

Monitoring of metal corrosion by electrochemical methods

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Abstract

The widespread use of metals and metal coatings in the manufacture of equipment and various products operated both in natural conditions and in technological environments requires the creation of means to control their corrosion behavior. This is relevant both in the process of developing these materials in the laboratory and for monitoring the current state of the equipment in operation. Methods based on the laws of electrochemical kinetics and coulometry make it possible to control the corrosion state of metal objects by measuring electrical characteristics such as current, potential, resistance and impedance. These electrical characteristics can be easily combined with the capabilities of modern microprocessor technology. To date, many methods and principles of interpreting the results of electrochemical measurements have been proposed to assess the corrosion state of metals, but it is not always easy to compare their capabilities and choose the optimal method for solving a particular problem, this publication compares various known methods of corrosion research based on electrochemical measurements. Their capabilities and the relationship of the parameters used are shown. The software for the implementation of the described methods is discussed.

Received: June 11, 2024. Published: July 17, 2024

doi: [10.17675/2305-6894-2024-13-3-7](https://doi.org/10.17675/2305-6894-2024-13-3-7)

Keywords: *corrosion, electrochemical methods, polarization resistance, electrochemical impedance.*

1. Introduction

During operation in natural conditions and technological environments, equipment made of metals and alloys is subjected to corrosion damage. The resulting damage is not limited to loss of mass or reduced structural strength. It is necessary to take into account the possibility of a subsequent “chain reaction”, leading to the failure of the entire complex, the detail of which is an element that has undergone corrosion destruction. At the same time, there is also a threat of environmental pollution, both by metal corrosion products themselves and by leakage of technological liquids and gases enclosed in metal structures (pipelines, tanks, *etc.*) Therefore, monitoring the corrosion state of metals in various environments is relevant [1].

Corrosion is a spontaneous process due to the lower thermodynamic stability of some metals compared to their oxidized compounds. It proceeds spontaneously with a decrease in free energy (and an increase in entropy) [2, 3]. Therefore, it is impossible to exclude corrosion of metals in principle. However, it can and should be significantly limited when

using various methods: – creation of special alloys, passivation of the metal surface by special treatment, application of protective coatings on metal, the use of corrosion inhibitors added to a corrosive environment or directly on the surface of the product, the use of protective or cathodic protection.

Metals in contact with solutions having ionic conductivity, as well as with some gases, especially in the presence of moisture, corrode by an electrochemical mechanism [2, 3]. Therefore, the use of electrochemical methods to monitor the corrosion state of a metal is not only fully justified, but also seems very convenient for objective registration of the rate of this process. It is obvious that the registration of electrical characteristics of an electrochemical process, such as current, charge, potential, resistance (impedance) can be easily implemented by means of modern electronics. And in combination with computer and microprocessor technology, it allows you to create hardware and software complexes for monitoring metal corrosion, both in the laboratory and in the field.

2. Coulometric Methods

All electrochemical methods are based on Faraday's law [2], which establishes the proportionality of the mass of the metal subjected to electrochemical transformation m (g) and the charge q (C) passed through the system during the time τ (sec):

$$m = Z \cdot q, \quad (1)$$

where: $Z = nM/F$ (g/C) is the electrochemical metal equivalent, n is the number of electrons in the reaction, M is the molecular weight, F is the Faraday constant ($F=96\,485.338\text{ C}\cdot\text{mol}^{-1}$).

Using (1), the mass corrosion rate K from the unit of the geometric surface of the metal per unit time can be determined as:

$$K = \frac{Z \cdot q}{S \cdot \tau} = Z \cdot i_{\text{corr}}, \quad (2)$$

where i_{corr} is the corrosion current density.

By calculating the density of the metal, equation 2 can be rewritten to calculate the rate of corrosion losses in thickness K_D :

$$K_D = Z \cdot i_{\text{corr}} / \rho \quad (3)^1$$

All electrochemical methods for assessing the corrosion rate of metals can be divided into two groups:

1. According to the concentration of metal ions that have passed into solution during corrosion;
2. By current densities or polarization resistance when an external polarization is applied to the system.

¹In equations 2 and 3, a scaling factor may be present to bring the values (sec – hour – year) and (μm – mm – cm – m) to the required dimensions.

The advantage of the first group of methods is the complete absence of external polarization of the sample during the corrosion experiment. However, at low corrosion rates, the concentration of oxidizing metal ions in the solution may be low. This requires the use of sensitive methods for analyzing the composition of the solution. One of the electrochemical methods for solving this problem is polarography. Among the polarographic techniques, the square wave inversion polarography with stationary amalgam anodes has a particularly high sensitivity [4].²

Another method may be based on measuring the charge required for the oxidation or reduction of the analyzed ion at its characteristic potential. In classical coulometry, using a potentiostat on an inert electrode (platinum, glass carbon), the electrolysis is provided at the characteristic potential that ensures the reduction or oxidation of the analyzed ion, and a change in current is recorded to its minimum background level. Then, the current is integrated for the entire time of electrolysis and the mass of the corrosion product is determined by (1). In [6], a modification of this coulometric technique is proposed, which does not require waiting for the current to decrease until the solution is fully depleted. Electrolysis with a characteristic potential³, which provided electrical transformations of the analyzed ion (metal corrosion product) is carried out for only 2–3 minutes and the kinetics of current decline over time is recorded. Then, using a special *ELFAN* program⁴ (Figure 4A), the parameters of the kinetic equation of current decay are determined.⁵

$$I = I_0 \cdot e^{-k\tau}; \quad (4)$$

where: I_0 is the initial electrolysis current, k is the kinetic constant.

Equation (4) with the found constants are integrated for a conditionally infinite time of solution production and the full charge required for complete electrical conversion of the analyzed ions is found for calculation according to (1):

$$q = \int_0^{\infty} I_0 \cdot e^{-k\tau} d\tau = I_0 / k \quad (5)$$

This method turned out to be quite fast compared to classical coulometry, where it is necessary to continue electrolysis until the solution is fully depleted. At the same time, it provides sensitivity and reproducibility at the level of spectral analysis methods.

