Improvement of the Linear Polarization Resistance Method for Testing Steel Corrosion Inhibitors

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Abstract—The linear polarization resistance method is used to improve the technique of corrosion control in liquid conducting according to GOST 9.514–99 (General Corrosion and Aging Protection System. Corrosion Inhibitors for Metals in Water Systems. Electrochemical Method of Determining the Protective Ability). Corrosion monitoring is shown to be performed by electronic devices with real-time data transfer to industrial controllers and SCADA systems.

INTRODUCTION

The corrosion damage in industrialized countries is known to be significant, 4–6% of the national income. The corrosion-induced metal losses can be substantially decreased when various corrosion protection methods are used. The successful application of these methods needs reliable fast methods for controlling the corrosion activity of a medium and determining the corrosion rate of metals and other corrosion parameters. The linear polarization resistance (LPR) method proposed by Stern and Geary in 1957 is in wide use among the device methods of corrosion control in liquid conducting media.

This electrochemical method is based on measuring the polarization resistance of the metal–medium interface ear a steady corrosion potential. Here, the corrosion rate expressed in terms of the metal dissolution current density is inversely proportional to the polarization resistance.

If medium resistance compensation devices are used, this method can be applied in water and water–oil media with an electrical conductivity of >2 µS/cm.

The measurement of LPR is the basis of the most widely used corrosion monitoring with electronic devices. In this case, the inversely proportional relation between the polarization resistance and the corrosion rate of a metal at its weak polarization with respect to a steady corrosion potential is applied.

The method of measuring LPR is the only method that can be used to (1–10 min) measure the corrosion rate rapidly and, thus, to provide on-line reaction to the failures in technological processes that cause corrosion growth. The on-line effect is maximal when the devices that provide real-time data transfer to a server. This approach ensures the maximum increase in the lifetime of equipment and the minimum corrosion-induced idle time.

In this method, two electrodes made of the material to be tested are placed in the aggressive corrosion medium and are polarized by an external current in the potential range where a linear character of the polarization curve in the current–potential coordinates is fulfilled. This range is as close as possible to the corrosion potential. The total resistance of the circuit between the electrodes is determined with allowance for the measured electrode potential, the initial emf (which is usually nonzero), and the current between the electrodes. This total resistance is the sum of the two polarization resistances of the electrodes, which are taken to be the same because they are made of the same metal, and the resistance of the solution. To determine the polarization resistance, the resistance of the solution should be subtracted from the total resistance of the circuit. Note that not all of the LPR devices take into account the ohmic resistance of working media, since this feature complicates a device (when measuring the resistance, the device operates as a conductometer). Therefore, the readings of the devices that do not take into account this factor deviate substantially from the actual corrosion rate.

The LPR method is used in a large number of laboratory and commercial corrosion rate control devices

used, which are widely applied under industrial conditions [1, 2].

The LPR method is implemented in Russian Monicor-2M and Monicor-3-GSM-LPR corrosion meters. The latter devices transfer real-time information to a web server through GSM/GPRS channels or to industrial controllers and SCADA systems through RS-485 according to the MODBUS protocol.

The LPR-based technique of determining corrosion has been successfully applied for almost all types of water-based aggressive media for more than thirty years. As an example, we note the water- and heat-supply systems of commercial enterprises of housing and public utilities, waste water cleaning systems, extraction of hydrocarbons with associated water [3–8], and the production of cellulose and paper.

Such devices are widely used in field and laboratory experience, since they can rapidly determine the efficiency of corrosion inhibitors (CIs) in 4- to 8-h tests [9].

Owing to its exceptional rate in obtaining results, the LPR method makes it possible to reveal high corrosiveness of a working medium at early stages and, hence, to prevent negative consequences of corrosion, to determine a correlation between corrosion and the accompanying technological process parameters (pressure, temperature, pH, flow rate), and to estimate the efficiency of inhibitor corrosion protection of other methods related to action on working media.

