

## Applications of exponential relaxation methods for corrosion studies and corrosion rate measurement<sup>§</sup>

V LAKSHMINARAYANAN and S R RAJAGOPALAN\*†

Raman Research Institute, Bangalore 560 080, India

† Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

**Abstract.** Investigations on the use of an exponential relaxation technique for studying corrosion systems are reported. It is shown that the polarisation resistance and the double layer capacitance of corrosion systems can be obtained by the small amplitude exponential relaxation technique (SAERT). It is demonstrated, that the rate of corrosion can be measured by the large amplitude exponential relaxation technique (LAERT). This technique yields 'accelerated Tafel plot' only when the charging current is negligible, which is seldom so. Methods for correcting for double layer charging are described. Double layer capacitance as a function of potential is obtained from LAERT. Therefore it can be used for studies on inhibitors. The utility of LAERT for corrosion systems with only one of the conjugate reactions under activation control is established. The effect of series resistance ( $R_s$ ) is discussed and an *in situ* method for its determination is described. A procedure for correcting the experimental data for errors due to  $R_s$  is given.

**Keywords.** Corrosion rate; polarisation resistance; ohmic drop and double layer capacitance; small amplitude exponential relaxation technique; large amplitude exponential relaxation technique; single transient and multi transient; accelerated Tafel plot.

### 1. Introduction

Two exponential relaxation techniques were proposed by Rangarajan (1971) and Prabhakara Rao and Rangarajan (1974) for the study of electrode kinetics. One of them employed a small amplitude exponentially decaying current pulse as input such that the resulting polarisation was in the linear regime of the current-potential relationship. This was called the exponential linear relaxation technique (Rangarajan 1971). The second technique which was termed the accelerated Tafel plot (ATP) (Prabhakara Rao and Rangarajan 1974) employed as input, a large amplitude exponentially decaying current pulse to polarise the electrode to the Tafel region. This technique, for reasons put forth in this paper, would be more aptly described by the term 'large amplitude exponential relaxation technique' (LAERT).

In spite of several attractive features of these techniques, they have been seldom used for the study of corrosion systems. There is no reported work on the use of exponential linear relaxation techniques for measuring polarisation resistances ( $R_p$ ) of corrosion systems. There is one paper (Prabhakara Rao and Yegnaraman 1982) describing the use of ATP for measuring the corrosion rate ( $i_{corr}$ ) of the system, iron

<sup>§</sup> Dedicated to Prof K. S. G. Doss on his eightieth birthday

\* To whom all correspondence should be addressed

A list of symbols is given at the end of the paper

in 0.5 M H<sub>2</sub>SO<sub>4</sub>. However, the results show an anomaly, namely  $i_{\text{corr}}$  is a function of the time constant,  $\tau$ , of the exponential current signal. The present authors showed that the anomaly is due to the neglect of double layer charging current and described methods of obtaining  $i_{\text{corr}}$  uncorrupted by charging current from the potential-time transient obtained in the so-called ATP technique (Lakshminarayanan and Rajagopalan 1985). In this paper, we show for the first time, that the small amplitude exponential relaxation technique (SAERT) could be used for measuring  $R_p$  and double layer capacity,  $C_d$ , of corrosion systems. In addition, we present here the results of the study of several corrosion systems by the ATP technique and show that it gives true  $i_{\text{corr}}$  and gives information on  $C_d$  as a function of potential as well.

## 2. Theory

### 2.1 Small amplitude exponential relaxation technique (SAERT)

Using the results of Rangarajan we give below the expressions, suitably modified for the corrosion systems, which are characterised by a pair of conjugate reactions. When an exponentially decaying current input of small magnitude is applied to a corrosion system which is purely under activation control, the linearised current-potential relationship takes the form,

$$-C_d \frac{d\eta}{dt} - \frac{(\alpha_c + \beta_a)nF\eta i_{\text{corr}}}{RT} = i = \Delta I \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where  $\Delta I \exp(-t/\tau)$  represents the current input,  $C_d$  is the double layer capacitance of the corrosion system,  $\alpha_c$  and  $\beta_a$  are respectively the transfer coefficients of the cathodic and anodic conjugate reactions of the corrosion system, and  $i_{\text{corr}}$  is the corrosion rate.

The solution of (1) is given by,

$$\eta = \frac{\Delta I R_p \tau_d}{(\tau_d - 1)} \left[ \exp\left(-\frac{t}{\tau}\right) - \exp\left(-\tau_d \frac{t}{\tau}\right) \right], \quad (2)$$

where  $R_p = \frac{RT}{(\alpha_c + \beta_a)nF i_{\text{corr}}}$  and  $\tau_d = \frac{\tau}{R_p C_d}$ .

