DETERMINATION OF THE CORROSION RATE AND THE EFFECTIVENESS OF INHIBITORS BY THE METHOD OF POLARIZATION RESISTANCE

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In recent years the attention of corrosion engineers has been drawn to the so-called method of polarization resistance, which makes it possible to determine the corrosion rate at any desired time. The starting point for the development of this method was the reverse proportionality between the corrosion rate and the slope of the $\mathscr{E} = f(i)$ curve close to the steady potential of the corroding metal observed by many investigators [1,2]. In [3-5] Stern gave the theoretical foundation of this dependence and indicated the areas of applicability and the possible error in the method.

THEORETICAL FOUNDATION OF THE METHOD

Stern [3-5] made a detailed examination of the case where the deceleration stage of the cathode reaction is the discharge of hydrogen ions and the deceleration stage of the anode reaction is the ionization of metal atoms. In this case the external polarizing current i_{ex}, which displaces the potential of the corroding metal from the steady potential ε_s toward more negative values by a small value $\Delta\mathscr{E}$, can be expressed as

$$i_{ex} = \vec{i}_1 - \overleftarrow{i_2} = k_1 [H^+]' e^{-\frac{\alpha F(\mathscr{E}_c + \Delta\mathscr{E})}{RT}} - k_2 e^{\frac{\beta z F(\mathscr{E}_c + \Delta\mathscr{E})}{RT}} \quad (1)$$

or

$$i_{ex} = i_c \left(e^{-\frac{\alpha F \Delta\mathscr{E}}{RT}} - e^{\frac{\beta z F \Delta\mathscr{E}}{RT}} \right), \quad (2)$$

where $[H^+]'$ is the surface concentration of hydrogen ions; a and β are the transport coefficients of the cathodic and anodic reactions; i_c is the rate of corrosion in the absence of external polarization.

For small values of $\Delta\mathscr{E}$ (small external current) the exponents in Eq. (2) can be expanded into series and the development can be limited to the first two terms

$$i_{ex} = -i_c \left(\frac{\alpha F \Delta\mathscr{E}}{RT} + \frac{\beta z F \Delta\mathscr{E}}{RT} \right).$$

By introducing

$$a = \frac{2.3RT}{b_k F}, \quad \beta = \frac{2.3RT}{b_a z F},$$

we obtain

$$i_{ex} = -2.3 \frac{(b_k + b_a)}{b_k b_a} i_c \Delta\mathscr{E}$$

or

$$\frac{\Delta\mathscr{E}}{\Delta i} = -\frac{b_k b_a}{2.3(b_k + b_a)} \frac{1}{i_c}. \quad (3)$$

$\Delta\mathscr{E} \to 0$

The case where the kinetics of the anodic reaction is determined by the ionization of the metal and the kinetics of the cathodic reaction is determined by the diffusion of some depolarizer (dissolved oxygen, for example) is no less interesting. The rate of the cathodic process under these conditions is equal to the limit diffusion current i_d, while the rate of the anodic process, as in the preceding case, is described by

the equation of the theory of decelerated discharge. The external polarization of the metal up to certain values of the potential affects only the rate of the second process. Therefore,

$$i_{ex} = \vec{i}_1 - \overleftarrow{i}_2 = i_d - k_2 e^{\frac{\beta z F (\mathscr{E}_c + \Delta\mathscr{E})}{RT}}$$

or

$$i_{ex} = i_c \left(1 - e^{\frac{\beta z F \Delta\mathscr{E}}{RT}}\right). \tag{4}$$

If $\Delta\mathscr{E}$ is small then expansion into series and transformation of (4) gives us

$$i_{ex} = -\frac{2.3}{b_a} i_c \Delta\mathscr{E}$$

or

$$\frac{\Delta\mathscr{E}}{\Delta i}_{\Delta\mathscr{E}^\circ \to 0} = \frac{b_a}{2.3} \frac{1}{i_c}. \tag{5}$$