In the general case, the Stern–Geary principle, which is the basis of the LPR method, is reduced to the following: corrosion critical density j_{cor} (mA/cm^2) is inversely proportional to polarization electrical resistivity R_p (Ω/cm^2), the electrode surface area, and corrosion potential E measured near a steady potential,

$$\left(\frac{dE}{dj}\right)_{dE \to 0} = R_p = \frac{b_a b_c}{2.3 j_{cor}(b_a + b_c)} = \frac{K}{j_{cor}}, \qquad (1)$$

where b_a and b_c are the slopes of the anode and cathode Tafel straight lines in semilogarithmic coordinates (mV).

From Eq. (1), we have

$$K = b_a b_c / 2.3(b_a + b_c), \ j = K/R_p,$$

where K is the coefficient of proportionality, which can change in the range 6.5–52.11 mV depending on the values of b_a and b_c. At room temperature, this coefficient is $K = 20–25$ mV for the majority of water media for iron and carbon steels [10, 11].

In practice, one constant is applied to measure the corrosion rate of carbon steels by LPR devices. Although these devices can change this constant, there are no clear recommendations on this point.

When analyzing the slopes of the Tafel segments of a polarization curve, which characterize different corrosion mechanisms, we can assume that the induced corrosion rate can differ from the real corrosion rate of sensor electrodes in inhibitor-free media by a factor

of 1.3. In inhibited oxygen-free media, this rate can be lower than that for inhibitor-free media by a factor of 1.3–2; in oxygen-containing media, it can be lower by a factor of 1–3 and even 6 in the case of very strong reagents. Although the Tafel slopes can be determined before every change in the measurement conditions to refine the constant, this procedure is not used because of the lack of necessity to determine the absolute corrosion rate. The experience of application of LPR devices in oil-field practice shows that the difference between the indicator-measured and the average corrosion rate in comparison with the classical method (from the mass losses of reference samples) reaches 20–50% in most oil-field oxygen-free media [12].

According to the Faraday law, the current corrosion index (j_{cor}, mA/cm^2) is converted into the depth corrosion index (v_{cor}, mm/year) for electrodes made of iron or low-carbon steel using the formula

$$v_{cor} = 11.7 j_{cor}. \qquad (2)$$

For the surface area of the electrodes entering in the set of a Monicor sensor ($S = 4.7$ cm^2), Eq. (2) is reduced to the form

$$v_{cor} = 11.7 \times 2K/4,$$
$$7R_p = 4.93 K/R_p = K_{sen}/R_p, \qquad (3)$$

where K_{sen} is the sensor constant, $K_{sen} = 2.16 b_a b_c/(b_a + b_c)$.

The purpose of this work is to improve the technique of laboratory corrosion investigations according to GOST 9.514–99 (General Corrosion and Aging Protection System. Corrosion Inhibitors for Metals in Water Systems. Electrochemical Method of Determining the Protective Ability), where the LPR is used.

EXPERIMENTAL

A new model of a corrosion rate indicator (Monicor-3-GSM-LPR) has been produced at OOO NPF Akrus-M since 2014. This device is intended for the LPR determination of the corrosiveness of a liquid medium and for real-time data transfer to a web server.

This device is applied to determine the efficiency of reagents according to GOST 9.514–99, which is used in Russia and the Eurasian Economic Community customs union for laboratory tests of CIs and choosing the most effective types. Similar specifications exist in the recommendations of NACE and other organizations abroad.

However, the noted standard and other norms do not imply the possibility of changing the sensor constant during measurements in different media. The sensor constant is specified by the user of a device and remains unchanged when a working medium changes or a reagent is introduced into it.

