POLARISATION MEASUREMENTS USED FOR CORROSION RATES DETERMINATION

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Abstract - In this paper, based on the literature data, are described the electrochemical theoretical concepts for the two methods used for determination of instantaneous corrosion rates from polarization measurements: extrapolation of the Tafel slopes with corrosion potential – Stern method and polarization resistance – Stern-Geary method. The error-producing factors are show also

Key words: corrosion rate, Tafel slopes extrapolation, polarisation resistance.

1. INTRODUCTION

In present there are many methods for determination of corrosion rates of metals, such as gravimetric-based mass loss, quartz crystal microbalance-based mass loss, electrochemical, electrical resistance, and solution analysis. The polarization measurement methods, based on electrochemical concepts, enable determination of instantaneous reaction rates at electrode/solution interface, such as the exchange current density in case of an electrode equilibrium and the corrosion current density in case of a corrosion system, from a single experiment. All other methods require multiple measurements over time for provide information on the corrosion rate.

There are two methods based on polarization measurements for determination of corrosion rates: Tafel slopes extrapolation with corrosion potential [1-7], so called Stern method, and polarization resistance method [1-7], so called Stern and Geary method. However, it must note that based on polarization measurements methods may implicate error-producing factors such as diffusion limitations, high solution resistance, presence of competing reduction-oxidation reactions, and no uniform current and potential distributions, etc.

The aim of this paper is to present the methods based on polarization measurements for determination of instantaneous corrosion rates, and to show conditions and circumstances where the error-producing factors are important.

2. THE POLARIZATION BEHAVIOUR OF CORROSION SYSTEMS

The total polarization curve of a corrosion system controlled by the charge transfer polarization is given in figure 1 (curve i_{app}). This is additively composed from partial anodic curve of metal oxidation ($i_{a,M}$) and partial cathodic curve of reduction of an oxidant from solution ($i_{c,Ox}$).
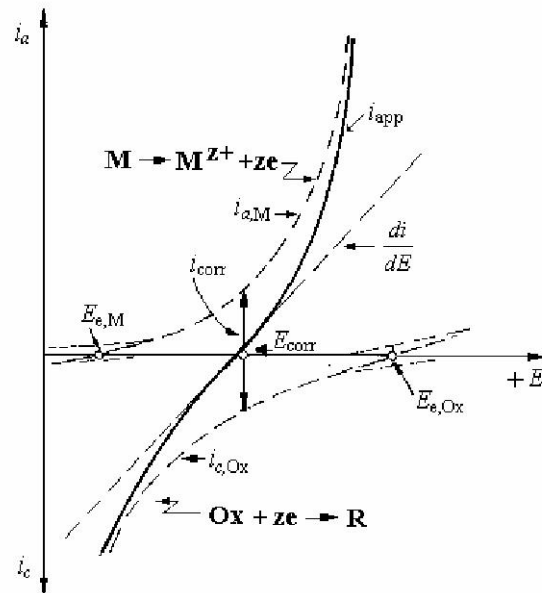
Fig. 1 – The polarisation diagram for a metal that corrodes under activation control, where:

i_{app} – total polarisation curve experimentally measured;
$i_{a,M}, i_{c,Ox}$ – partial anodic and cathodic polarisation curves, respectively;

$E_{e,M}, E_{e,Ox}$ – equilibrium potentials for metal and oxidant reactions, respectively;

$\dfrac{di}{dE}$ - tangent to polarisation curve in corrosion potential.

The experimental polarization curve (i_{app}) is described by a relation similar to the Butler-Volmer [8] equation for reversible reactions:

$$i_{app} = i_{corr} \left\{ \exp\left[\frac{\alpha_{a,M} zF}{RT}\left(E - E_{corr} \right) \right] - \exp\left[-\frac{\alpha_{c,Ox} zF}{RT}\left(E - E_{corr} \right) \right] \right\} \qquad (1)$$

where:

i_{app} is applied or measured current density;

i_{corr} – corrosion current density;

$\alpha_{a,M}$, $\alpha_{C,Ox}$ - charge transfer coefficients for anodic and cathodic reactions, respectively;

E- E_{corr} –polarization, given by difference between applied and corrosion potential;

z – metal valence; F – Faraday constant; R – gas constant; T – absolute temperature.