In some cases the corrosion rate is controlled by the stage of discharge of hydrogen ions and by the diffusion of the products of dissolution of the metal. The density of the external cathode current in this case is found by the equation

$$i_{ex} = \vec{i}_1 - \overleftarrow{i}_2 = k_1 [H^+]' e^{-\frac{\alpha F (\mathscr{E}_c + \Delta\mathscr{E})}{RT}} - i_d$$

or

$$i_{ex} = i_c \left(e^{-\frac{\alpha F \Delta\mathscr{E}}{RT}} - 1\right). \tag{6}$$

By expanding into series and transforming this equation we obtain

$$i_{ex} = -\frac{2.3}{b_k} i_c \Delta\mathscr{E}$$

or

$$\frac{\Delta\mathscr{E}}{\Delta i}_{\Delta\mathscr{E}^\circ \to 0} = \frac{b_k}{2.3} \frac{1}{i_c}. \tag{7}$$

Equations (3), (5), and (7) show that the ratio $\Delta\mathscr{E}/\Delta i$, called the polarization resistance, is inversely proportional to the corrosion rate. This relationship is satisfied as long as we can limit ourselves to the first two terms of the expansion into series of the indicated exponential functions. In the case described by Eq. (2) the magnitude of the polarization up to which this limitation is preserved with a given error can be calculated if, as in [5], we assume that $b_a = b_k = b$. For this purpose one must solve Eq. (2) with respect to $\Delta\mathscr{E}$

$$i_{ex} = i_c \left(e^{-\frac{2.3\Delta\mathscr{E}}{b_k}} - e^{\frac{2.3\Delta\mathscr{E}}{b_a}}\right),$$

$$i_{ex} = -2i_c \operatorname{sh} \frac{\Delta\mathscr{E}}{b} 2.3,$$

$$\Delta\mathscr{E} = -\frac{b}{2.3} \operatorname{Arsh} \frac{i_{ex}}{2i_c}. \tag{8}$$

The expansion of this function gives a series with alternating signs:

$$\Delta\mathscr{E} = -\frac{b}{2.3 \cdot 2} \frac{i_{ex}}{i_c} + \frac{b}{2.3 \cdot 48} \left(\frac{i_{ex}}{i_c}\right)^3 - \ldots.$$

The first term of this series corresponds to Eq. (3), and therefore the maximum possible error e is expressed by the second term

$$e \leqslant \frac{b}{2.3 \cdot 48} \left(\frac{i_{ex}}{i_c}\right)^3. \tag{9}$$

From (9) we can find the ratio i_{ex}/i_c for given values of b and e and by introducing it into Eq. (8) we calculate $\Delta\mathscr{E}$ with a given error. Figure 1a shows the values of $\Delta\mathscr{E}$ up to which one can polarize an electrode at different values of b so that the error e does not exceed the given permissible error.

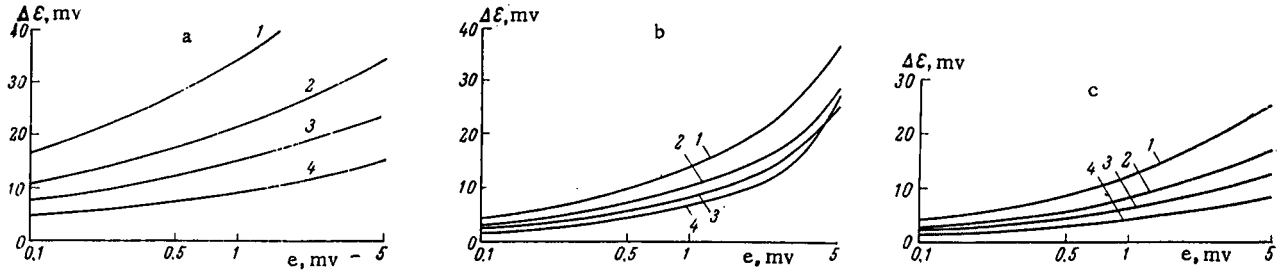

Fig. 1. Dependence of the acceptable magnitude of polarization on the error for the following cases: a) Decelerated discharge (ionization); b) decelerated diffusion (ionization); c) decelerated discharge (diffusion). The values of the coefficients are: 1) 0.20; 2) 0.10; 3) 0.06; 4) 0.03.