From (2) it is evident that the potential-time transient exhibits a maximum. This arises due to a time lag in over-potential ( $\eta$ ) following current ( $i$ ). We discuss below the methods of obtaining  $R_p$  and  $C_d$  from  $\eta$ - $t$  transient.

2.1a *Single transient method for measurement of  $R_p$  and  $C_d$* : For a corrosion system under activation control, the double layer charging current [ $-C_d (d\eta/dt)$ ] is zero at the maximum point and the entire current is purely faradaic. Utilising this fact it can be shown,

$$R_p = \frac{-\eta_{\text{max}}}{\Delta I \exp\left(-\frac{t_{\text{max}}}{\tau}\right)}, \quad (3)$$

where  $\eta_{\max}$  and  $t_{\max}$  are the co-ordinates of the maximum of  $\eta$ - $t$  transient.

It can also be shown for the same case,

$$T_{\max} = \left( \frac{t_{\max}}{\tau} \right) = \frac{\ln \tau_d}{(\tau_d - 1)}. \quad (4)$$

It is clear that using (3) and (4)  $R_p$  and  $C_d$  can be obtained from a single transient for a corrosion system, which is under activation control.

Another method of obtaining  $R_p$  and  $C_d$  would be by fitting a curve represented by (2) to the experimental data.

**2.1b Multi transient method for measurement of  $R_p$  and  $C_d$ :** A third method is to plot  $\eta_{\max}$  against  $i$  (corresponding to  $t_{\max}$ ) obtained from several transients and evaluate the slope ( $d\eta/dt$ ) which is equal to  $R_p$ .

All the three methods yield  $R_p$  values uncorrupted by double layer charging, since at  $\eta_{\max}$ ,  $(d\eta/dt) = 0$  and therefore the charging current is also zero whatever be the value of  $C_d$ .

Most of the systems exhibiting uniform corrosion fall into one of the following categories.

(i) Both cathodic and anodic reactions are one-step tafelium electron transfers and are under activation control.

(ii) The anodic reaction is a one-step tafelium electron transfer and is under activation control, but the cathodic reaction is partly under mass transfer control or is mass transfer limited.

$$R_p = (RT)/(\beta_a n F i_{\text{corr}}).$$

(iii) The anodic reaction is passive dissolution while the cathodic reaction is a one-step tafelium electron transfer on the passive area

$$R_p = (RT)/(\alpha_c n F i_{\text{corr}}).$$

In all these cases  $R_p$  and  $C_d$  can be measured by the small amplitude exponential relaxation technique (SAERT). In the case (i)  $R_p$  can be found by polarising in either direction. In the case (ii) it is found by polarising in the anodic direction, while cathodic polarisation is to be employed for the case (iii).

**2.1c Effect of series resistance:** The model considered above is  $C_d$  across  $R_p$ . Experimental measurement always includes a series resistance,  $R_e$ . This may have contributions from the resistance of the working electrode, resistance of electrolyte existing between working electrode and the Luggin tip. The presence of  $R_e$ , in a current controlled experiment, leads to an additional ohmic drop being included in the measured potential and hence (2) is to be modified as,

$$\frac{\Delta I R_p \tau_d}{(\tau_d - 1)} \left[ \exp\left(-\frac{t}{\tau}\right) - \exp\left(\tau_d \frac{t}{\tau}\right) \right] + \Delta I R_e \exp\left(-\frac{t}{\tau}\right). \quad (5)$$

The coordinates of the maximum of  $\eta$ - $t$  transient change due to the presence of  $R_e$ . Employing (5) it can be shown

$$T_{\max}^* = T_{\max} - \{\ln[1 + (R_e/R_p) (\tau_d - 1)/\tau_d]\}/(\tau_d - 1), \quad (6)$$

and

$$\eta_{\max}^* = \eta_{\max} \left[ \exp \left( \frac{-\ln a^*}{\tau_d - 1} \right) \right] \left[ 1 + \frac{R_e}{R_p} \frac{(\tau_d - 1)}{\tau_d} \right], \quad (7)$$

where  $a^* = R_p / \left[ R_e \frac{(\tau_d - 1)}{\tau_d} + R_p \right]$ .

$\eta_{\max}^*$  and  $T_{\max}^*$  are coordinates of the maximum of the  $\eta-t$  transient, when  $R_e \neq 0$ , and  $\eta_{\max}$  and  $T_{\max}$  are coordinates of the maximum of  $\eta-t$  transient when  $R_e = 0$ .

