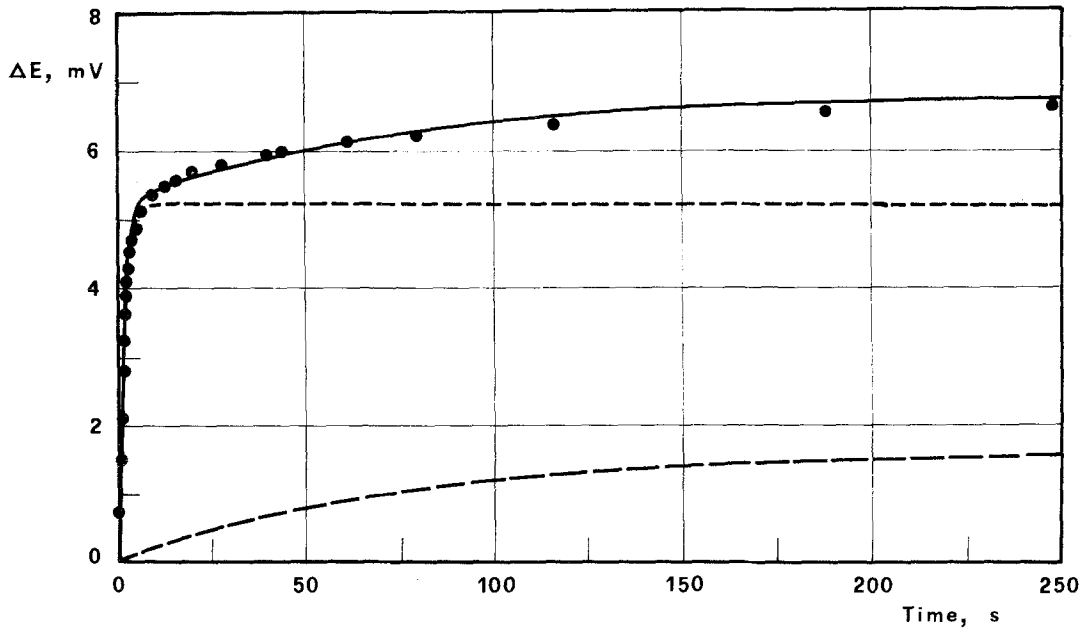
Fig. 2. Typical potential-time response to a galvanostatic anodic step ($i = 2.5\,\mu\text{A cm}^{-2}$) on the experimental steel specimen after 94 h of free corrosion (experimental dots). Solid line is the computer interpolation according to Equation 4. Dashed lines are the partial contributions to Equation 4: --------- true charging curve; ———— noise function.
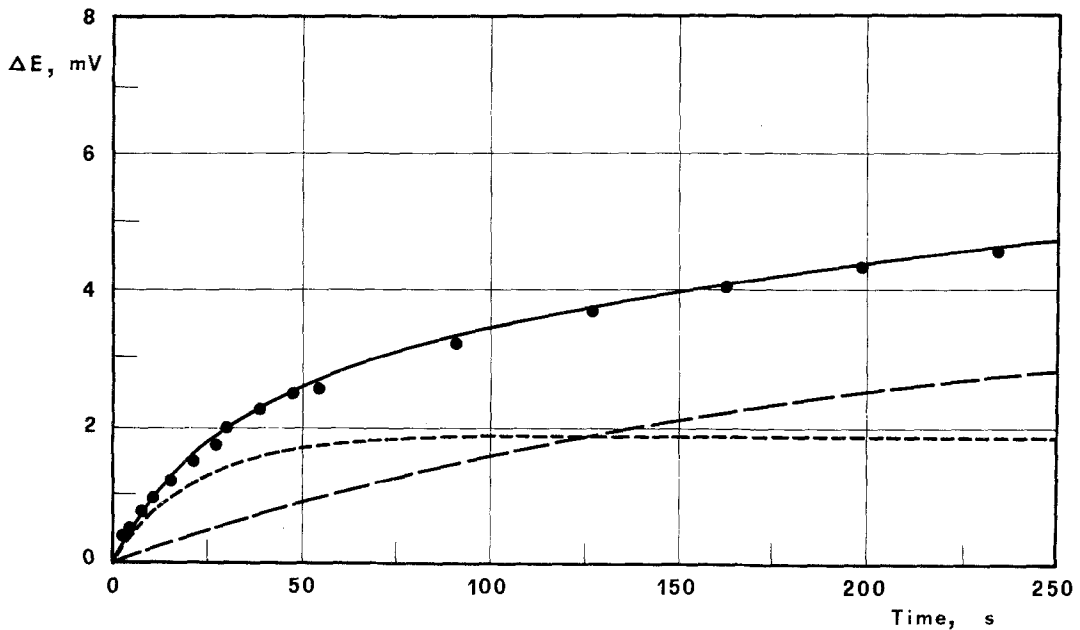