Table 1. Experimental results for the water of the Ety-Purovsk deposit

CI		I_{cor}, mA	j_{cor}, mA/cm²	v_{cor}, mm/year	b_c	b_a	K	K_{sen}	Volume fraction, %	
no.	C_{CI}, mg/L						mV		water	oil
Control		0.00500	0.00106	0.0124	86	42	12.3	60.9		
1	10	0.00035	0.00007	0.0009	100	57	15.8	78.4		
	25	—	—	—	100	58	15.9	79.3		
2	10	0.00018	0.00004	0.0004	100	40	12.4	61.7	50	50
	25	0.00090	0.00019	0.0022	106	50	14.8	73.4		
3	10	0.00023	0.00005	0.0006	85	60	15.3	76.0		
	25	0.00038	0.00008	0.0009	80	65	15.6	77.5		
Control		0.10200	0.02170	0.2539	142	40	13.6	67.4		
1	10	0.00011	0.00002	0.0003	110	52	15.4	76.3		
	25	—	—	—	100	43	13.1	65.0		
2	10	0.00060	0.00013	0.0015	160	44	15.0	74.5	30	70
	25	0.00105	0.00022	0.0026	92	64	16.4	81.5		
3	10	0.00013	0.00003	0.0003	98	72	18.0	89.7		
	25	0.00033	0.00007	0.0008	90	88	19.3	96.1		
Control		0.01050	0.00223	0.0261	120	42	13.5	67.2		
1	10	0.00019	0.00004	0.0005	118	55	16.3	81.0		
	20	0.00140	0.00030	0.0035	196	48	16.8	83.3		
2	10	0.00106	0.00023	0.0026	80	60	14.9	74.1	100	0
	20	0.00017	0.00004	0.0004	116	52	15.6	77.6		
3	10	0.00068	0.00014	0.0017	96	58	15.7	78.1		
	20	0.00029	0.00006	0.0007	100	80	19.3	96.0		

The efficiency of CI is estimated by the formula

$$Z = \frac{K_0 - K_1}{K_0} \times 100\%, \qquad (4)$$

where Z is the protective action of CI (%) and K_0 and K_1 are the corrosion rates without and with an inhibitor (g/(m² h)), respectively.

According to Eq. (4), the sensor constant is the same for tests without and with an inhibitor and does not affect Z. However, is it the same in these tests? This is the question a negative answer to which can sharply change the results of ranking reagents, since the corrosion rate determined without and with an inhibitor should be calculated by formulas having different coefficients in their numerators.

The determination of the Tafel slopes before every change in experimental conditions for refining the constant and, hence, the absolute corrosion rate takes time and needs complex equipment. Therefore, the sensor constant of an LPR device is taken to be 120 for an electrode area of 4.7 cm². The designers of an LPR device note in the instruction of a corrosion meter that

the induced corrosion rate can differ from the real corrosion rate of the sensor electrodes because of the fact that, theoretically, the sensor constant is not constant in all cases of application of the sensor.

In this work, we determine the constant of an LPR sensor during CI tests for two model media in West Siberian deposits (Sutormin and Ety-Purovsk deposits) in order to improve the technique of laboratory corrosion rate investigations according to GOST 9.514–99 and other LPR techniques.

We determine the LPR sensor constant from the Tafel slopes in the polarization curves recorded in uninhibited and inhibited (at various concentrations) water–oil media of two compositions. Based on the calculated Tafel slopes in the recorded polarization curves, we calculated method constant K and sensor constant K_{sen} under certain conditions.

RESULTS AND DISCUSSION

The results obtained for the waters of the Sutormin and Ety-Purovsk deposits are presented in Tables 1–4 and Figs. 1 and 2.

Table 2. Constants for testing CI reagents 1−3 in the water of the Ety-Purovsk deposit

CI	C_{CI}, mg/L	K, mV	$\Delta K = \Delta K_{sen}$, %	Water/oil, %/%
1	Control	13.5	0	
	10	16.3	+20.58	100/0
	20	16.8	+2.78	
	Control	12.3	0	
	10	15.8	+28.66	50/50
	25	15.9	+1.11	
	Control	13.6	0	
	10	15.4	+13.14	30/70
	25	13.1	−14.84	
2	Control	13.5	0	
	10	14.9	+10.20	100/0
	20	15.6	+4.72	
	Control	12.3	0	
	10	12.4	+1.25	50/50
	25	14.8	+18.91	
	Control	13.6	0	
	10	15.0	+10.58	30/70
	25	16.4	+9.37	
3	Control	13.5	0	
	10	15.7	+16.22	100/0
	20	19.3	+22.92	
	Control	12.3	0	
	10	15.3	+24.64	50/50
	25	15.6	+1.96	
	Control	13.6	0	
	10	18.0	+32.99	30/70
	25	19.3	+7.20	