It is readily seen from (6) and (7) that in the presence of series resistance, it is not possible to calculate  $R_p$  from  $\eta_{\max}^*$  and  $T_{\max}^*$  if  $R_e$  is not known. Generally, in current controlled experiments, the error due to ohmic drop in  $R_e$  is easily corrected since the value of current is precisely known at each instant if the value of  $R_e$  is known. However, the real problem is in knowing the value of  $R_e$ .

The exponential relaxation technique provides an elegant method for the *in situ* measurement of  $R_e$ . When  $R_e \neq 0$ , at  $t = 0+$ , a potential jump occurs in the  $\eta-t$  transient, which is due to the ohmic drop,  $iR_e$ . From the magnitude of the potential drop,  $R_e$  can be readily calculated. Using this value of  $R_e$  recovered experimentally, the  $\eta-t$  profile can be corrected for the ohmic drop due to  $R_e$  by using the relation

$$(\eta)_t = (\eta^*)_t - R_e \Delta i \exp(-t/\tau). \quad (8)$$

This technique can therefore be used to evaluate  $R_p$  and  $C_d$  even without *a priori* knowledge of  $R_e$ .

## 2.2 Large amplitude exponential relaxation technique (LAERT)

When a current input of the form  $\Delta I \exp(-t/\tau)$ , where  $\Delta I$  is sufficiently large to keep the system in the Tafel region, is applied to a corrosion system under activation control, the resulting current-potential relationship can be shown to be

$$i = \Delta I \exp\left(-\frac{t}{\tau}\right) = -C_d \frac{d\eta}{dt} + i_{\text{corr}} \exp\left(\frac{2.303\eta}{bc}\right), \quad (9)$$

or

$$i = \Delta I \exp\left(-\frac{t}{\tau}\right) = -C_d \frac{d\eta}{dt} - i_{\text{corr}} \exp\left(\frac{2.303\eta}{ba}\right), \quad (10)$$

where  $bc$  and  $ba$  are the Tafel slopes of cathodic and anodic reactions of the corrosion system. If the charging current [ $= -C_d(d\eta/dt)$ ] is zero, then (9) and (10) become Tafel relations. Under such conditions,  $\eta-t$  transient will be a straight line in the large polarisation range, and an accelerated Tafel plot (ATP) is obtained. However, charging current is generally not zero for corrosion systems when transient methods are used for studying them. Therefore, corrosion rates calculated from the linear section of the  $\eta-t$  transient will be in error. Even when the double layer charging current cannot be neglected, it can easily be corrected using an elegant approach suggested by Rangarajan (1971) and Prabhakara Rao and Rangarajan (1974). Hence, this method is better called the large amplitude exponential relaxation technique (LAERT) rather than accelerated Tafel plot (ATP). Methods of obtaining true  $i_{\text{corr}}$  by LAERT after correcting for charging current are described below.

2.2a *Multitransient method for measurement of  $i_{\text{corr}}$* : The  $\eta$ - $t$  transient exhibits a maximum when both activation and charging are present. At  $t_{\text{max}}$ , the current is entirely faradaic since  $(d\eta/dt)$  is zero at that instant. Hence a Tafel plot free from the effects of double layer charging can be derived from  $\eta_{\text{max}}$  and  $i$  at  $t_{\text{max}}$  of several transients, obtained by varying  $\Delta I$  at constant  $\tau$ . Getting  $I_{\text{corr}}$ ,  $ba$  and  $bc$  from the Tafel plot is straightforward.

2.2b *Single transient method for measurement of  $i_{\text{corr}}$  and  $C_d(E)$* : The double layer charging current can be corrected using a single  $\eta$ - $t$  transient. At each  $\eta$  value, the total current is equal to the sum of faradaic current ( $i_F$ ) and non-faradaic current ( $i_{nF}$ ). For every  $\eta$  (excepting  $\eta_{\text{max}}$ ) there are two values of current; one in the rising ( $i_{t_1}$ ) and another in the falling portion ( $i_{t_2}$ ). However, as  $i_F$  is the same, both in the rising and falling portions, at constant  $\eta$ , it is easy to show,

$$(i_F)_{t_1} = (i_{t_1}) + C_d \left( \frac{d\eta}{dt} \right), \quad (11)$$

where

$$C_d = [(i_{t_2}) - (i_{t_1})] / \left[ \left( \frac{d\eta}{dt} \right)_{t_1} - \left( \frac{d\eta}{dt} \right)_{t_2} \right]. \quad (12)$$

A similar expression has been given by Rangarajan (1973) while discussing the theory of double pulse galvanostatic technique. At each  $\eta$ ,  $i_F$  can be calculated by (11). By plotting these values of  $i_F$  against the corresponding values of  $\eta$  on semilog paper,  $i_{\text{corr}}$  and Tafel slopes can be found. Incidentally  $C_d$  as a function of potential is recovered from (12).