²This method is implemented for ECOTEEST and IPC potentiostats using a specialized *POLINA* program [5].

³In particular, during corrosion of iron alloys in solution, two components are analyzed separately: for the Fe^{2+} ion, its oxidation potential to Fe^{3+} can be selected, and for the Fe^{3+} ion, on the contrary, its reduction to Fe^{2+} can be carried out. In the future, the individual charges required for the electrical conversion of these ions can be summarized to calculate the mass of the corroded metal.

⁴Electrochemical Faraday Analysis. The program controls the operation of the potentiostat and performs the necessary calculations.

⁵In this example, the equations for a solution containing steel oxidation products in the form of Fe^{2+} and Fe^{3+} ions are given.

Table 1.⁶ A comparative assessment of the mass loss Δm of St20 in 3% NaCl, pH=5.5 at exposure times of 168 and 672 h.

Measurement method	Ion	168 h	672 h
		$\Delta m, \text{g}$	$\Delta m, \text{g}$
Mass lost	–	0.040±0.002	0.15±0.02
Express coulometry	Fe ³⁺	0.0127±0.0001	0.050±0.002
	Fe ²⁺	0.0092±0.0003	0.0378±0.0008
	Fe ³⁺ + Fe ²⁺	0.0219±0.0002	0.088±0.002

3. Methods Based on Polarization Measurements

The second group of methods is based on the laws of electrochemical kinetics. When a metal comes into contact with an electrolyte, two mutually contradictory processes occur simultaneously on its surface: oxidation of the metal, leading to its corrosion and reduction of the depolarizer (for example, H⁺ ions or reactive oxygen species and other oxidants). Equilibrium is established between the currents expended on these reactions. In case of corrosion without external polarization, these currents are equal in magnitude but opposite in sign. Therefore, there is no any external current in such a system. The metal surface (within the local area) can be considered equipotential. It has a so-called “open circuit potential” (E_{OCP}), also called a stationary or corrosion potential. This potential is a compromise between the potentials of the anodic metal oxidation reaction and the cathodic reduction reaction of the depolarizer.

This is shown graphically on the Evans diagram [7], from which it can be seen (Figure 1) that the open circuit potential is established when the anode and cathode currents of partial reactions 1 and 2 are equal. In this case, the anode current corresponds to the metal corrosion current I_{corr} . The general polarization curve 3 is an algebraic sum of curves 1 and 2. In the overlap region, these partial curves mutually neutralize each other. Outside this zone, the general curve is increasingly approaching one of the partial branches.

The E_{OCP} value allows one to qualitatively assess the corrosion state of a given system. Using the Pourbaix diagram, the E_{OCP} value for the metal under study can be used to determine its thermodynamic stability in a given type of electrolyte, as well as the possible forms of its oxidation products. Some products (for example, insoluble oxides) can contribute to the passivation of metal and reduce its corrosion rate. In any case, by measuring only the E_{OCP} value it is impossible to quantify the corrosion rate, but only to assess whether the system is within certain boundaries where the risk of corrosion increases. In this case, the very limits of metal resistance to corrosion should first be determined experimentally. However, monitoring the state of the system using the E_{OCP} value is widely used in practice due to the ease of measurement. All you need is a high-resistance voltmeter and there is no

⁶The results are taken from [6].

need to apply external polarization to the object under study, which could disrupt its state. This monitoring method can be used both for laboratory tests and in field conditions for real objects.

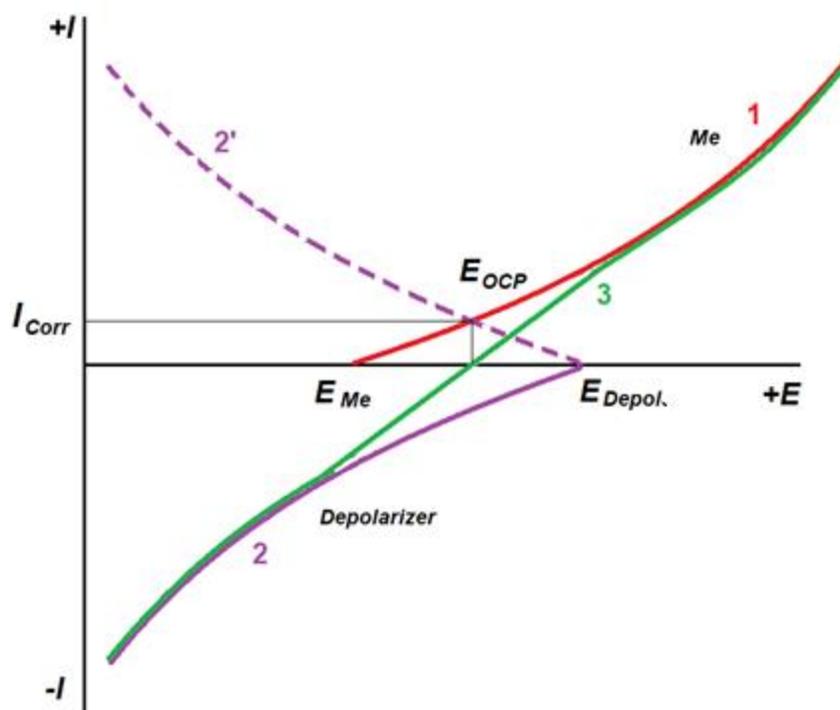


Figure 1. Evans corrosion diagram. 1: partial anodic polarization of the metal; 2: partial cathodic polarization curve of the depolarizing reaction; 2': cathodic curve “modulo” for determining the potential and corrosion current; 3: general polarization curve of the corrosion process.