Table 3. Experimental results for the water of the Sutormin deposit

CI		I_{cor}, mA	j_{cor}, mA/cm²	v_{cor}, mm/year	b_c	b_a	K	K_{sen}	Volume fraction, %	
no.	C_{CI}, mg/L						mV		water	oil
Control		0.20000	0.04255	0.4979	72	46	12.2	60.6		
1	10	0.00014	0.00003	0.0003	140	42	14.1	69.8		
	25	0.00250	0.00053	0.0062	160	52	16.8	83.4		
2	10	0.00024	0.00005	0.0006	186	24	9.2	45.9	50	50
	25	0.00035	0.00007	0.0009	140	26	9.5	47.4		
3	10	0.00068	0.00014	0.0017	65	52	12.6	62.4		
	25	0.00120	0.00026	0.0030	100	45	13.5	67.0		
Control		0.11000	0.02340	0.2738	106	30	10.2	50.5		
1	10	0.00096	0.00020	0.0024	134	32	11.2	55.8		
	25	0.00050	0.00011	0.0012	102	56	15.7	78.1		
2	10	0.00170	0.00036	0.0042	80	50	13.4	66.5	90	10
	25	0.00100	0.00021	0.0025	148	50	16.3	80.7		
3	10	0.00110	0.00023	0.0027	120	52	15.8	78.4		
	25	0.00040	0.00009	0.0010	144	52	16.6	82.5		