It is worthwhile pointing out that in LAERT also the presence of  $R_e$  will lead to an error in the measurement of  $i_{\text{corr}}$ . The method of correction described in §2.1c is valid here also.

Employing the methods described above,  $i_{\text{corr}}$  can be measured for the following types of corrosion systems:

- (i) When both the conjugate reactions are under activation control: In this case  $i_{\text{corr}}$  is obtained by polarising in both the directions.
- (ii) In the case of systems having one conjugate reaction under activation control and the other partially mass transfer controlled,  $i_{\text{corr}}$  is obtained by polarising in the direction of the activation controlled reaction.
- (iii) If one of the conjugate reactions is activation controlled and the other diffusion limited, then faradaic current is related to overpotential by

$$i_a = i_{\text{corr}} \left[ 1 - \exp \left( \frac{2.303\eta}{ba} \right) \right], \quad (13)$$

if the cathodic reaction is diffusion limited ( $bc \rightarrow \infty$ ) and

$$i_a = i_{\text{corr}} \left[ \exp \left( -\frac{2.303\eta}{bc} \right) - 1 \right], \quad (14)$$

if the anodic polarisation has an infinite slop ( $ba \rightarrow \infty$ ).

To obtain  $i_{\text{corr}}$  in this case, the system will have to be polarised in the direction of the reaction which is under activation control and the true faradaic current calculated by the above methods. Using this current,  $i_{\text{corr}}$  can be obtained from (13) and (14) by curve fitting.

### 3. Experimental

An ASTM G-72 type corrosion cell is used for the study. The electrode specimen is masked with Araldite (an epoxy resin) to define the area exposed to the electrolyte. The systems studied are (i) mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, (ii) Armco iron in 0.5 M H<sub>2</sub>SO<sub>4</sub>, (iii) mild steel in 1 M HCl (for inhibitor study), (iv) copper in 1 M NaCl, (v) Armco iron in 0.52 M NaCl.

For the first four systems, the electrolyte was deaerated with oxygen-free hydrogen. For copper in neutral 1 M NaCl, experiments were conducted both in aerated and deaerated conditions. Measurements were carried out one hour after the attainment of the steady state. Steady state logarithmic polarisation measurements of  $i_{\text{corr}}$  were carried out immediately after recording ATP.

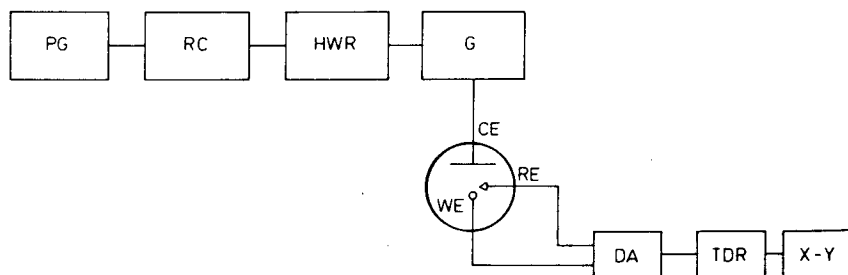
The block diagram of the experimental set-up is shown in figure 1. An exponentially decaying waveform is generated by applying a rectangular pulse to a RC network and half-wave rectifying the resulting waveform. This is applied to the cell using a fast response potentiostat in the galvanostatic mode developed for this purpose (V Lakshminarayanan, Aithu Poojary and S R Rajagopalan 1981, unpublished results). The transients obtained by SAERT and LAERT are corrected for ohmic drop due to  $R_e$  by the method given in § 2.1c.

### 4. Results and discussions

Figure 2 shows a typical  $\eta-t$  transient obtained for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

$R_p$  values obtained by all the three methods described above are given in table 1 for several corrosion systems studied in this work. They are in good agreement with the steady state linear polarisation value. Hence, the small amplitude exponential relaxation method can be considered a transient analogue of the linear polarisation technique.

To assess the validity of the method of correction for the ohmic drop due to  $R_e$  given in § 2.1c, experiments were conducted using a dummy cell ( $R_e = 100\Omega$ ,  $R'_p \equiv 10\mu\text{cm}^2$  and  $C'_d \equiv 10\mu\text{F/cm}^2$ ). The values of  $R'_p$  calculated from uncorrected and corrected transients are 108.4 $\Omega$  and 9.83 $\Omega$  respectively. It is clear that the method suggested in this work effectively corrects for the ohmic drop due to  $R_e$ .