3.1. Extrapolation of Tafel polarization curves

To quantify the corrosion rate, various techniques are used that involve applying external polarization to the system. It is impossible to measure the corrosion current directly in the experiment, since it flows in the metal body and is not registered in the external circuit.

Traditionally, to determine the corrosion current, polarization curves are used, taken at a low scanning speed near the potential E_{OCP} and plotted in semi-logarithmic coordinates, since the dependence of the current on the potential in a wide range has an exponential character [2, 8] (Figure 2).

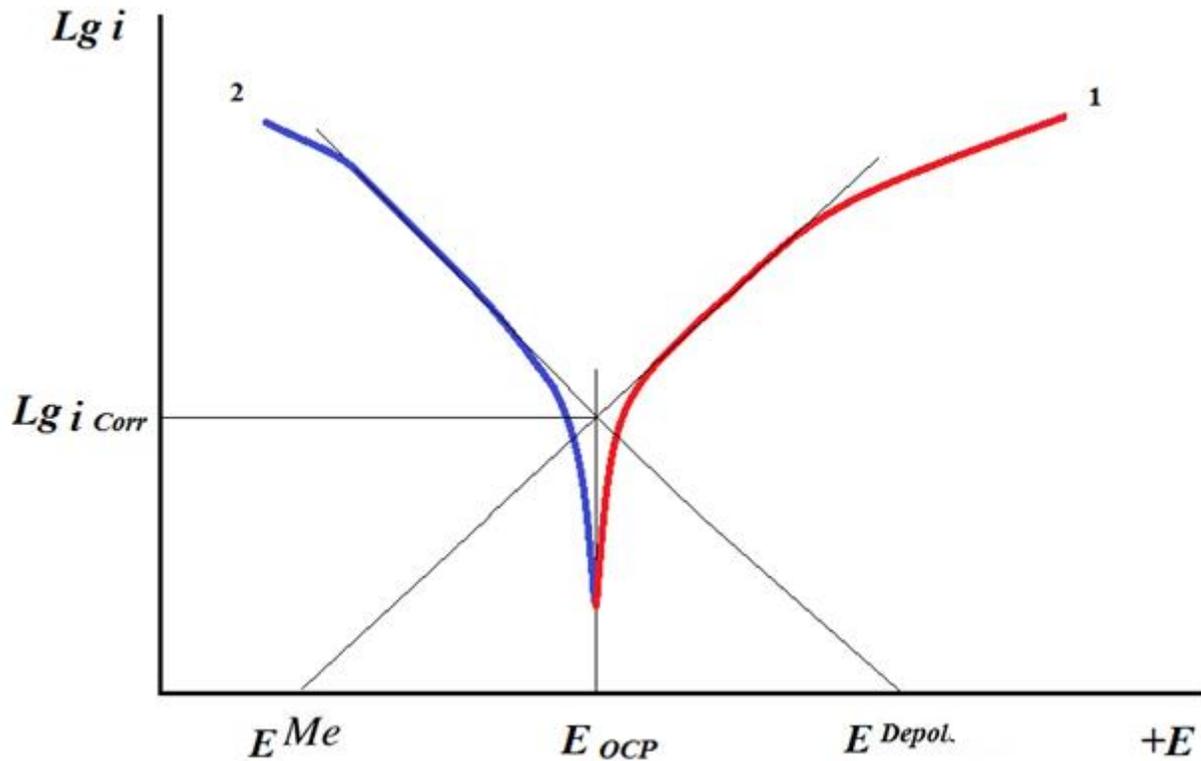


Figure 2. Polarization diagram of the corrosion process in Tafel coordinates. 1 is anodic branch of the polarization curve. 2 is cathode branch of the polarization curve.

This diagram shows the current densities recorded in the external circuit when external polarization is applied to the system. In the region close to the E_{OCP} potential, the recorded currents decrease and change sign, since, in accordance with the Evans diagram, mutual neutralization of the cathodic and anodic partial reactions occurs. On semi-logarithmic axes this appears as a pointed V-shaped area. In this case, its minimum value reflects the logarithm of the smallest absolute value of the recorded current.

In areas outside the overlap zone of the partial curves in Figure 1, straight sections are observed on the polarization curve in Figure 2, obeying the Tafel equation:

$$\eta = a + b \log i \quad (6)$$

In this equation, for each branch, η refers to the overvoltage of the corresponding reaction (deviation from E^{Me} or E^{Depol}); i is the current density, a and b are constants:

$$a = \frac{2.303RT}{\alpha nF} \log i_0 \quad b = \frac{2.303RT}{\alpha nF} \quad (7)$$

Here R is the universal gas constant, T is the absolute temperature, α is the transfer coefficient, i_0 is the exchange current of the corresponding reaction. The constant b represents the slope of the straight-line Tafel section of the polarization curve. As one moves

away from E_{OCP} , this slope can change for various reasons, in particular when the nature and/or mechanism of the electrochemical reaction changes [2, 3, 8], as well as under the influence of the ohmic factor.

Since each of the partial reactions 1 and 2 in Figure 1 obeys equation 6, therefore, in semi-logarithmic coordinates (Figure 2), their intersection point can be found by extrapolating their straight sections. In such a way, this method allows you to graphically simultaneously determine the E_{OCP} value and the logarithm of the corrosion current. Therefore, it is widely used in corrosion research.

However, the Tafel slopes method can be used only in laboratory conditions, since it requires a potentiostat that provides potential sweeping and registration of a current that varies by several orders of magnitude during polarization (usually from several mA to fractions of μA). To obtain clearly defined rectilinear Tafel sections, it is necessary to ensure good preparation of the metal surface and uniform distribution of current over its surface. This factor is influenced by the shape of the electrode and its location in the cell relative to the auxiliary electrode⁷ and the reference electrode. In addition, in high-resistance environments, the straightness of the sections may be disrupted due to the influence of the ohmic factor with increasing current density. Therefore, when using the Tafel curve method to determine the corrosion current, some experience is needed in determining the boundaries of linear sections for extrapolating lines.