Control		0.16500	0.03510	0.4107	65	48	12.0	59.6		
1	10	0.00050	0.00011	0.00125	240	23	9.1	45.3		
	20	0.00011	0.00002	0.0003	152	34	12.1	60.0		
2	10	0.00023	0.00005	0.0006	105	42	13.0	64.8	100	0
	20	0.01150	0.00245	0.0286	88	50	13.9	68.9		
3	10	0.00740	0.00157	0.0184	132	40	13.3	66.3		
	20	0.00060	0.00013	0.0015	66	90	16.6	82.2		
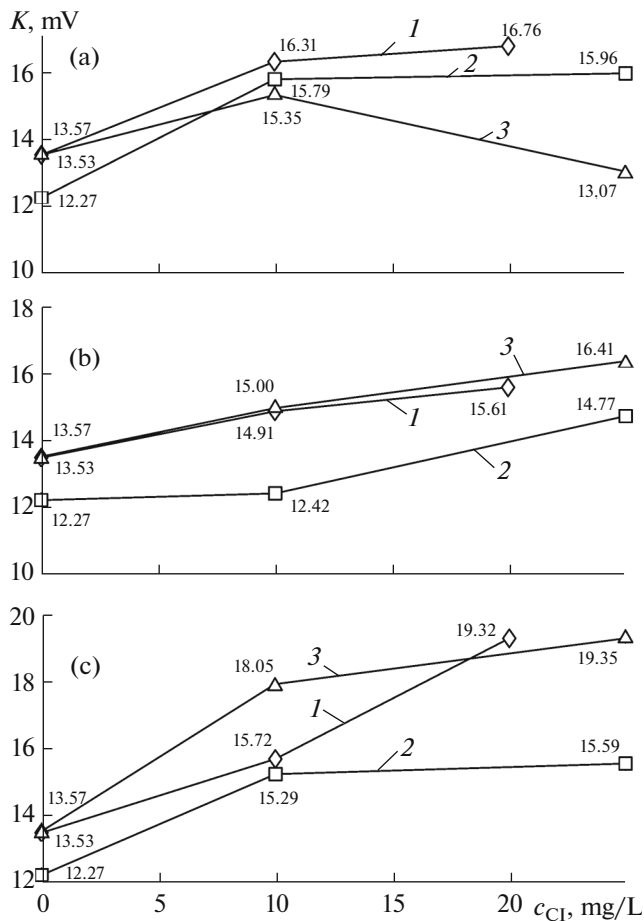
Fig. 1. Constant K vs. concentration C_{CI} in the water of the Ety-Purovsk deposit: (a–c) reagents 1–3, respectively. (*1–3*) Curves for the fraction ratio water : oil (vol %) of 100 : 0, 50 : 50, and 30 : 70, respectively.
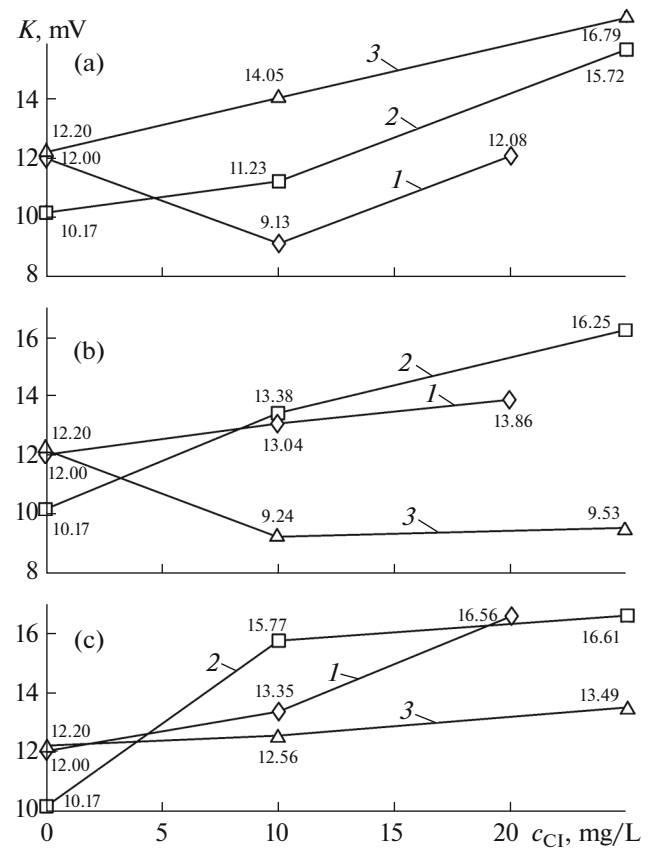
Fig. 2. Constant K vs. concentration C_{CI} in the water of the Sutormin deposit: (a–c) reagents 1–3, respectively. (*1–3*) Curves for the fraction ratio water : oil (vol %) of 100 : 0, 90 : 10, and 50 : 50, respectively.