**Figure 1.** Block diagram of the set-up used for exponential relaxation technique. PG - pulse generator; RC - RC network; HWR - half-wave rectifier; G - galvanostat; CE - counter electrode; RE - reference electrode; WE - working electrode; DA - differential amplifier; TDR - interfacing circuit (transient data recorder); X-Y - X-Y recorder.

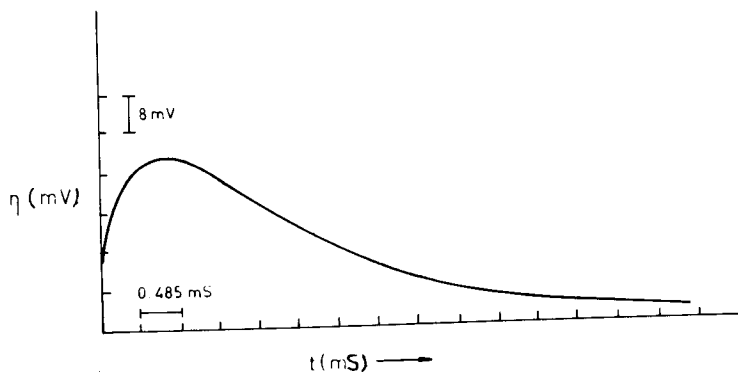


Figure 2. Potential-time transient obtained at  $\tau = 1$  ms and  $\Delta I = 10$  mA/cm<sup>2</sup> for MS/0.5 M H<sub>2</sub>SO<sub>4</sub>.

Table 1. Polarisation resistance ( $R_p$ ) of some corrosion systems obtained by SAERT.

System	Method	$\tau$ (m sec)	$R_p$ from cathodic polarisation (ohm cm <sup>2</sup> )	$R_p$ from anodic polarisation (ohm cm <sup>2</sup> )
MS/0.5 M H <sub>2</sub> SO <sub>4</sub> (deaerated)	Method 1	1	14.71	14.21
	[by using (3)]	1000	13.98	14.56
	Method 2 (by curve fitting)	1	15.38	14.25
	Method 3 (Multi-transient approach)	1	14.85	14.52
	Steady state linear polarisation (SSLP)	1000	13.72	13.85
Armco iron/ 0.5 M H <sub>2</sub> SO <sub>4</sub> (deaerated)	1	—	14.02	14.07
		100	194	208
		1000	196	197.2
	2	100	201.6	205.1
	3	100	202.3	207.2
Armco iron in 0.5 M NaCl (aerated)	1	1000	205.0	205.0
	SSLP	—	—	79.48
	1	100	—	82.34
		1000	—	80.10
	2	100	—	81.50
Copper in 1 M NaCl (aerated)	3	100	—	80.90
		1000	—	82.00
	SSLP	—	—	292
	1	100	—	312
		1000	—	305
Copper in 1 M NaCl (deaerated)	2	100	—	295
	3	100	—	301
		1000	—	310
	SSLP	—	—	3.55 × 10 <sup>3</sup>
	1	500	—	3.57 × 10 <sup>3</sup>
Copper in 1 M NaCl (deaerated)		5000	—	3.33 × 10 <sup>3</sup>
	2	500	—	3.70 × 10 <sup>3</sup>
	3	500	—	3.45 × 10 <sup>3</sup>
		5000	—	3.5 × 10 <sup>3</sup>
	SSLP	—	—	—

$C_d$  values obtained by SAERT are given in table 2. The values of  $C_d$  obtained for systems containing acid solutions or deaerated NaCl are of the expected order of magnitude. In the case of systems having aerated NaCl solution  $C_d$  values are large. This is presumably due to large pseudo-capacitance. Similar observation has been reported in literature (Kanno *et al* 1980) for mildsteel in aerated NaCl.

Figure 3 shows  $i_{\text{corr}}$  of MS in 0.5 M  $\text{H}_2\text{SO}_4$  (deaerated) obtained from the straight line portion of the  $\eta$ - $t$  curve. No correction for charging current has been carried out in this case. It is seen that  $i_{\text{corr}}$  increases with increasing  $\tau$  and  $\Delta I$ . It tends to a value corresponding to steady state logarithmic polarisation at higher time constants and lower  $\Delta I$ . Table 3 gives  $i_{\text{corr}}$  of MS in 0.5 M  $\text{H}_2\text{SO}_4$  obtained at various  $\tau$  values after correcting for charging current by using the procedures described. It is seen that  $i_{\text{corr}}$  calculated after correcting for double layer charging is independent of  $\tau$ . This clearly shows that the correction for charging current is a must in this transient technique for getting true  $i_{\text{corr}}$ . It is also seen that  $i_{\text{corr}}$

