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Limitations of the linear polarization method to determine stainless steel corrosion rate in concrete environment

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Abstract

The linear polarization is a non-destructive way of estimating the instantaneous corrosion rate of a metal. In case of reinforced concrete, the method is restricted mainly because of a concrete resistance, unknown area of the polarized reinforcement and non-uniform corrosion. In spite of that, thanks to the polarization resistance it is possible to estimate whether the reinforcement corrodes in activity or passivity. The results imply that sometimes even the knowledge of R_p is insufficient for stating activity or passivity of the material. It has been proved, however, that the shape of the curve determining R_p by linear polarization may frequently indicate the corrosion behaviour. It is possible to evaluate the deviation of the point of zero current from the free corrosion potential which was measured prior to the linear polarization and also to evaluate the deviation of the polarization curve from the regression line, which is defined by the coefficient of determination.

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1. Introduction

Linear polarization is a non-destructive method designed for measuring polarization resistance. Therefore, it serves for identification of corrosion rate at or near free corrosion potential. The potentiodynamic way of linear polarization technique is based on a continuous change of an electrode's potential in the vicinity of free corrosion potential. Prior to each measurement, free corrosion potential must be identified with a reference electrode. Subsequently, a counter electrode makes the working electrode's potential skip in the cathodic direction. Polarization of the working electrode in anodic direction follows with a constant scan rate up above the value of corrosion potential. The working electrode gets thus slightly excited, symmetrically in the vicinity of the corrosion potential within the potential range $\Delta E = E - E_{\mathrm{corr}}$ in both anodic and cathodic direction.

The standard ASTM G 59–91 (Standard test method for conducting potentiodynamic polarization resistance measurements) [1] defines the polarization resistance by the relation Eq. (1).

$$R_p = \left(\frac{\partial \Delta E}{\partial i}\right)_{i=0,\mathrm{d}E/\mathrm{d}t \to 0} \tag{1}$$

It means that the polarization resistance of a corroding electrode is defined as a slope of a potential-versus-current density line within the zero current point $i = 0$. The rate of polarization should be close to zero.

The polarization resistance value is then used for calculating the corrosion rate in a form of the corrosion current density (i_{corr}) by using Eq. (2).

$$i_{\mathrm{corr}} = \frac{B}{R_p} \tag{2}$$

However, for the coefficient B, Stern–Geary coefficient, the Tafel slopes b_a, b_c must be known (Eq. 3). Mostly, the coefficient is strictly empirical for a given corrosion system.

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Nomenclature

List of symbols

E	electrode potential
R_p	polarization resistance
E_{corr}	free corrosion potential
i	current density
I	current
R_e	electrolyte resistance
t	time
i_{corr}	corrosion current density
B	Stern–Geary coefficient
b_a, b_c	Tafel slopes
E_{oc}	open-circuit potential prior to linear polarization
$E_{i=0}$	zero current potential (potential of the intersection of polarization curve and zero current coordinate)
R^2	coefficient of determination of linear regression

$$B = \frac{b_a b_c}{2.303(b_a + b_c)} \tag{3}$$

Fortunately, it is not essential to know the Tafel slopes in case of steel reinforcement in concrete because the knowledge of the limit value of polarization resistance itself is sufficient for distinguishing between corrosion in activity or in passivity. The following conversion of polarization resistance into corrosion rate is merely an implication of a new error into results. Moreover, corrosion attack is of a localized character in case of concrete reinforcement, thus it is impossible to identify corrosion rate within the attack with the calculated corrosion rate representing a mean value of corrosion rate in a polarized area of an electrode.

In case of steel in chloride-free concrete pore solution, it can be expected that linearity of linear polarization curves will be affected by difference in values of anodic and cathodic Tafel slopes which correspond to diffusion control and charge-transfer control, respectively. In this case, a plot of E versus i will tend to curve to an asymptote parallel to the potential axis. The difference between the values b_a and b_c not only modifies the equation for calculating the coefficient B but it affects the technique of polarization resistance determination. The higher the difference between the values b_a and b_c, the narrower the range that would be utilizable for the analysis [3]. The problems of polarization curves' non-linearity in the vicinity of corrosion potential were thoroughly dealt with by Mansfeld [4]. Mansfeld proved that linear curves can be expected only in exceptional cases ($b_a = b_c$) and that determination of polarization resistance through linearization procedure can lead to erroneous values [4]. No curve, however, can ever be said to be linear. For cases where b_a approaches infinity (stainless steel in oxygen saturated acids) or b_c approaches infinity (corrosion under diffusion control), the deviation from linearity would be even larger [6]. Many errors in polarization resistance results, which were obtained by means of commercial corrosion monitoring probes, originate in the assumption that the polarization curve is linear up to the specified overvoltage, usually 10 mV [7]. These devices determine the current at a given potential and calculate the slope between this point on the polarization curve and the origin ($E - E_{corr}$).

It is expected for correct measuring by means of linear polarization that free corrosion potential is stationary prior to polarization [3]. During the measurement, the system being polarized with a given rate of polarization requires some time to achieve a steady-state [2]. High rate of polarization contributes to non-stationarity of the system by a double layer capacitance charging effect [1]. In case of potentiodynamic polarization, the requirement of the steady-state could be achieved by a low rate of polarization. For very fast polarization, when t approaches 0, the equation of a current response can be simplified to [2]:

$$\frac{dI}{dE} = \frac{1}{R_e} \tag{4}$$

and for very low polarization rate [2]

$$\frac{dI}{dE} = \frac{1}{R_e + R_p} \tag{5}$$

Assuming these two equations and low electrolyte resistance, it can be expected, when performing the potentiodynamic measurement within short potential range in the vicinity of free corrosion potential, that the polarization curve will be of a very sharp slope ($1/R_e$) at the beginning of polarization and $1/(R_e + R_p)$ after a long period of time, resulting in a non-linear polarization curve.

This study discusses the results of determination of polarization resistance by means of linear polarization which were primarily collected to estimate the threshold chloride level for activating several types of stainless steel in fresh as well as in carbonated concrete pore solutions. Some unexpected values of R_p led to a detailed survey of the originally measured data. The paper presents results of the non-linear polarization curves analysis.

2. Experimental

Since the linear polarization method was primarily used for assessing the threshold chloride level at which several types of stainless steel became locally activated, five stainless steel grades were selected and exposed to concrete pore solutions differing in pH (8, 12.5, 13.5) and chloride content (from 0.1 up to 150 g of chloride ions/l). It is not

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