Fig. 3. Typical potential-time response to a galvanostatic anodic step ($i = 5\,\mu\text{A cm}^{-2}$) on the ARMCO iron specimen after 245 h of free corrosion (experimental dots). Solid line is the computer interpolation according to Equation 4. Dashed lines are the partial contributions to Equation 4: --------- true charging curve; ———— noise function.

Table 1. Calculation of parameters of Equation 4 from experimental data

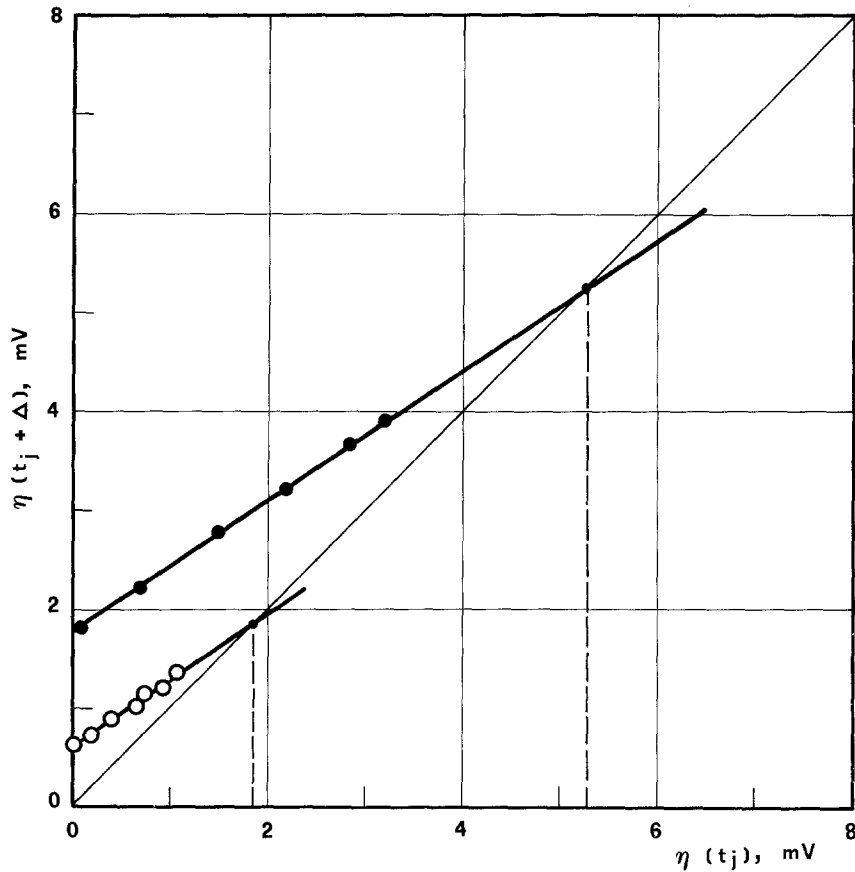| Parameters	Experimental steel after 94 h (Fig. 2)	ARMCO iron after 245 h (Fig. 3)
$R_p (\Omega \, cm^2)$	2100	380
$C(mF \, cm^2)$	0·79	58
$R'(\Omega \, cm^2)$	650	800
$C'(mF \, cm^2)$	122	270
Applied $i(\mu A \, cm^{-2})$	2·5	5