**Table 2.** Double layer capacitance ( $C_d$ ) for some corrosion systems obtained by SAERT.

System	Method	$\tau$ (m sec)	$C_d$ from cathodic polarisation ( $\mu\text{F}/\text{cm}^2$ )	$C_d$ from anodic polarisation ( $\mu\text{F}/\text{cm}^2$ )
MS/0.5 M $\text{H}_2\text{SO}_4$	Curve fitting (i)	1	86.71	93.56
	From $\eta_{\text{max}}$ and $t_{\text{max}}$ [using (3) and (4)] (ii)	1	89.78	91.80
Armco iron/ 0.5 M $\text{H}_2\text{SO}_4$	(i)	100	83.13	77.15
	(ii)	100	80.0	78.00
Armco iron in 0.52 M NaCl (aerated)	(i)	100	—	1395
	(ii)	100	—	827
Copper in 1 M NaCl (aerated)	(i)	500	—	290
	(ii)	500	—	275
Copper in 1 M NaCl (deaerated)	(i)	500	—	134
	(ii)	500	—	139

**Table 3.** Corrosion rate of MS in 1 M  $\text{H}_2\text{SO}_4$  (deaerated) obtained at various  $\tau$  values by LAERT.

Method	$\tau$ (m sec)	$i_{\text{corr}}$ (mA/cm <sup>2</sup> ) from cathodic Tafel line	$i_{\text{corr}}$ (mA/cm <sup>2</sup> ) from anodic Tafel line	$bc$ (mV)	$ba$ (mV)
Multi-transient	1	1.45	1.30	93	76
	100	1.40	1.35	99	83
	1000	1.35	1.35	99	83
Single transient	5	1.40	1.40	103	83
	10	1.40	1.40	96	86
	50	1.40	1.40	96	83
Logarithmic polarisation	—	1.35	1.35	96	83



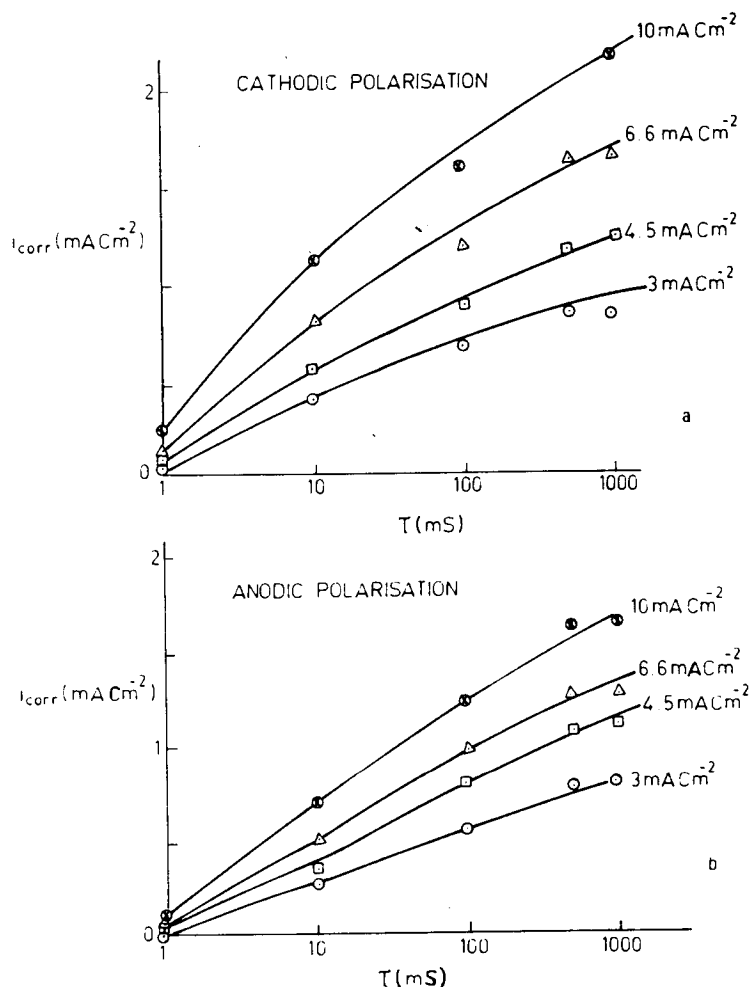


Figure 3. (a) Plot of  $i_{\text{corr}}$  vs.  $\eta$  obtained at several applied current densities ( $\Delta I$ ) from cathodic accelerated Tafel plots. (b) Plots of  $i_{\text{corr}}$  vs.  $\eta$  obtained at several applied current densities ( $\Delta I$ ) from anodic accelerated Tafel plots.

obtained by the two procedures of correcting for charging current are in good agreement with logarithmic polarisation value.