One can examine the case described by Eq. (4) in a similar way. Let us solve this equation with respect to $\Delta\mathscr{E}$

$$\Delta\mathscr{E} = \frac{b_a}{2.3}\ln\left(1 - \frac{i_{ex}}{i_c}\right). \tag{10}$$

After expanding (10) into series we find

$$\Delta\mathscr{E} = -\frac{b_a}{2.3}\frac{i_{ex}}{i_c} - \frac{b_a}{2.3}\frac{i_{ex}}{2i_c^2} - \frac{b_a}{2.3}\frac{i_{ex}}{3i_c^3} - \ldots.$$

The error e at $i_{ex}/i_c \ll 1$ is determined by the inequality

$$e < \frac{b_a i_{ex}}{2.3 \cdot 2i_c^2}. \tag{11}$$

By replacing i_{ex}/i_c calculated by (11) for different values of b_a and e in Eq. (10) we obtain the dependence of the polarization $\Delta\mathscr{E}$ on the acceptable error (Fig. 1b).

For the conditions described by Eq. (6) similar transformations give us

$$\Delta\mathscr{E} = -\frac{b_k}{2.3}\ln\left(\frac{i_{ex}}{i_c} + 1\right) \tag{12}$$

$$\Delta\mathscr{E} = -\frac{b_k}{2.3}\frac{i_{ex}}{i_c} + \frac{b_k}{2.3}\frac{i_{ex}}{2i_c^2} - \frac{b_k}{2.3}\frac{i_{ex}}{3i_c^3} + \ldots$$

$$e \leqslant \frac{b_k}{2.3}\frac{i_{ex}}{2i_c^2}. \tag{13}$$

The corresponding dependence $\Delta\varepsilon = f(e)$ is shown in Fig. 1c.

EXPERIMENTAL RESULTS

In the first series of experiments the sample was polarized by a current of known intensity and the potentials were measured with a PPTV potentiometer, using the ordinary circuit. Variations of this circuit used for similar purposes are described in [6, 7]. Round samples were stamped out of low alloyed iron; they were degreased electrochemically in an alkaline solution. The experiments were continued for 24 h at 20 ± 0.5 °C in 1 NH_2 SO_4 and also in the same solution with some additional elements. The polarization resistance $\Delta\mathscr{E}/\Delta i$ was determined after different periods of time from the beginning of the experiment; the corrosion rate i_c at the same moment of time was calculated by Eq. (3). The results were used to draw a curve (Fig. 2) representing the variation of corrosion as a function of time. The average value of i_c over the whole period of the experiment, determined from these curves, was compared with the results obtained by the gravimetric method. The difference between the results obtained by the two methods did not exceed 10%.

To improve the method, we developed an apparatus which records the polarization resistance during fractions of a second [8]. The reduction in the polarization time decreases the excitations in the system induced by the external currents, and this is particularly important when one uses solutions containing in-

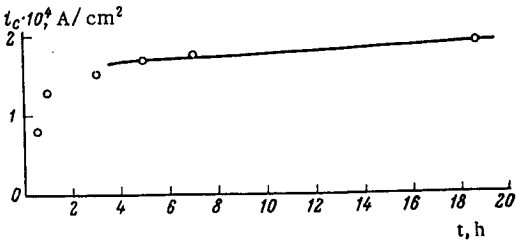

Fig. 2. Dependence of the corrosion rate of iron on time in 1 N H_2SO_4 obtained by using ordinary polarization equipment.

hibitors. Also, it makes it possible to determine more precisely the time to which the corrosion rate corresponds.

The diagram of the apparatus is shown in Fig. 3. The main parts of the apparatus are the electrochemical cell 1, a switch 2, a time relay 3, a direct current amplifier 4, and an automatic recording potentiometer 5. The structure of the cell is such that one can place in it eight samples around the circumference and the same number of reference electrodes. Each sample can be either a working sample or an auxiliary electrode. In this way a two-sided polarization is carried out in the cell and all eight samples are tested at the same time. The polarizing current in the circuit of the cell has six limits determined by the polarization resistances $R_1 - R_6$. The potential of the working electrode (W.E.) is measured with respect to a reference electrode (R.E.) made of the same metal and immersed in the same solution. The initial difference of potentials created between W.E. and R.E. is compensated by the amplifier simultaneously with tuning of the amplifier to zero. The duration of the current pulse for the polarization of the working electrode is determined by the time relay 3. The difference of potentials occurring during polarization is applied to the amplifier 4 and then to the automatic recorder 4; the scale of the automatic recorder is graduated in units of polarization resistance.