3.2. Methods based on polarization resistance

With a small polarization dE relative to the corrosion potential, the change in the current dI of the general polarization curve 3 in Figure 1 turns out to be proportional to the shift in the potential. On the polarization curve, this looks like a linear section in straight coordinates, the nature of which is due to the mutual influence of partial curves 1 and 2 in the overlap region. The dE/dI ratio is an important process parameter called the polarization resistance R_{pol} .

Back in the 50s of the last century, it was empirically discovered [9, 10] that the corrosion rate is inversely proportional to the polarization resistance, which is much easier to measure experimentally than the slopes of the Tafel curves. If the corrosion rate is expressed in terms of the I_{Corr} parameter, it can be formally represented by the equation:

$$I_{\text{Corr}} = B/R_{\text{pol}}, \quad (8)$$

where B is the empirical coefficient of proportionality, depending on the corrosion system.

The values of the coefficient B for specific systems were determined by various methods, including comparing the loss of metal mass during corrosion and the measured value of R_{pol} [10].

⁷In some cases, it is necessary to use several auxiliary electrodes to distribute the current on the electrode more evenly, for example, to polarize a two-sided flat sample.

In classical works [11, 12], Stern and Geary established the relationship of the kinetic parameters of partial cathode and anode reactions with the value of B coefficient:

$$B = \frac{b_a b_c}{2.303(b_a + b_c)} \quad (9)$$

In this formula, b_a and b_c are the coefficients of Tafel's equation (6) for the anode and cathode sections of the polarization curve, respectively. Thus, if the kinetics of electrode reactions has been previously studied for a certain system, it is possible to calculate the corrosion rate value.

To monitor the corrosion rate by polarization resistance, a small dE polarization from an external source is periodically applied to the metal sample relative to its actual E_{OCP} potential (for example, $dE = 10 \text{ mV}$ ⁸) and R_{pol} is determined by the resulting current. Then, I_{Corr} is found using formula (8) and actual corrosion rates are calculated using formulas (2) and (3).

Specialized *CorrosionMeter* devices work on this principle [13]. This can also be done using a potentiostat under the control of a special program [14].

This method of polarization resistance is relatively simple to implement, and almost does not disturb the state of the object at low dE . It should be borne in mind that the corrosion rate determined by this method is not accurate, since it is calculated using a predefined constant B , which can change significantly over time when the state of the metal changes. For example, for the active state of steel, the Tafel coefficients usually take the values $b_a = 120 \text{ mV}$ and $b_c = 120 \text{ mV}$, which gives $B = 26 \text{ mV}$. In the passive state, the coefficient $b_a = \infty$, which will double the coefficient $B = 52 \text{ mV}$ [12]. Therefore, the values of the corrosion rates by this method should be taken as estimates, which may differ from the true ones, as a rule in the direction of overestimation (sometimes by 2 or more times). Also, for more accurate results, it is sometimes necessary to calibrate measurements based on the results of corrosion mass lost (gravimetry) [15]. In addition, it should be borne in mind that the polarization resistance method gives instantaneous corrosion values, and gravimetry gives integral values.

The *CorrosionMeter*-based technique can be used in laboratory tests of various materials, as well as in the field. In the latter case, the samples from the material of the object under study are used, placed in a corrosive environment interacting with the object.

3.3. Modified Mansfeld method

Although the measurement of polarization resistance is not difficult, in order to monitor the corrosion rate by this method, it is necessary to first determine the Tafel coefficients in a separate experiment, or use their theoretical values to calculate B . To reliably determine the Tafel slopes of the polarization curves, it is required to polarize the object from the corrosion

⁸The magnitude of the potential shift should be minimal so as not to cause irreversible changes in the state of the metal, but at the same time sufficient to register the current that has arisen.

potential, both in the cathode and anode regions, by at least 100 mV. However, in some cases this may not be enough. Obviously, this effect on the metal will be stronger the wider the boundaries of the potential change. This can irreversibly change its state and lead to reactions with the components of the solution (and inhibitors). To overcome these problems, F. Mansfeld proposed a modification of the polarization resistance method, which makes it possible to quickly determine the current value of the coefficient B in each individual measurement. In this case, the potential deviation from the E_{OCP} may not exceed 30 mV in each polarity [16].

This method is based on taking into account some nonlinearity of the polarization curve near the corrosion potential. It can be seen from Figure 1 that the nature of the general current dependence on the potential near E_{OCP} (curve 3) is determined by the shape of the partial polarization curves of the anode (curve 1) and cathode (curve 2) processes in the region of their mutual overlap. The current for each partial curve depends exponentially on the potential. The general current i can be expressed as a dependence on the polarization $\Delta E = E - E_{\text{OCP}}$ [17]:

$$i = i_{\text{Corr}} \left(e^{\frac{2.3\Delta E}{b_a}} - e^{-\frac{2.3\Delta E}{b_c}} \right) \quad (10)$$

It is obvious that only with the same kinetic parameters of partial reactions ($b_a = b_c$), the current of the general polarization curve will have a strictly linear dependence on the polarization only. Consequently, in the general case, a quasi-linear curve is formed near the corrosion potential, the curvature of which depends on the kinetics of the cathode and anode processes.

If we replace i_{Corr} in equation (10), expressing it in terms of R_{pol} , b_a and b_c from equations (8) and (9), we get:

$$i = \frac{b_a b_c}{2.303(b_a + b_c)R_{\text{pol}}} \left(e^{\frac{2.3\Delta E}{b_a}} - e^{-\frac{2.3\Delta E}{b_c}} \right) \quad (11)$$

Mansfeld proposed to rearrange the terms of this equation so that unknown coefficients remain on the right side:

$$2.303 \cdot i \cdot R_{\text{pol}} = \frac{b_a b_c}{2.303(b_a + b_c)} \left(e^{\frac{2.3\Delta E}{b_a}} - e^{-\frac{2.3\Delta E}{b_c}} \right) \quad (12)$$

The polarization resistance can be defined as the tangent to the polarization curve at the E_{OCP} potential:

$$R_{\text{pol}} = dE/dI \quad (13)$$

Taking into account the found R_{pol} , it is necessary to calculate the value of the new variable $2.303 \cdot i \cdot R_{\text{pol}}$ for each point of the polarization curve and obtain its dependence on the polarization ΔE (Figure 3).