Table 4 gives the  $i_{\text{corr}}$  obtained for the systems Armco iron in 0.5 M  $\text{H}_2\text{SO}_4$ , Armco iron in 3% NaCl (0.52 M) and copper in 1 M NaCl. The values obtained by both single and multi-transient methods are in good agreement with the steady state logarithmic polarisation.

In the case of copper and iron in NaCl, the cathodic reactions are under partial mass transfer control while the anodic reaction is under activation control. Hence in these, corrosion rate has been obtained from anodic transients alone.

From (4) it is seen that any errors in the estimation of slope will affect the calculation of charging current, which in turn will affect the accuracy of calculation of faradaic current ( $i_F$ ). To minimise errors while employing the single transient approach, it is better to use data where the faradaic current is greater than the

Table 4. Corrosion rates of some corrosion systems obtained by LAERT.

System	Method	$\tau$ (m sec)	From	From	<i>bc</i> (mV)	<i>ba</i> (mV)
			cathodic plot (mA/cm <sup>2</sup> )	anodic plot (mA/cm <sup>2</sup> )		
Armco iron in 0.5 M H <sub>2</sub> SO <sub>4</sub>	Multi-transient	100	0.074	0.074	93	73
		1000	0.074	0.072	93	73
	Single transient	100	0.074	0.074	90	73
		1000	0.070	0.070	90	76
Copper in 1 M NaCl	Logarithmic polarisation	—	0.072	0.072	93	73
		100	—	0.062	—	51.5
	Multi-transient	1000	—	0.060	—	56.0
		100	—	0.065	—	52.5
Copper in 1 M NaCl (deaerated)	Single transient	1000	—	0.068	—	57.1
		500	—	0.060	—	53.5
	Logarithmic polarisation	—	—	0.060	—	53
		5000	—	0.0032	—	54.8
Copper in 1 M NaCl (deaerated)	Multi transient	500	—	0.0034	—	53
		5000	—	0.0030	—	53
	Single transient	500	—	0.0030	—	53
		—	—	0.0032	—	56.48
Armco iron in 3% NaCl (aerated)	Logarithmic polarisation	—	—	0.0032	—	56.48
		100	—	0.180	—	79.7
	Multi-transient	1000	—	0.180	—	79.7
		100	—	0.180	—	79.7
Single transient	100	—	0.180	—	79.7	
	1000	—	0.170	—	83.7	
Logarithmic polarisation	—	—	0.180	—	83.7	

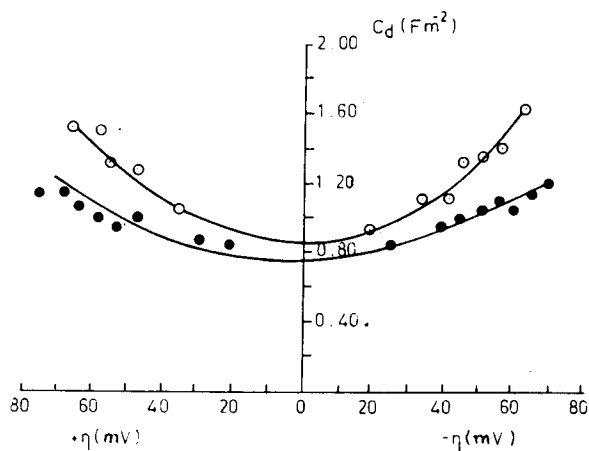
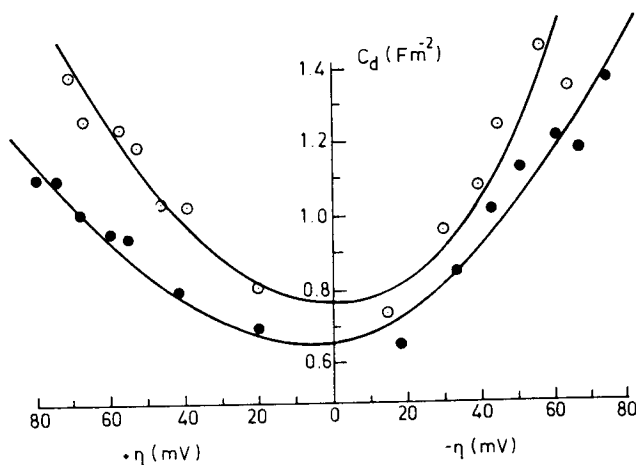


Figure 4.  $C_d$  as a function of potential for the system of MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> (deaerated) with and without hexamine inhibitor. ○ without inhibitor; ● with 10 mM hexamine inhibitor.

non-faradaic. The ratio of faradaic to non-faradaic current depends on  $\tau$ . For systems with low corrosion rate which have large  $R_p C_d$ , faradaic current is larger than non-faradaic current only at higher time constants. On the other hand, systems exhibiting high  $i_{\text{corr}}$  (low  $R_p C_d$ ) gives  $i_F$  greater than charging current even



**Figure 5.**  $C_d$  as a function of potential for the system of MS in 1 M HCl (deaerated) with and without acetyl acetone inhibitor.  $\circ$  without inhibitor;  $\bullet$  with 0.1 M acetyl acetone inhibitor.