Using this equipment, we obtained curves of the variation of polarization resistance with time for the media indicated in the table. From the curves we determined the average value of the polarization resistance; the loss of weight of the samples was used to determine the corrosion rate. By replacing these values in Eq. (3) we calculated the coefficient

$$K = \frac{b_k b_a}{2.3(b_k + b_a)}.$$

The table shows that the value of K for the media investigated remains almost constant and equal on the average to $2 \cdot 10^{-2}$, which is in agreement with the values found from the slopes of the cathodic and anodic polarization curves. Therefore, we may assume that the theoretical concepts upon which the method is based are correct for the iron-oxygen system and that the dissolution of iron in this case is the result of hydrogen depolarization without the formation of insoluble compounds.

Figure 4 shows the variation of the corrosion rate with time obtained on the basis of the results relative to the polarization resistance in pure acid solution. The variation of the corrosion rate during the initial period may be due to the presence of an oxide film on the surface of the metal and its dissolution with time. The subsequent linear increase in the dissolution rate is apparently due to the increase of the real surface area of the sample. For the linear sections of the curves we can write equations of the dependence of the corrosion rate on time (these equations are given below each of the figures). In these equations the free terms are found by extrapolating the straight lines to the axes of ordinates, i.e., they represent the rate at which the metal would dissolve at the first moment of contact with the acid if the metal were not covered with a protective (oxide) film. These values characterize the comparative agressivemess of the corrosive medium, and therefore we can rightly call them coefficients of aggressiveness. The values of the agressiveness coefficients for the media investigated are given in the table. It can be seen that the 6 NH_2SO_4 solution is the most aggressive medium.

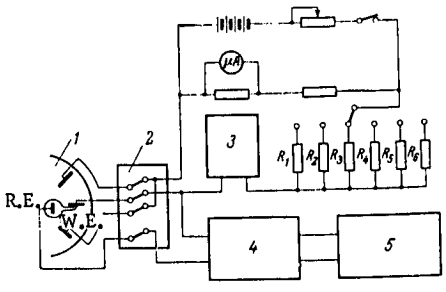

Fig. 3. Diagram of the apparatus for determining the corrosion rate by the method of polarization resistance.

The curves relative to the corrosion rate in acid solutions containing surface active elements have a different shape than those relative to pure acids (Fig. 5). Apparently in the presence of these elements the process of dissolution of the surface film is different. For weak inhibitions such as α - picoline (curve 1) the corrosion rate is linear after a given time, which may be due, as in the case of pure acids, to the increase of the real surface area of the sample. For the KPI-1 inhibitor (curve 2, Fig. 5) the dependence of the corrosion rate of time differs

Corrosion of Iron in Acid Solutions at 20 °C

Medium	i_c (average), A/cm²	$\frac{\Delta\varepsilon}{\Delta i}$ (average), Ω	K (from weight losses)	K (from polarization curves)	Aggressiveness coefficient, A/cm²	Deceleration coefficient, γ
6N H_2SO_4	—	50	$1.8\cdot10^{-2}$	—	$3\cdot10^{-4}$	—
1N HCl	$2.0\cdot10^{-4}$	106	$2.1\cdot10^{-2}$	$2.1\cdot10^{-2}$	$1.6\cdot10^{-4}$	—
1N H_2SO_4	$1.9\cdot10^{-4}$	120	$2.2\cdot10^{-2}$	$1.8\cdot10^{-2}$	$1.5\cdot10^{-4}$	—
1N H_2SO_4 + 3g/liter PB-8-2	$1.5\cdot10^{-4}$	108	$1.6\cdot10^{-2}$	$1.3\cdot10^{-2}$	$1.5\cdot10^{-4}$	1
1N H_2SO_4 + 0,1 M α-picoline	$0.4\cdot10^{-4}$	470	$1.9\cdot10^{-2}$	—	$0.3\cdot10^{-4}$	5
1N H_2SO_4 + 0,01 M monomethylolthiourea	$1.6\cdot10^{-5}$	1400	$2.2\cdot10^{-2}$	$1.7\cdot10^{-2}$	$0.16\cdot10^{-4}$	9.4
1N HCl + 3 g/liter PB-8-2	$1.6\cdot10^{-5}$	2850	$4.5\cdot10^{-2}$	$1.6\cdot10^{-2}$	$0.13\cdot10^{-4}$	12.3
1N H_2SO_4 + 0,01 M decylpyridine chloride	—	2500	—	$1.1\cdot10^{-2}$	$0.07\cdot10^{-4}$	21.4
1N H_2SO_4 + 0,01 M KPI-1	—	3400	—	$1.1\cdot10^{-2}$	$0.04\cdot10^{-4}$	37.5

