Assessment of Various Techniques for Corrosion Rate Measurements

P. Radhakrishnamoorthy, V. Sivan & Sandip Roy

Central Electrochemical Research Institute, Karaikudi-623006

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Various methods for electrochemical corrosion rate measurements have been discussed briefly giving the basic theoretical aspects and experimental techniques used. The conditions of applicability of various methods are outlined.

Corrosion in its broadest sense encompasses electrochemical corrosion (wet corrosion), chemical oxidation (dry corrosion), mechanical corrosion etc. We have confined our discussion to electrochemical or wet corrosion in this paper. An understanding of the mechanism and a way of measuring the rate of corrosion takes one a long way in his ability to prevent corrosion. The various methods that are available to measure the corrosion rates are: 1. Weight loss measurements, 2. Logarithmic polarisation measurements, 3. Linear polarisation technique, 4. Impedance measurements, 5 Relaxation techniques, 6. Faradaic rectification techniques.

The basic theory underlying the above techniques, the experimental aspects and the conditions of applicability of these methods are given below:

1. Weight loss measurements

Faraday's Law is the basis of this method. The loss in weight of the metal due to corrosion is given by the following equation:

$$W = \frac{i_{cor}\ t}{F} \cdot \frac{M}{N} \qquad \ldots (1)$$

knowing M, F, Z and measuring W and t, i_c can be calculated.

Experimentally this is the simplest method. This method is applicable irrespective of the mechanism of corrosion (i.e. whether $\triangle E$ is large or small, anodic or cathodic controlled etc), but the method suffers from the following drawbacks. 1. Time-consuming, 2. Destroys the sample, and 3. If the corrosion rate is small, the changes in weight over short periods of time will be small and hence, the accuracy of the method will be low. On the other hand, if the corrosion is allowed to take place for a long time to get an appreciable change in weight, there is every possibility of a change in the nature of the surface and hence in the corrosion rate, as a consequence of which one gets an average corrosion rate.

2. Logarithmic polarisation measurements.

The basis of this method is the Butler-Volmer equation. Generally cathodic polarisation data are preferred inasmuch as these are easy to measure experimentally, and when E is sufficiently negative with respect to E_{cor}, the equation is

$$i = -i_{cor} \exp\left[\frac{\alpha_c\ nF\ \triangle E}{R'T}\right] \qquad \ldots (2)$$

Taking logarithm

$$\log i = -\log i_{cor} - 2.303\ \alpha_c\ nF\ \triangle E/R'T \qquad \ldots (3)$$

Therefore, the intercept of log i vs $\triangle E$ plot gives the value of i_{cor}.

Under ideal conditions the accuracy of the logarithmic polarisation method is equal to or greater than the conventional weight loss methods This technique enables one to measure extremely low corrosion rates, and it can be used to continuously monitor the corrosion rate of a system. Athough this method yields accurate values for corrosion rates, it suffers from the following shortcomings: i) to ensure reasonable accuracy, the Tafel region must extend over a current range of at least one order of magnitude; ii) concentration polarisation should not be present: iii) the corrosion reaction must

have only one reduction processs, since the Tafel region is usually distorted if more than one reduction process is present; and iv) the nature of the surface may also change over the region of potentials studied.

3. Linear polarisation technique

This method was suggested by Stern and Geary[1]. When the corrosion potential is far away from the reversible potentials of both the anodic and cathodic reactions, the contribution of the current due to their conjugate reactions are negligible. Under these conditions, i_{cor} is given by : $i = i_a - i_c$

$$i = i_{cor} \{\exp.(\alpha_a nF \triangle E/R'T) - \exp.(-\alpha_c nF \triangle E/R'T)\} \quad .... (4)$$

When $\triangle E << R'T/\alpha_a nF$ or $R'T/\alpha_c nF$

the exponential terms can be expanded and consequently we get

$$i = i_{cor} \left[\triangle E \frac{nF}{R'T} (\alpha_a + \alpha_c) \right] \quad ... (5)$$

This equation predicts a linear relation between i and E, the slope of which is given by $i_{cor} \frac{nF}{R'T} (\alpha_a + \alpha_c)$

If α_a and α_c are obtained from other experiments, i_{corr} can be obtained. The advantages of this method are: 1. It permits rapid corrosion rate measurements, and 2. The changes in the nature of the surface during polarisation are kept to a minimum. The method suffers from the following drawbacks: a) a serious limitation is imposed by the requirement that the E_{cor} must be far from the reversible potentials of both the anodic and cathodic reactions of the corrosion process and also both the reactions must be under activation control. b) α_a and α_c are to be obtained from saparate experiments. Stern-Geary's linear polarisation technique has been subjected to criticism by Mansfeld and Oldham[2-4] and Mathews[5]; they showed that d^2i/dE^2 is not equal to zero as would be expected from Stern-Geary's equation.