The summarized data for these waters are given in Table 5.

When inhibitors at $C_{CI} = 10$ mg/L were introduced into the model water of the Ety-Purovsk deposit, constant K increased by 18% on average and was 13.5 mV. At $C_{CI} = 20$ and 25 mg/L, the constant still increased by 6% and was 16.3 mV. At a watering of 90–100%, we have $K = 13.5$–19.3; at a watering of 30–50%, we have $K = 12.3$–19.4 mV.

When inhibitors at $C_{CI} = 10$ mg/L were introduced into the model water of the Sutormin deposit, constant K increased mainly by 9% and was 12.4 mV. At $C_{CI} = 20$ and 25 mg/L, the constant still increased by 17% and was 14.5 mV. At a watering of 90–100%, we have $K = 9.1$–16.6; at a watering of 30–50%, we have $K = 9.2$–16.8 mV.

CONCLUSIONS

(1) Our experimental data demonstrate that the LPR sensor constant increases by 20% during tests in the same medium when various reagents are introduced into it. The LPR sensor constant changes by 13% during the passage from a certain medium without a reagent to another medium.

(2) If an increase in the sensor constant by 10–20% is not taken into account, the efficiency of using CI changes by $(10-20)K_1/K_0$, where K_0 is the corrosion rate in a medium without CI (g/(m² h)) and K_1 is the metal dissolution rate in the medium with CI (g/(m² h)). This circumstance should be taken into account to obtain correct results under the stringent requirements imposed by oil producing companies on the laboratory investigations of reagents for choosing the best ones (protective ability of 90% in OAO NK Rosneft and 95% in PAO ANK Bashneft).

(3) Before estimating the efficiency of reagents, we recommend determining the sensor constant from polarization curves. If the constant cannot be determined, we recommend calculating the efficiency of a reagent by the LPR method with allowance for a 20% increase in the sensor constant during tests with CI.

Table 4. Constants for testing CI reagents 1−3 in the water of the Sutormin deposit

CI	C_{CI}, mg/L	K, mV	$\Delta K = \Delta K_{sen}$, %	Water : oil, vol %
1	Control	12.0	0	
	10	9.1	−23.98	100 : 0
	20	12.1	+32.38	
	Control	10.2	0	
	10	11.2	+10.47	90 : 10
	25	15.7	+39.95	
	Control	12.2	0	
	10	14.1	+15.11	50 : 50
	25	16.8	+19.52	
2	Control	12.0	0	
	10	13.0	+8.65	100 : 0
	20	13.9	+6.28	
	Control	10.2	0	
	10	13.4	+31.59	90 : 10
	25	16.2	+21.46	
	Control	12.2	0	
	10	9.2	−24.27	50 : 50
	25	9.5	+3.15	
3	Control	12.0	0	
	10	13.4	+11.18	100 : 0
	20	16.6	+24.04	
	Control	10.2	0	
	10	15.8	+55.16	90 : 10
	25	16.6	+5.31	
	Control	12.2	0	
	10	12.6	+2.93	50 : 50
	25	13.5	+7.43	

Table 5. Summarized results of determining constant K under various conditions

CI	Deposit	Watering, %	Value of K (mV) at C_{CI} (mg/L)				Maximum deviation from K without CI, %
			0	10	20	25	
1	Ety-Purovsk	100	13.5	16.3	16.8	—	23.9
	Sutormin	100	12.1	9.1	12.1	—	0.6
2	Ety-Purovsk	100	13.6	14.9	15.6	—	15.4
	Sutormin	100	12.0	13.0	13.9	—	15.5
3	Ety-Purovsk	100	13.5	15.7	19.3	—	42.9
	Sutormin	100	12.0	13.5	16.6	—	37.9
1	Ety-Purovsk	30	13.6	15.4	—	13.1	13.1
	Sutormin	90	10.2	11.2	—	15.7	54.6
2	Ety-Purovsk	30	13.6	15.0	—	16.4	20.9
	Sutormin	90	10.2	13.4	—	16.2	59.8
3	Ety-Purovsk	30	13.6	18.1	—	19.4	42.6
	Sutormin	90	10.2	15.8	—	16.6	63.4
1	Ety-Purovsk	50	12.3	15.8	—	16.0	30.1
	Sutormin	50	12.2	14.1	—	16.8	37.6
2	Ety-Purovsk	50	12.3	12.4	—	14.8	20.4
	Sutormin	50	12.2	9.2	—	9.5	−21.9
3	Ety-Purovsk	50	12.3	15.3	—	15.6	27.1
	Sutormin	50	12.2	12.6	—	13.5	10.6

(4) For the media studied in this work, we derived the following formulas, which take into account the increase in the sensor constant for determining the efficiency of CI:

for the water of the Ety-Purovsk deposit,

$$Z_1 = \frac{(K_0 - K_1 \times 1.21) \times 100}{K_0},$$

for the water of the Sutormin deposit,

$$Z_2 = \frac{(K_0 - K_1 \times 1.19) \times 100}{K_0}.$$

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