At the corrosion potential (E_{corr}), the anodic and cathodic rates are exactly equal; thus the applied current density is zero. All electrons generated by oxidation metal in dissolution reaction are consumed by oxidant reduction reaction on the same metal surface.

The equation (1) can be use for determinenation of instantaneous corrosion rates (in current units) from polarization measurements, as follows.

2.1. Tafel slopes extrapolation method

At large polarization, in the potential region where the rate of a single partial corrosion reaction predominates, the graphical representation in coordinates E–log i_{app}, for reactions under pure activation control give straight lines (so called Tafel lines), as in figure 2. At potentials well away from the corrosion potential, the applied current density reflects the kinetics of only one of the corrosion reactions.
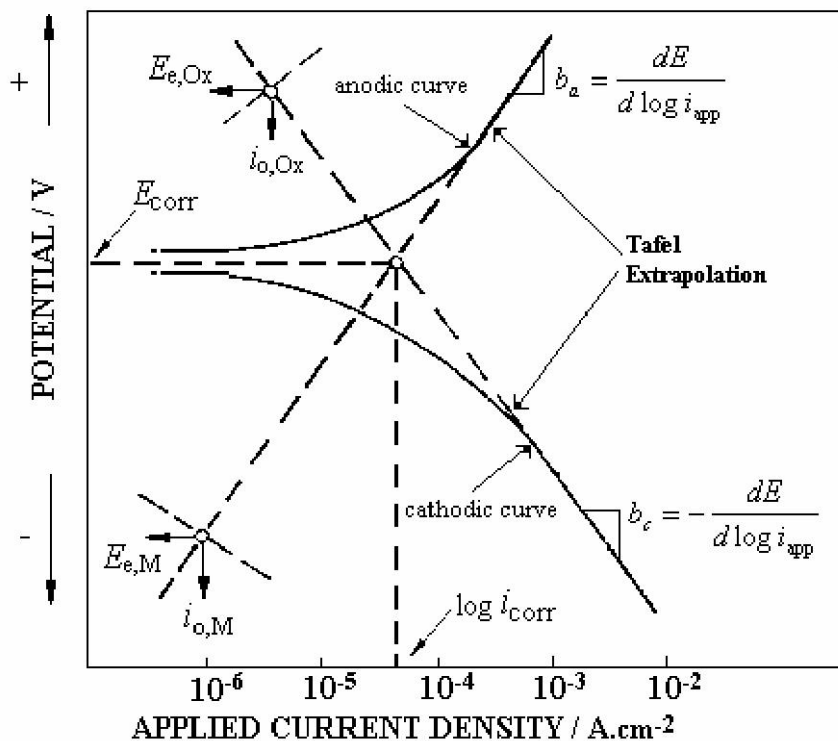

Fig. 2 – Semilogarithmic polarization curves for a corrosion system under activation control (Tafel behaviour).

Thus, when $E >> E_{corr}$ and $i_{a,M} >> \left| i_{c,Ox} \right|$ it obtains the Tafel slope of the anodic reaction, conform to the relation:

$$b_a = \left(\frac{dE}{d\log i} \right)_{E \rangle\rangle E_{cor}} = +\frac{2,3RT}{\alpha_{a,M} zF} \qquad (2)$$

For cathodic curve, when $E << E_{corr}$ and $i_{a,M} << \left| i_{c,Ox} \right|$, Tafel slope is given by relation:

$$b_c = \left(\frac{dE}{d\log i} \right)_{E \langle\langle E_{cor}} = -\frac{2,3RT}{\alpha_{c,Ox} zF} \qquad (3)$$

The both Tafel lines intersect in the point of coordinates (E_{corr}, $\log i_{corr}$) that makes possible the estimation of the corrosion current density by the extrapolation of the Tafel slopes with corrosion potential. As assuming uniform metal dissolution across the surface, Faraday's laws can be used to convert it to rate of weight loss in g/m²h [9] or rate of penetration in mm/year [2].

In spite of the fact that method was accepted by ASTM, the graphical extrapolation method for determination of the corrosion current can lead to the various values [10]. A poor selection of the slope to be used can change the corrosion current density by a factor of 5 to 10 [4]. Two rules should be applied when using Tafel extrapolation. For an accurate extrapolation, at least one of branches of the polarisation curve should exhibit Tafel behaviour (i.e., linear on semilogarithmic scale) over at least one decade of current density. In addition, the extrapolation should start at least 50 to 100 mV away from E_{corr}.