Fig. 4. Graphical extrapolation of two charging curves: ● experimental conditions as in Fig. 2; ○ experimental conditions as in Fig. 3.

on experimental steel after 94 h and on Armco iron after 245 h respectively: the first curve is an example of a rapid attainment of the stationary state, while the second one shows a sluggish potential variation.

From application of the non-linear least squares method [6], a set of parametric values is calculated in both cases (Table 1) considering each

recorded curve as the sum of two partial curves, according to Equation 4. The partial curves plotted in Figs. 2 and 3 have been calculated from the parameters of Table 1.

As the parameters of Table 1 indicate $R_p C \ll R'C'$ in both cases, the R_p values can be also obtained from the graphical extrapolation of the very initial part (i.e., $t \ll R'C'$) of the potential
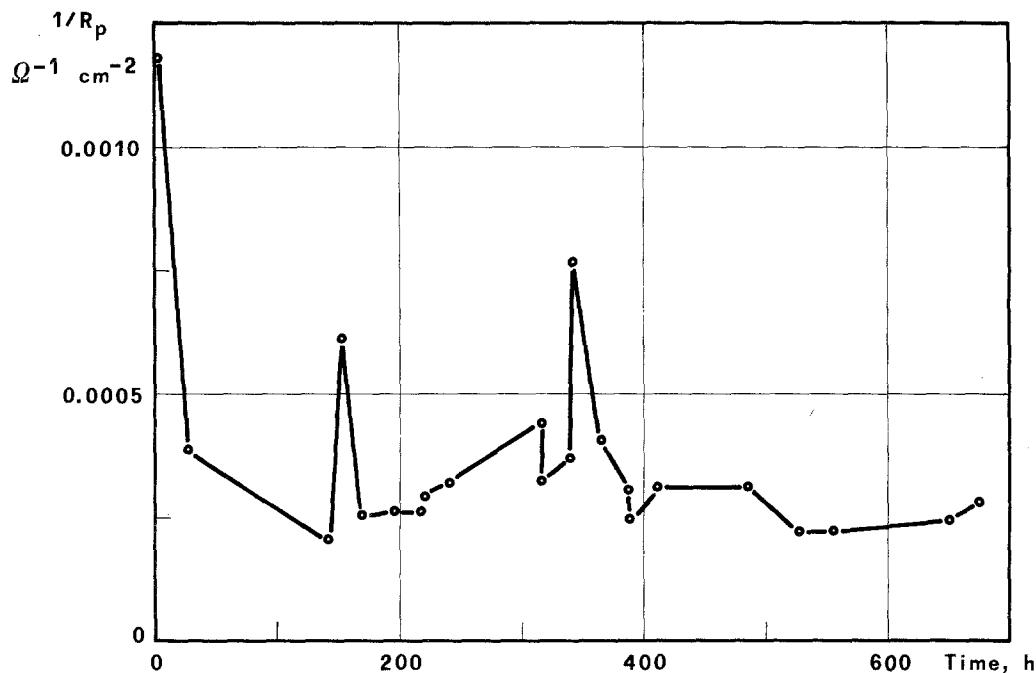
Fig. 5. Typical plot of $1/R_p$ versus time for the experimental steel specimen through 674 h of corrosion.

rise due to a galvanostatic step. For this purpose the experimental response is plotted as $\eta(t_j + \Delta)$ versus $\eta(t_j)$, where Δ is a small time increment; the intersection of this plot with the 45° line gives the asymptotic value IR_p [7] and therefore R_p.