However, it should be realised that Stern-Geary's equation is an approximate result (linearised form of experimental) and hence bound to differ from the exact result.

But this would not be the case if one differentiates the original $i-E$ equation three times and then imposes the condition $E = E_{cor}$. However, it must be stated that Oldham and Mansfeld in their subsequent papers[6] acknowledged the valdity of Stern-Geary's method, subject to the limitations it had and even advocates[7]. it for i_{cor} measurements by showing as to how some of the drawbacks can be overcome.

Barnett[8] had analysed the theoretical aspects of the linear corrosion kinetics and by model calculations showed the requirements for the applicability of Stern-Geary method. Albaya et al[9] have developed expressions taking into account mixed control (mass transfer and activation) for the cathodic reaction which in the limit mass transfer polarisation is zero, tends the Stern-Geary equation. Mathews[5] in his paper showed that the linearity of the current potential relation holds good only over very small ranges of potential e.g. 2mV. The potential range over which the Stern-Geary equation is valid depends, on the mechanism of reaction (could vary from 3 to 60 mV) and hence is not predictable[8].

4. Impedance Method

Sinusoidal or alternating square wave singals[10-12] based on the measurements of impedance of the interface (at corrosion potential) and a constant which comprises a number of electrochemical constants that are characteristics of the metal and the solution have been used for corrosion rate measurements. It may be pointed out that in linear polarisation method, the input is constant voltage. The disadvantage of using a constant voltage is that it will permanently polarise the electrode and this might alter the course of the corrosion reaction. In impedence method alternating voltage is used. The advantages of using low frequencies are stressed by Prazak and Barton[12] as is evident from the fact that, as frequency tends to zero, the response of the interface tends to that of d.c. response; at the same time, the interface would not be permanently polarised. The permissible amplitude for electrochemical measurements by electrode impedance method is 5 to 15mV[13,14]. The apparatus[15] for measuring R_p is shown in Fig. 1. The working electrode A is polarised by controllable, stabilised alternating current of a rectangular type wave form with a frequency f = 0.5 to 10 Hz from a source 1 with

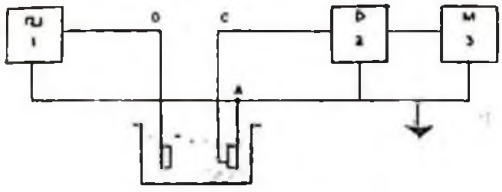


FIG 1 APPARATUS FOR MEASURING R_p

1 SOURCE OF LOW FREQUENCY RECTANGULAR TYPE OSCILLATIONS
2 AMPLIFIER
3 CATHODE BRIDGE WITH A MEASURING INSTRUMENT
A WORKING ELECTRODE
C REFERENCE ELECTRODE WITH A PROBE
D AUXILIARY ELECTRODE

a high internal resistance by means of an electrode D made of inert metal The alternating polarisation of the working electrode A is picked up using a reference electrode C with a probe and after amplification and rectification, is indicated by a microammeter connected into a cathode-type bridge 3. The advantagee of this method are: 1. The electrodes are not polarised. 2. Corrosion rates can be measured faster by impedance method than by linear polarisation method.

5. Relaxation methods

Relaxation methods namely the Potentiostatic, Galvonostatic and Accelerated Tafel plots have been suggested[16-19] for corrosion rate measurements. Hewever, no experimental detail are available.

6. Faradaic rectification method

In general, the current potential curves for electrode-electrolyte interface are assymmetric about the equilibrium potential. This natural assymmetry in the behaviour of interfaces is responsible for the rectification property Faradaic rectification). As a result of Faradaic rectification, the input of the type shown in Fig. 2 transforms to an output shown in Fig. 2b.

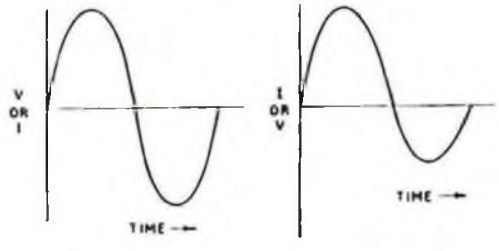


FIG 2(a) INPUT FIG 2(b) OUTPUT

This output can be split into a d.c. component with twice the frequency as the signal and an a.c. component with the same frequency (Fig. 3A). This changing direct current can be represented by a constant, time-average, value of a d.c. (Fig. 3B).