**Table 5.** Effect of inhibitors on corrosion rates.

System	$\tau$ (m sec)	Inhibitor	Inhibitor concentration (M)	$i_{corr}$ (mA/cm <sup>2</sup> ) Single transient		$i_{corr}$ (mA/cm <sup>2</sup> ) Multi-transient	
				From cathodic Tafel line	From anodic Tafel line	From cathodic Tafel line	From anodic Tafel line
MS/0.5 M H <sub>2</sub> SO <sub>4</sub>	50	Hexamine	0	1.393	1.428	1.428	1.428
			0.01	0.385	0.385	0.385	0.400
MS/1 M HCl	20	Acetyl- acetone	0	0.7	0.7	0.72	0.70
			0.1	0.310	0.320	0.300	0.310

at low  $\tau$ . As a rule of thumb, it is better to use  $\tau \geq 10 R_p C_d$ . Too large a  $\tau$  should be avoided since it might lead to concentration polarisation at large  $\Delta I$ .

Figure 4 shows  $C_d$  as a function of potential for MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> obtained at  $\tau = 50$  msec. The effect of adding hexamine (10 mM) is also shown in figure. The lowering of  $C_d$  brought about by the adsorption of inhibitor is clearly seen. Figure 5 shows similar behaviour for MS in 1 M HCl with 0.1 M acetyl acetone as inhibitor. Table 5 shows the effect of hexamine (10 mM) on the corrosion rate of MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> and the effect of acetyl acetone on the corrosion rate of MS/1 M HCl.

## 5. Conclusions

1. SAERT can be considered a transient analogue of the steady state linear polarisation technique, while LAERT can be considered that of the steady state logarithmic polarisation technique. The straight line portion of the  $\eta-t$  curve

cannot be considered the 'accelerated Tafel plot' (ATP) as it contains contributions from the double layer charging current also. Hence it is preferable to call this the large amplitude exponential relaxation technique (LAERT).

2. SAERT involving both multitransients and single transients can be used to obtain polarisation resistances  $R_p$  and double layer capacitances  $C_d$  of corrosion systems.
3. With the single transient method one can get either  $R_p$  (by SAERT) or  $i_{\text{corr}}$  (by LAERT) by perturbing the electrode for very small time periods and thus preventing excessive polarisation of the electrode. Besides, the single transient method is quite fast for close monitoring of  $R_p$  and  $I_{\text{corr}}$ .
4. LAERT using a single transient provides information on  $C_d$  as a function of potential which is useful in the study of inhibitors and for investigating area changes with time.
5. Both the relaxation techniques have an in-built advantage of *in situ* measurement of  $R_e$  which permits correction for the ohmic drop due to  $R_e$ .

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### List of symbols

$b_a$ and $b_c$	– anodic and cathodic Tafel slopes of conjugate reactions of the corrosion system;
$C_d$	– double layer capacitance;
$\Delta I$	– amplitude of exponentially decaying current input;
$i_{\text{corr}}$	– corrosion rate;
$i_F$	– faradaic current;
$i_{nF}$	– non-faradaic current;
$i_{t_1}$	– total applied current at the rising portion of $\eta-t$ curve;
$i_{t_2}$	– total applied current at the falling portion of $\eta-t$ curve;
$R_p$	– polarisation resistance;
$R_e$	– solution resistance;
$t_{\text{max}}$	– time corresponding to maximum of $\eta-t$ curve;
$T_{\text{max}}$	– $t_{\text{max}}/\tau$ ;
$T_{\text{max}}^*$	– $t_{\text{max}}/\tau$ in the presence of solution resistance;
$\alpha_c$ and $\beta_a$	– cathodic and anodic transfer coefficients respectively for the conjugate reactions of the corrosion system;
$\eta_{\text{max}}$	– overpotential corresponding to maximum of the $\eta-t$ curve;
$\eta_{\text{max}}^*$	– overpotential corresponding to maximum of the $\eta-t$ curve in the presence of solution resistance $R_e$ ;
$\tau$	– time constant of the exponentially decaying current input;
$\tau_d$	– $\tau/R_p C_d$ .

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