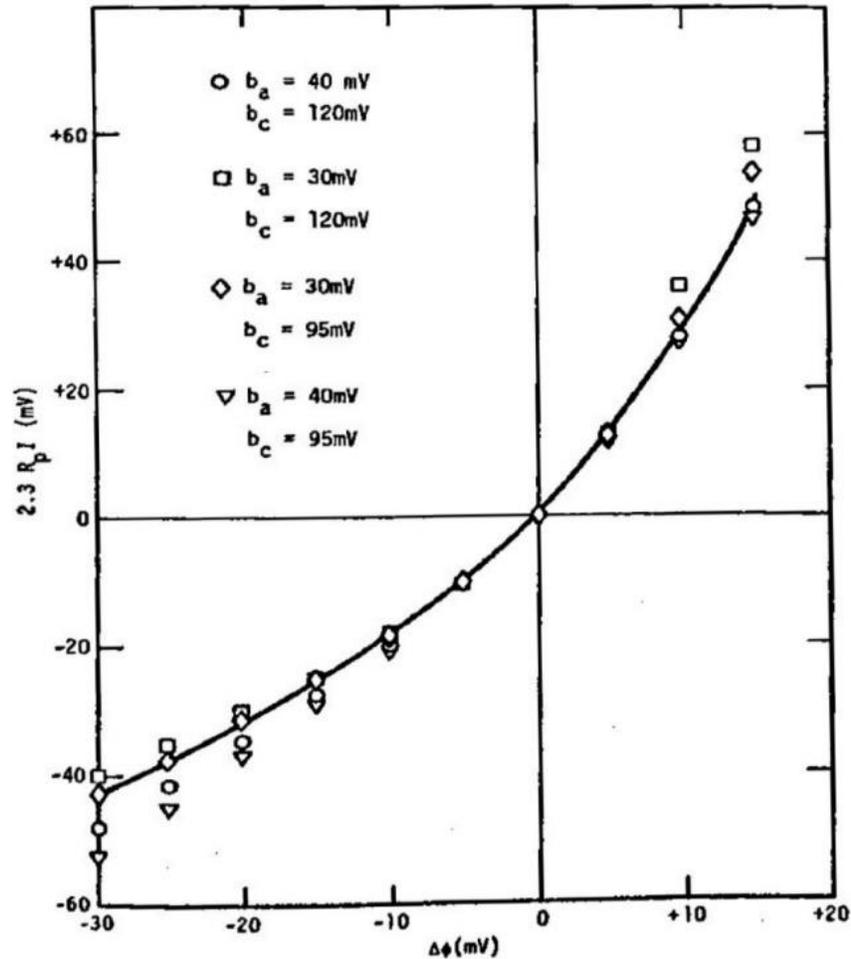


Figure 3. An example of a polarization curve in Mansfeld coordinates. Taken from [16]. The solid line shows the experimental dependence. The dots show the values calculated by (12) from the lab values shown in the figure.

The shape of the resulting curve $Y=f(\Delta E)$ is determined by the values of b_a and b_c coefficients, which can be selected based on theoretical assumptions, or calculated by optimization methods using a computer. In the 70s of the last century, when this technique was developed, the latter method could not be widely used. Nowadays, the use of computer optimization is not a problem. In particular, F. Mansfeld reports on the development of the *POLFIT* application [18], which provides the necessary calculations for determining corrosion currents along a quasi-linear section of the polarization curve according to equation (12).

Recently, there has been renewed interest in the practical use of the Mansfeld method, in particular, for the study of reinforcement corrosion in concrete. D. Shevtsov [19] critically analyzed the theoretical assumptions adopted in the derivation of equations (9–11) and showed that these equations are valid not only for processes occurring in the kinetic region on a homogeneous metal surface with a uniform current distribution. Moreover, similar

equations can be used for corrosion systems where the cathode and/or anode process is not provided by a single reaction. They also act in the presence of pitting corrosion.

It is important to note that it has been shown that for a quasi-linear section of the curve, the parameters of equation (12) b_a and b_c should be considered not as true Tafel's slopes, but as effective coefficients determining the nature of the dependence of current on the potential in this area. A comparison of the results obtained by the Mansfield method with the results obtained by the classical polarization resistance method showed their greater accuracy with respect to gravimetric measurements. For example, for corrosion of steel reinforcement in concrete in the marine atmosphere, the polarization resistance method overestimates the corrosion rate by 10 times, and according to the Mansfeld method by only 2.3 times [19].

This method seems promising and can be used on a par with the polarization resistance method.

3.4. Electrochemical impedance

Electrochemical impedance is also related to polarization resistance and is widely used in electrochemical and corrosion studies [20, 21]. However, in this case, the deviation of the potential of the test sample from the stationary state is performed by applying a harmonic AC signal of low amplitude. The current response signal will also be harmonic and, in general, may have a phase shift φ relative to the superimposed potential signal. Thus, the impedance of the system is a vector Z^*

$$Z^* = Z \cos \varphi + j Z \sin \varphi, \quad (14)$$

Here Z is the impedance modulus, equal to the ratio of the amplitudes of the potential signals and the current caused by it, φ is the phase shift, j is an imaginary unit. It can be seen from (14) that in the absence of phase shift, the impedance corresponds to the polarization resistance (13). However, the manifestation of capacitive and diffusion phenomena in electrochemical systems causes a phase shift between current and potential signals. The latter changes with the frequency of the harmonic signal. The nature of its frequency dependence is determined by the nature of the object.