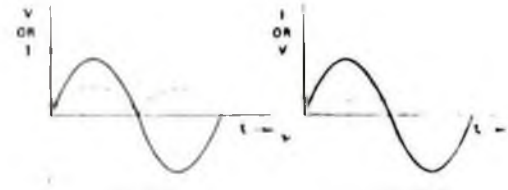


FIG 3(a) V OR I VS TIME INPUT FIG 3(b) I OR V VS TIME OUTPUT

Satyanarayana[20] suggested and applied the method of Faradaic rectification to evaluate the corrosion current. The basis of the method is fairly simple and is as follows: When an alternating voltage of the type $E = E_m$. Cos wt is applied across the working electrode-solution interface, the output current i consists of a direct current component $\bar{i}$ and an alternating current component $\tilde{i}$

$$i = \bar{i} + \tilde{i} \quad \ldots (6)$$

$\bar{i}$ can be expressed as

$$\bar{i} = i_{cor}\left\{\exp\left[\frac{-2.303\,(E_1 - E_{cor})}{b_c}\cdot X\right] - \exp\left[\frac{2.303\,(E_1 - E_{cor})}{b_a} Y\right]\right\} \quad \ldots (7)$$

$$\text{where } X = I_o \frac{(-2.303\,F_m)}{b_c} \text{ and} \quad \ldots (8)$$

$$Y = I_o \frac{(2.303\,E_m)}{b_a} \quad \ldots (9)$$

where I_o is the modified Bessel function of the first kind and order zero.

It can be seen that the above equation is similar to the one that is obtained when a constant voltage E is applied across the interface, except for the multiplication of the anodic component of the current by the constant factor X and the cathodic component of the current by the constant factor Y When E_m is low compared with $b_a/2.303$ or $b_c/2.303$

$$\bar{i} \simeq i_{cor} \cdot 1.32\left[E^2_m\,(b_c^{-2} - b_c^{-2}) - 2.303\,\bar{i}\,R\,(b_c^{-1} + b_a^{-1})\right] \quad \ldots (10)$$

because $\bar{E}_1 = \bar{i} R$ where R is the total resistance of the circuit including thh solution resistance. Therefore, if b_c and d_a are known, a single measurements of $\bar{i}$ will give of the valve of i_{cor}. Satyanarayana[21] showed that a knowledge of one Tafel slope is adequate to get the corrosion current in view of the fact that b_c and b_a are related through the following equation :

$$\phi = 0.576\ E_m^2\ (b_c^{-1} - b_a^{-1}) \qquad \ldots \quad (11)$$

Further

$$\bar{i} = 2.303\ i_{cor}\ (b_c^{-1} + b_a^{-1})\ (\psi - \bar{i} R) \qquad \ldots \quad (12)$$

By measuring $\bar{i}$ and ϕ for a given alternating voltage of amplitude $\gtrsim$ 30mV applied to the corroding electrode and by knowing one of the Tafel slopes, both the corrosion rate and the other Tafel slope may be readily evaluated. The value of R required above may be estimated from the geometry of the electrode and the conductivity of the electrolyte or experimentally determined.

The experimental setup is also fairly simple and is shown schematically in Fig. 4. The same metal as the

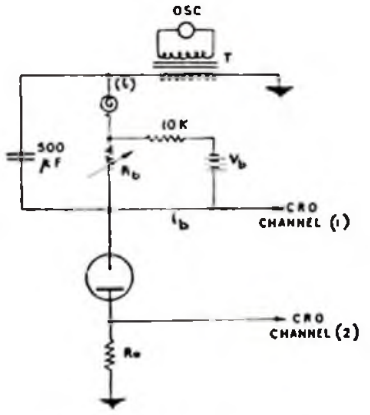


FIG. 4 CIRCUIT DIAGRAM FOR FARADAIC RECTIFICATION METHOD

working electrode, with a large surface area (to minimise the polarisation) is made use of as the counter electrode. The inter-electrode distance is kept to a minimum. The $\bar{i}$ and ψ are measured as follows. Tne circuit was completed with zero alternating voltage applied to the cell. The back-off voltage was adjusted to V_1 by changing R_b until the current through the galvanometer was reduced to zero. Alternating voltage was now applaied to the cell and the magnitude and direction of the steady value of the direct current $\bar{i}$ through the galvanometer was noted. This current was again reduced to zero by adjusting the back-off voltage to V_2 which gives the value of Ψ as $(V_1 - V_2)$. The alternating voltage across R_c and between working electrode and ground as well as the phase shift between the two were then measured with an oscilloscope. This latest technique of corrossion rate measurements leads to the following significant advantages :

1. In this method only one of the Tafel slopes is necessary. Hence, the experimentation takes less time and the attack on the specimen is small.