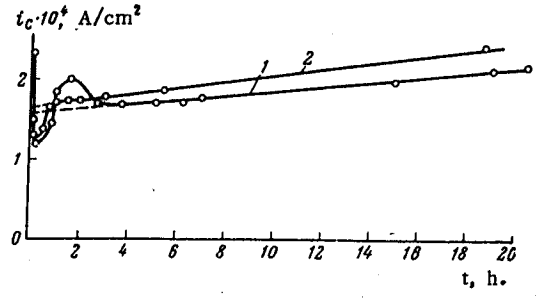

Fig. 4. Dependence of the corrosion rate of iron on time in 1N H_2SO_4 (1) and 1N HCl (2). The linear sections of the curves are described by the equations: 1) $i_c = 1.54\cdot10^{-4} + 0.035\cdot10^{-4}t$; 2) $i_c = 1.64\cdot10^{-4} + 0.043\cdot10^{-4}t$.

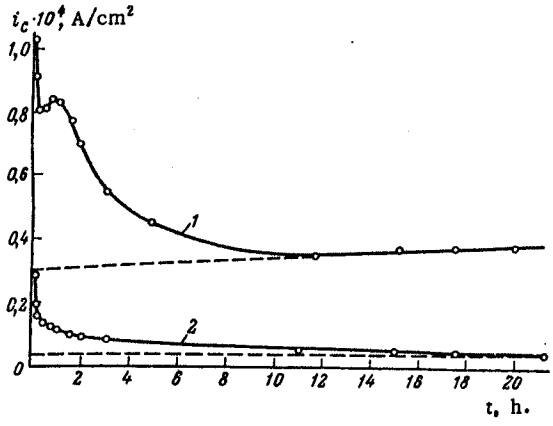

Fig. 5. Dependence of the corrosion rate of iron on time in 1N H_2SO_4 + 0.1 M α-picoline (1) and in 1 N H_2SO_4 + 0.01 M KPI-1 (2) The linear section of curve 1 is described by the equation: $i_c = 0.3\cdot10^{-4} + 0.004\cdot10^{-4}t$.

from those examined before in that there is no linear increase in the corrosion rate. The aggressiveness coefficient, found by extrapolation of the rectilinear section, is very small in this case (see table).

The protective action of inhibitors is characterized by the deceleration coefficient γ, which indicates by what factor the corrosion rate is decreased as the result of adding the inhibitor. This coefficient is calculated on the basis of the weight losses of samples in a pure and in an inhibited acid. One can use the ratio between the aggressiveness coefficients as a modified method of determining the deceleration coefficients. Then all complications due to the change in the surface during corrosion and the dependence of the corrosion rate on time are eliminated. Some of the coefficients γ determined in this manner are given in the table.

CONCLUSIONS

1. We have examined the theoretical foundation of the method of polarization resistance.
2. We found that this method can be used to determine the corrosion rate of iron in acid media and to calculate the protective action of inhibitors.
3. We formulated the concept of the aggressiveness coefficient, which is a quantitative measure of the effect of the medium on the pure surface of the corroding metal. We proposed a modified method of determining the deceleration coefficient γ based on the use of the aggressiveness coefficients.

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