In Fig. 4 the graphical extrapolation is applied to the experimental data of Fig. 2 and 3; R_p values of 2100 and 370 $\Omega\,cm^2$ are obtained, in good agreement with those of Table 1. In order to test more thoroughly the validity of the assumption necessary for the graphical extrapolation (i.e. $R'C' \ll R_p C$), the corrosion kinetics of experimental steel specimens were followed.

In Table 2, calculated values of $R_p C$ and $R'C'$ are reported as a function of corrosion time, together with values of R_p obtained either by means of a computer or through graphical extrapolation. The results show that in general, for this corrosion system, the two exponential functions of Equation 4 are distinguishable and the graphical extrapolation is applicable; the extrapolated values are greater than the calculated ones by less than 10%.

A typical plot of $(1/R_p)$ versus time, (experimental steel), is shown in Fig. 5. Integration of such plots, obtained on each specimen, is

compared with weight loss determinations in Figs. 6 and 7 for experimental steel and Armco iron respectively. The correlation coefficients result was found to be 0·9982 and 0·9943. From the slopes of the straight lines of Figs. 6 and 7, respectively 1·69 × 10⁵ and 1·89 × 10⁵ s $\Omega^{-1} . g^{-1}$, the value of K can be obtained through Equation 5: thus, assuming n and M equal for both steels, K is 54 V^{-1} for the experimental steel and 49 V^{-1} for Armco iron. Such values are consistent with the theory as shown in the Stern and Weisert diagram [8] $(1/R_p$ versus weight loss rate), they fall within the theoretical lines described by $b_a = 0·06$ V, $b_c = 0·10$ V and $b_a = 0·06$ V, $b_c = \infty$, as shown in Fig. 8. Such agreement with the theoretical prediction confirms the validity of the proposed model and the consistency of the method used to separate the polarization resistance from spurious contributions.

5. Conclusions

When the polarization resistance method is applied to a metal electrode corroding in film-forming environments, a practical difficulty arises from the long time necessary to obtain a measurable steady

Table 2. Comparison between computer and graphical analyses of experimental data

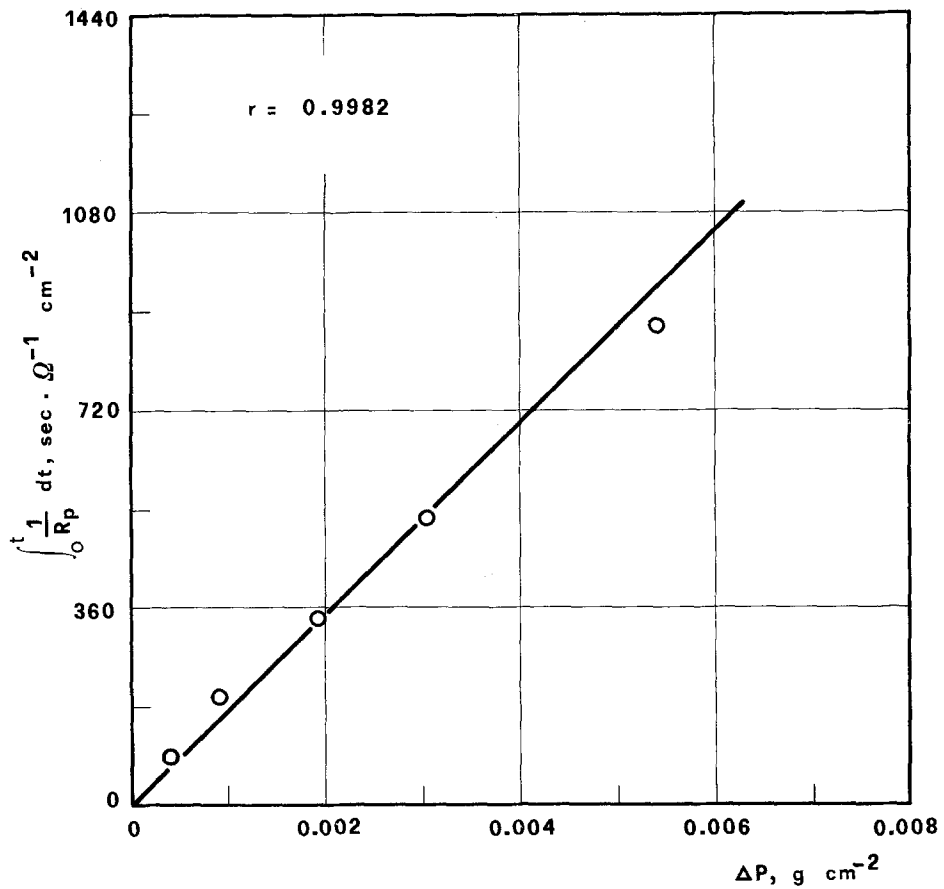| Corrosion time (h)	$R_p C$ (s)	$R'C'$ (s)	R_p (comp. analysis) (Ω cm^2)	R_p (graph. analysis) (Ω cm^2)
4	0·95	59·5	1060	1100
6	0·95	56·1	1640	1800
21	1·69	293	4250	4500
56	0·81	203	1190	1160
95	1·18	118	1300	1400
116	1·51	1008	2640	2600
245	22·1	214	1980	2220
532	19·6	1364	1080	1100