2. One has a choice as to which of the Tafel slope be determined experimentally. That reaction which gives a well-defined Tafel slope may be selected for this purpose, increasing thus the accuracy of the result ; for example, the anodic reaction on non-passivating metals or the cathodic reaction on passive metals may be chosen.

3. For several practical corrosion systems, one of the Tafel slopes may be regarded as already known ; for example, b_a tends to infinity for normally passive metals and b_c tends to infinity where the cathodic reaction is under diffusion control. In such cases, this method becomes an absoute method for corrosion rate determination.

4. This method provides minimum change in the nature of the working electrode in view of the fact that the shift of the electrode potential from the corrosion potential to the mean potential is one or two orders of magnitude less than in the linear polarisation technique.

5. The measured current i is independent of frequency of the excitation voltage unlike in the impedance method.

6. There is no need for introducing a reference electrode because single electrode potentials are not required. It must be mentioned, however, that this method applies to situations where the anodic and cathodic Tafel slopes are unequal But cases are rare where anodic and cathodic Tafel slopes are equal and hence the applicability of the method does not suffer from the above-mentioned drawback.

Again, this method will not yield correct values for the corrosion current in situations where either one of the reactions, viz. cathodic or anodic is under near-equilibrium conditions at the corrosion potential.

CONCLUSION

From the various methods discussed in this paper for corrosion rate measurement only the linear polarisation and Faradic rectification methods appear to be competitive in that both disturb the nature of the electrode surface to a minimum extent. However, the Faradic rectification method has a distinct advantage over the linear polarisation method because in the former case one needs only one of the Tafel slopes b_a or b_c and hence there is a choice; whereas the linear polarisation needs both b_a or b_c. Again, the accuracy with which the corrosion rate can be measured is a note worthy feature of Faradaic rectification method.

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NOMENCLATURE

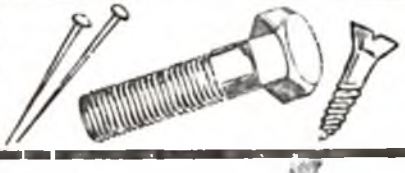
b_a Anodic Tafel slope; b_c Cathodic Tafel slope; E Electrode potential; E_1 Mean potential of the working electrode corresponding to $\bar{i}$; E_{cor} Corrosion potential; $\triangle E = E - E_{cor}$; E_m Amplitude of AC signal; F Faraday; i Current passing through the cell; i_{cor} corrosion current; i_a Anodic current; i_c Cathodic current; $\bar{i}$ Faradic rectification current; $\tilde{i}$ Alternating Current; M Molecular weight; n Number electrons; R' Gas constant; R total resistance of the circuit; T Temperature; W Weight; α_a transfer coefficient for anodic recaction; α_c transfer coefficient for cathodic reaction.

REFERENCES

1. M. Stern and A. Geary, J. Electrochem. Soc. 104 (1957) 56
2. F. Mansfeld and K.B. Oldham, Corrosion, 26(1970) 207
3. K.B. Oldham and F. Mansfeld, Corrosion, 27(1971) 434
4. F Mansfeld and K.B Oldham, Corrosion, 28 (1972) 180
5. D.B. Mathews, Aust. J. Chem. 28 (1975) 243
6. F. Mansfeld and K.B. Oldham, Corros. Sci. 11 (1971) 787
7. F. Mansfeld. J. Electrochem. Soc. 120 (1973) 515
8. S. Barnett, Corros. Sci. 9 (1969) 145
9. H.C. Albaya, O.A. Cobo and J.B. Bessone, Corros. Sci. 13 (1973) 287
10. W. Schewenk and H.E Buhler, Corros. Science 3 (1963) 261
11. J.C. Rowland and M.N. Bently, Brit Corros. J. 2 (1967) 92
12. M. Prazak and K. Barton, Corrosion Science, 7 (1967) 159
13. A. N. Frumkin, Kinetica Electrodynch Processov, p-19, 1952 Mascow University Publishers, Moscow
14. K J. Vetter, Electrochemische Kinetik, p.481 1961, Springer, Berlin
15. M. Prazak, Slabopr. obz., Electronics and Telecommunic. Rev. 27 (1966) 219
16. K.S Rajagopalan, G. Venkatachari, N.C. Dey and V.S. Muralidharan, J. Electrochem Soc. India 24 (1975) 17
17. G. Prabhakara Rao and S.K Rangarajan, J .Electroanal. Chem. 55 (1974) 151
18. Private communication
19. Principles of current methods for the study of electrochemical reactions. Boris B. Damaskin, 1967, McGraw Hill Co. New York
20. S. Sathyanarayana, J. Electroanal. Chem. 50 (1974) 411
21. S. Sathyanarayana, to be published.

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