Thus, by performing a series of impedance measurements at different frequencies of the harmonic signal and obtaining the impedance spectrum, it becomes possible to determine the nature of the interaction of active and reactive factors. To do this, you can choose an equivalent circuit made up of a set of simple elements (resistor, capacitance, inductance, constant phase element, *etc.*), the method of interconnection and the values of which provide a frequency dependence of the impedance, similar as for the experimental spectrum. At the same time, the nominal values of some resistive elements of an equivalent circuit can be judged from the rate of corrosion processes, using approaches similar to the polarization resistance method. To analyze impedance spectra in terms of equivalent circuits, programs based on the Simplex method optimization algorithms are used [22]. To work with IPC

potentiostats, we have developed the *DCS*⁹ software that allows us to process experimental impedance spectra in terms of equivalent circuits in automatic and manual mode.

The method of impedance spectroscopy allows not only assessing the intensity of corrosion processes, but also provides information about their mechanism. A significant amount of information about the methods of impedance spectroscopy and the analysis of its results does not allow us to consider them in detail in this publication. In relation to corrosion, they are given, for example, in [23, 24].

4. Development of Corrosion Monitoring Software

Modern electrochemical complexes provide computer registration of experimental results. For their processing and calculation of corrosion parameters, there are several specialized programs, for example, [25, 26]. We have also developed software for processing the results of the above described techniques performed with IPC potentiostats [27]. These software packages for the Windows operating system are designed taking into account the data format and the command system of these instruments. A number of programs (*ELFAN*, *POLINA*) were mentioned earlier. Two programs will be discussed in more detail below.

4.1. The *CorrMeter* program

This software package (Figure 4B) allows you to emulate the corrosion meter mode on an IPC potentiostat, as described in Section 3.2. The measuring cell may consist of two or three electrodes. In the program settings options, time intervals are set that control the moments of polarization activation, the magnitude of the potential shift dE , the constants of the electrode material under study (necessary for equations (2) and (3)), and the surface area. The program provides control of the potentiostat for periodic monitoring of the E_{OCP} in the absence of external polarization. And also calculates the polarization resistance to R_{pol} when applying the polarization of the dE . In accordance with the value of R_{pol} , the loss of mass and thickness as a result of corrosion is calculated taking into account the specified constants for various metals. The results are displayed graphically on the computer screen and saved in files, which allows you to study the change in the corrosion situation over time.

A detailed description of the *CorrMeter* program and examples of its operation are given in [14].

⁹ Dummy Circuits Solver.

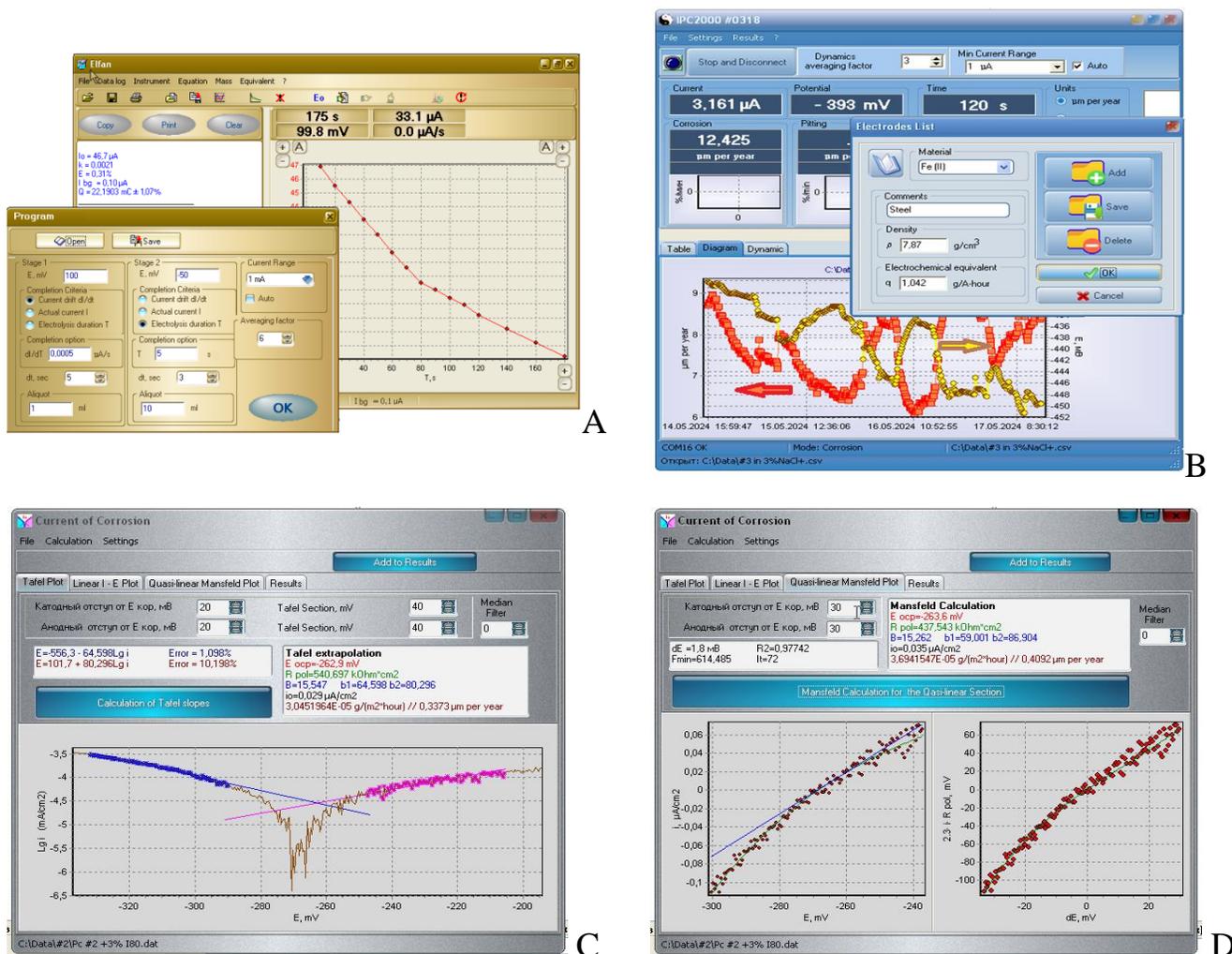


Figure 4. Examples of the program interfaces. A – Efan; B- CorrMeter; C, D – CurrCorr.