There are several factors that can lead to non-Tafel behaviour. The diffusion limitations on a reaction; ohmic losses in solution can lead to a curvature of the Tafel region, leading to erroneously high estimation of corrosion rate if not compensated for properly.; the presence of oxidation reactions that are not metal dissolution.

For consideration of the polarisation curves, the assumption of a steady-state system is implicit. The corrosion is a no equilibrium process that occurs at steady state. In many cases steady state is only approached and never achieved. The most used means of monitoring the approach to steady state of a corrosion system is the measurement of the corrosion potential with time. Generally, the E_{corr} changes most rapidly at the beginning of immersion. As the conditions at metal/solution interface approach steady state, the time-rate of change in E_{corr} decreases. A reasonable criterion for steady state would be change of less 5 mV in E_{corr} over a 10 minute period [4].

2.2. The polarisation resistance – Stern-Geary method

Many investigators have experimentally observed that i_{app} was approximately linearly to applied potential within a few milivolts of polarisation from E_{corr}. The equation (1) can be mathematically linearized by taking its series expansion (e.g. $e^x = 1 + x + x^2/2! + x^3/3! + \dots$) and by neglecting higher terms when $\Delta E / b < 0.1$, obtaining the relation:

$$i_{app} = i_{corr}\left\{\left[1 + \frac{\alpha_{a,M}zF}{RT}(E - E_{corr})\right] - \left[1 - \frac{\alpha_{c,Ox}zF}{RT}(E - E_{corr})\right]\right\}$$

$$= i_{corr}\left[\left(\frac{\alpha_{a,M}zF}{RT} + \frac{\alpha_{c,Ox}zF}{RT}\right)(E - E_{corr})\right]$$

$$(4)$$

Replacing:

$$\frac{\alpha_{a,M}zF}{RT} = \frac{2.3}{b_a}; \frac{\alpha_{c,Ox}zF}{RT} = \frac{2.3}{b_c},$$

$$\text{and } (E - E_{corr}) = \Delta E$$

and rearranged the terms, equation (4) becomes:

$$i_{corr} = \frac{1}{2,3} \cdot \frac{b_a b_c}{b_a + b_c} \cdot \left(\frac{\Delta i_{app}}{\Delta E}\right)_{E_{corr}} = \frac{B}{R_p} \quad (5)$$

where:

$$B = \frac{1}{2,3} \cdot \frac{b_a b_c}{b_a + b_c}$$

and

$$R_p = \left(\frac{\Delta E}{\Delta i_{app}}\right)_{(E - E_{corr})^{-\infty}}$$

is the polarisation resistance given by slope of linear part (dE / di) at $t = \infty$, $\Delta E = 0$, [ohm·cm²]

The relation (5) known as Stern-Geary equation or polarisation resistance method correlates the slope (dE / di) of the polarisation curve (see tangent at curve i_{app} from figure 1) for an electrode that corrodes at the open-circuit potential (E_{corr}) of corrosion current density (i_{corr}) at the same potential. The knowledge of R_p, b_a and b_c enables direct determination of corrosion rate at any instant in time using Eq. (5) [2-7]

Conform to ASTM standards [11] the procedures for determination of the linear $E-i$ behaviour for an electrode near E_{corr} and therefore to conducting polarisation resistance measurements can be: potentidynamic, potential-step and current-step. The

current step method has been cited to be faster than potentiodynamic and potential-step methods and less susceptible to error associated with drift in E_{corr}. Using this method, the independent determination of b_a and b_c is still required.

The complications with polarisation resistance method by linear polarisation method are given by error-producing, as [4]:

➢ invalidation of the results through oxidation of some other electroactive species besides the corroding metal in question;

➢ a change in the open-circuit or corrosion potential during the time to perform the measurement;

➢ use of ΔE that is too large, invalidating the assumption of a linear relationship between i_{app} and E required by Eq. 4 (i.e. $\Delta E/b < 0.1$);

➢ too fast a voltage scan rate or insufficient potential hold time;

➢ ohmic solution resistance;

➢ non uniform current and potential distributions.

CONCLUSIONS

The methods based on polarization measurements: Tafel slopes extrapolation with corrosion potential and polarization resistance method, enable determination of instantaneous corrosion rates from a single experiment. However, the methods are susceptible of error-producing that must be avoided.

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