Fig. 6. Integral values of $1/R_p$ plots as a function of corresponding weight losses of five experimental steel specimens, according to Equation 5.
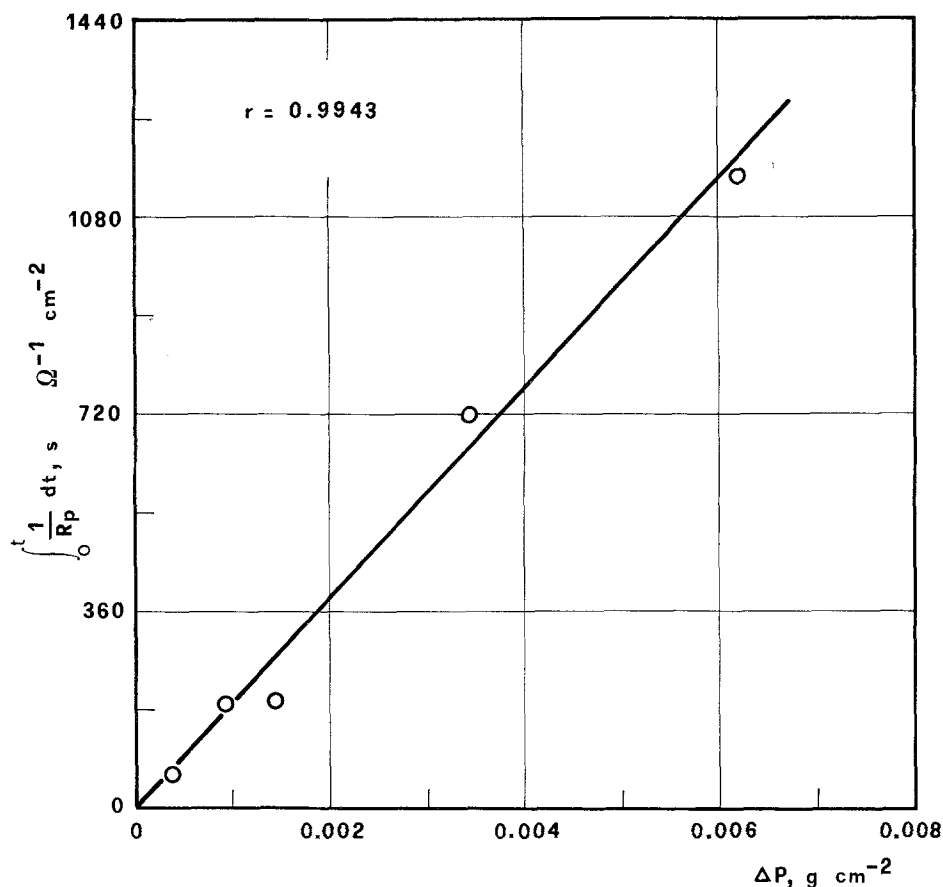
Fig. 7. Integral values of $1/R_p$ plots as a function of corresponding weight losses of five ARMCO iron specimens, according to Equation 5.