4.2. The CurrCorr program

This program is designed to calculate the corrosion current from files of polarization curves obtained experimentally with IPC potentiostats, but can also be used with other devices with appropriate coordination of the file format. The program provides three independent methods for I_{corr} determining:

- By extrapolation of Tafel curves;
- By linear polarization resistance;
- According to the Mansfeld method.

Based on the found I_{corr} values, the mass and thickness corrosion rate are calculated. For all three methods, a common program block is used, the algorithm of which is based on equations (2) and (3) with the ability to edit constants corresponding to the metal being studied.

- The module, based on the extrapolation of Tafel curves, provides data representation in the form of a semi-logarithmic graph (Figure 4C). Unlike similar programs [25], there is no automatic allocation of linear sections of the graph, since in many cases this can lead to an error. Using the settings, the user sets the potential boundaries of the Tafel linear sections separately for the cathode and anode branches of the polarization curve. Within these specified boundaries, the coefficients of the linear regression equation of the form are calculated for each branch:

$$E_c = a_c + b_c \log i \quad (15)$$

$$E_a = a_a + b_a \log i \quad (16)$$

The obtained straight lines for the Tafel plots are superimposed on a graph of experimental points for visual control. In addition, the level of error between the experimental and approximating data is calculated in order to assess the correctness of the selected site boundaries.

Comparing these expressions (15) and (16) with the Tafel equation (6), it is obvious that they differ in the use of absolute potentials E_c and E_a instead of overvoltage η . This accordingly affects the values of a_c and a_a . In this case, the coefficients b_c and b_a correspond to the slopes of Tafel curve branches.

The intersection point of the approximating lines in accordance with Figure 2 allows to determine the E_{OCP} and $\log i_{\text{corr}}$.

$$\log i_{\text{corr}} = \frac{b_a - b_c}{a_c - a_a} \quad (17)$$

$$E_{\text{OCP}} = b + a_c \log i_{\text{corr}} \quad (18)$$

According to the i_{corr} values mass and thickness corrosion rate is obtained. The values b_c and b_a using equations (8) and (9) are used to calculate the Stern–Geary coefficient B and R_{pol} . These values can be used for calculation and comparison with other methods.

- The second module of the program allows you to determine the slope of a linear section of the polarization curve near the corrosion potential within user-defined boundaries. The linear regression equation in this case has the form:

$$E = E_{\text{OCP}} + R_{\text{pol}} \cdot i \quad (19)$$

As in the previous method, the linearization line is plotted on the graph of experimental points and the approximation error is calculated. In accordance with the found resistance R_{pol} and the Stern–Geary coefficient entered by the user¹⁰, it is calculated by the corrosion current (8). The corrosion rate in the general module is calculated by the value of i_{corr} . In addition, from the found R_{pol} value, it is possible to determine the exchange current i_0 for a reversible reaction [8] using the formula:

¹⁰ B – values obtained from the Tafel curves or the Mansfeld method can be used.

$$i_0 = \frac{RT}{nFR_{\text{pol}}} \quad (20)$$

- The third module of the program provides the implementation of the Mansfeld algorithm based on the analysis of the nonlinearity of a quasi-linear section of the polarization curve near the corrosion potential (Figure 4D). To use equation (12), the experimental values of the absolute potential E must be replaced by the polarization ΔE , taking into account the previously found open circuit potential. In addition, the R_{pol} value should be calculated as tangent to the polarization curve at the E_{OCP} point. Thus, to implement the Mansfeld method, two mutually dependent parameters (E_{OCP} and R_{pol}) must be determined. If the section of the polarization curve near the corrosion potential is linear, then its slope and, consequently, the polarization resistance do not depend on the error in determining E_{OCP} . However, this section of the polarization curve usually has some curvature. Since the polarization resistance R_{pol} is calculated as tangent to the polarization curve at the point of stationary potential, therefore, the error in determining E_{OCP} will inevitably affect the results of the calculation of corrosion by the Mansfeld method.

In turn, the error in determining the potential may be due to a number of factors. In particular, Mansfeld believes that it may be the result of the influence of ohmic error, especially noticeable in poorly conducting media [18]. In our opinion, a systematic imbalance of the recording device when measuring currents and potentials can have a significant impact on the error in determining of E_{OCP} . Since the currents in the process of potential sweep when passing the E_{OCP} point become vanishingly small (and change sign), even a slight imbalance of the recorder at the level of several nanoamperes can cause an error in the actual determination of the value of the non-current potential of several millivolts, which may affect the correctness of determining the slope of the potential–current curve. To overcome this difficulty, equation (12) can be complicated by adding an additional variable ξ to be selected, taking into account the possible error in E_{OCP} value, regardless of the cause of its occurrence. The criterion for the correctness of this method will be the reduction of the error of the calculated dependence in comparison with the experimental points.

Thus, equation (12) in the case of three selected parameters (b_a , b_c , ξ) takes the form:

$$2.303 \cdot i \cdot R_{\text{pol}} = \frac{b_a b_c}{2.303(b_a + b_c)} \left(e^{\frac{2.3(\Delta E + \xi)}{b_a}} - e^{\frac{-2.3(\Delta E + \xi)}{b_c}} \right) \quad (21)$$

We performed comparative calculations using equations (12) and (21) for the same set of experimental points formed by their polarization curve of steel (St3) in an alkaline solution. The type of approximating curves obtained as a result of optimizing the parameters of the equations (12) and (21) is shown in Figure 5, and the numerical values of the parameters in Table 2.

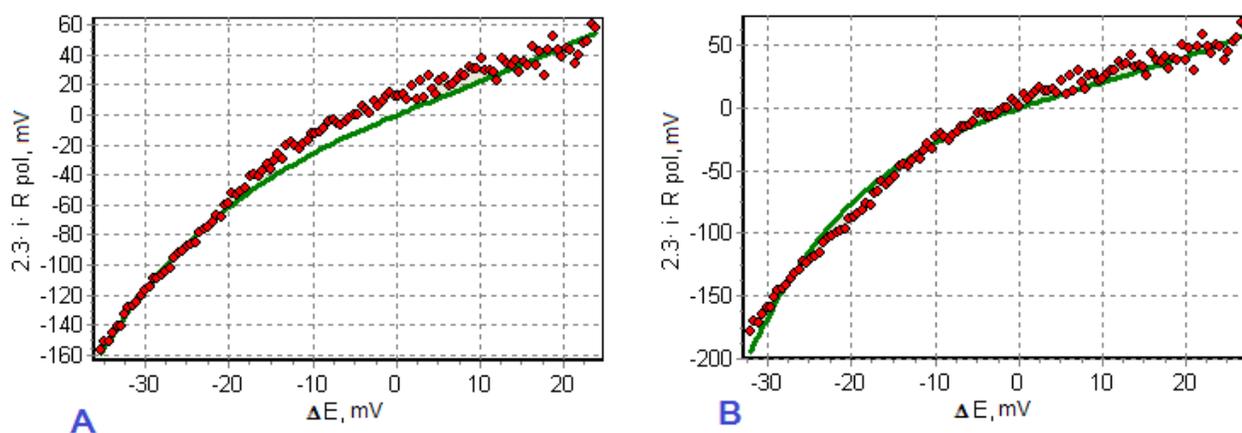


Figure 5. An example of optimizing the parameters of the Mansfeld function. The experimental points are shown in red. The green line is the result of optimizing the parameters of the equation. A – calculation for two parameters b_a , b_c . B – calculation for three parameters b_a , b_c and ξ .

It can be seen from the results obtained that when using equation (21), taking into account the additional parameter ξ makes it possible to increase the convergence of the approximating function with experimental points. Even a small correction of 3.6 mV to E_{OCP} value has a significant impact on the results of determining corrosion indicators.

Table 2. Parameters of the Mansfeld equation and corrosion indicators determined using them.

Equation	b_a , mV/dec	b_c , mV/dec	ξ , mV	Correlation coefficient R^2	The Stern–Geary coefficient B , mV	R_{pol} , $\text{k}\Omega \cdot \text{cm}^2$	i_{corr} , $\mu\text{A}/\text{cm}^2$
(12) Two parameters	43.310	60.958	–	0.9777	10.997	251.86	0.044
(21) Three parameters	32.629	57.797	3.3	0.9927	9.057	285.18	0.032

Thus, for the numerical solution of the Mansfeld equation, the principle of multidimensional optimization with sequential approximation is used until a constant value of ξ is reached. The described program uses the following algorithm for this purpose:

1. It is preliminarily assumed that there is no error at the experimental points ($\xi_0=0$) and the E_{OCP} potential will be determined at the point of changing the polarity of the current. At this potential, R_{pol} is calculated as a tangent to the polarization curve and, taking into account these values, the experimental data are converted as a dependence $Y=f(\Delta E)$, where

$$Y = 2.303 \cdot i \cdot R_{\text{pol}} \quad (22)$$

2. Using the Simplex method algorithms [22], three-factor optimization is performed and the values of b_c and b_a and ξ are found to ensure the best compliance with experimental data.
3. If $|\xi_0 - \xi| > 1$ mV, adjust the value of the open circuit potential ($E_{OCP} + \xi$) and at this point re-determine R_{pol} . Taking into account the updated result, the dependence $Y = f(\Delta E)$ is recalculated and rebuilt. Then the new value $\xi_0 = \xi$ is stored and the optimization is repeated according to point 2.
4. Otherwise, if $|\xi_0 - \xi| < 1$ mV, the optimization process is completed and the Stern–Geary coefficient is calculated based on the found values b_c and b_a , which allows calculating corrosion rate using the general program module.

The adequacy of the calculation is controlled by calculating the error and is visualized on the graph (Figure 4D).

In subsequent publications, a comparison of the results of the determination of corrosion indicators obtained by these three methods will be presented.

Conclusion

1. An overview of various methods for monitoring the corrosion state of metal based on electrochemical principles is provided. Of the considered methods, only potential measurements can be implemented in full-scale conditions. However, this method does not allow us to obtain quantitative indicators of the corrosion rate, but only to assess the transition from active dissolution to passivation. The remaining methods require laboratory application and allow you to monitor changes in the corrosion rate of a metal sample.
2. The possibilities of the considered methods are compared and it is shown how the same corrosion indicators can be obtained in different ways. At the same time, the values of the obtained corrosion indicators may differ.
3. A description of specialized computer programs designed to monitor the corrosion characteristics of objects is provided. These programs were developed by the author in relation to the command system and the data format of the IPC potentiostatic complex. However, some of them (*DCS* and *CurrCorr*), which are not related to the instrument control, can be used with other devices, provided that the data file format is consistent.
4. A discussion of the results of the calculation of corrosion characteristics obtained using various methods described above will be presented in a subsequent publication.

Acknowledgments

This study was carried out as part of R&D (2022–2024): “Chemical resistance of materials, protection of metals and other materials from corrosion and oxidation” (EGISU registration number 122011300078-1, inventory number FFZS-2022-0013).

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