state. Sources of error are represented by free corrosion potential variation and electrode equilibria modifications.

In these cases, the electrode potential rise consequent to a galvanostatic step can be analysed in terms of two superimposed charging curves: the first one depending on polarization resistance and total electrode capacity, the second one depending on the electrode pseudo-capacity which takes into account all disturbing processes. When the time constant of the biasing curve is larger than that of the true charging curve, it is possible to calculate each curve numerically and the corresponding R_p value from the experimental potential rise.

Under favourable conditions (i.e., $R_p C \ll R'C'$), which have been found in this work, the R_p value is more easily obtainable from a graphical extrapolation of the initial part of the potential rise curve; R_p values determined in this way are within 10% of those calculated by means of the least squares method and are consistent with weight losses.

This method is now being applied extensively in the laboratory corrosion monitoring of several experimental steels for sea water service.
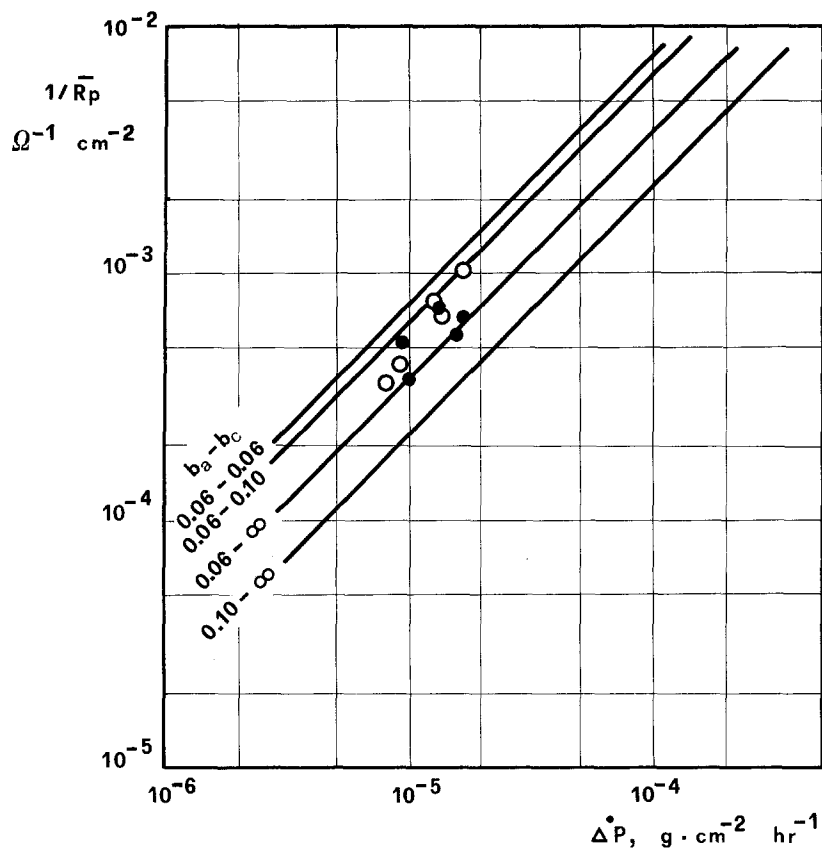
Acknowledgements

Fig. 8. Stern and Weisert-type diagram including experimental results of this work.

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