A coulometric method for estimation of the anti-corrosion efficiency of polymer coatings

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Abstract
This study presents the results of a qualitative estimation of the protective efficiency of anti-corrosion coatings obtained by coulometric determination of corrosion products (CDCP). Using this technique, studies of an epoxy compound in demineralized water with a conductivity of $L = 10^{-6}$ S at $T = 20°C$ were carried out. As an example, the service life of a coating for the protection of storage tanks for chemically demineralized water at nuclear plants was estimated based on the results obtained.

Keywords: coulometric method, estimation of protective efficiency, anticorrosion coating

1. Introduction

Development of new anti-corrosion materials and coatings made it necessary to provide an objective estimation of the service life of protective coatings in corrosive media. However, for various reasons, today's measurement standards cannot objectively estimate the time period beyond which a coating starts to lose its protective properties, though numerous methods and instruments are used [1].

In fact, months are required to test coatings under operating conditions, whereas the necessity of "fast" testing requires that the measurement conditions be simplified and made more drastic. However, so-called "accelerated" tests provide information about the durability of a coating under *forced destruction* conditions instead of the natural ageing mechanism, whereas "instrumental" estimation methods based on electrical analogues just replace the method of forced coating destruction while creating an illusion that they study the mechanism objectively. Physical methods are complicated in use and poorly suitable for routine tests of real coatings [2]. What is more, all the measurement approaches mentioned above do not make it possible to determine the *initial time interval* when the coating loses its protective properties.

One of the attempts to estimate the "*time of corrosion start*" was made using the impedance method. Measurements in the frequency range of $25 \div 10^8$ Hz made it possible to judge on the state of the coating in a corrosive medium based on changes in the frequency response characteristics of a "capacitor with losses" where the coating is the dielectric, while the electrolyte and the base metal are the capacitor "plates".

However, worldwide experience has revealed that this method has a fundamental limitation: an "elementary electrochemical cell" is replaced by a virtual model of "capacitor with losses". The latter fact deprives "electric" simulation of physical meaning, because any model combination "capacitance-resistance" in an "electrolyte-coating-metal" system corresponds to a *fundamentally undefinable* number of real system states. Furthermore, in case of a nonconducting coating, polarization current

can distort the real behavior of the metal under the film. In case of conducting coatings, the electronic behavior of the coating rather than the metal is described.

As a result, recording of the frequency characteristics of the coating capacitance and resistance are only suitable for comparative estimates [3-4].[1)]

In fact, out of the methods widely used for testing the corrosion resistance of metals, only the *mass loss method* makes it principally possible to determine the main process parameter, namely the metal mass loss (Δm). However, though the estimation criterion $\Delta m/\Delta t$ (where Δt is exposure time) is quite demonstrative, the mass loss method does not allow one to identify the kinetics of changes in the ionic composition of corrosion products (*e.g.*, Fe^{2+} and Fe^{3+} ions) that plays an important role in studies on steel and alloy corrosion or efficiency of protective systems. Using the mass loss method, it is difficult to estimate the trends of corrosion kinetics in case of microgram mass losses: in the initial period of metal corrosion, under a layer of a protective coating (inhibitor), in a multicomponent alloy, or in a zone of phase changes of the metal structure in the weld adjacent zone of welded joints, *etc*.

As shown in our studies [5-7], overcoming the difficulties in correct corrosion estimation in the microgram range, and in particular, the protective efficiency of coatings, directly depends on solving the problem of selecting an adequate estimation criterion and experimental parameter for determining micro quantities of corrosion products.

The use of the advantages of the main corrosion parameter $\Delta m/\Delta t$ while eliminating the limitations of the mass loss method and other approaches allowed us to state the following requirements for the *measurement criterion*:
- quantitative measurement of the main corrosion parameter $\Delta m/\Delta t$ without any reference standard;
- elimination of the effects of the measuring system on the specimen being tested during the measurement;
- clarity, accuracy, and repeatability of the results and technological efficiency of *in situ* measurements.

2. CDCP method and criterion for estimation of coating anti-corrosion efficiency

An approach to the fulfillment of the above set of requirements for determination of the metal corrosion kinetics and estimation of the protective properties of coatings was considered both experimentally and theoretically in the previous publications [8, 9]. In fact, it was suggested to use ions (corrosion products) formed on a metal surface upon exposure to corrosive factors as the main corrosion characteristics. It was noted that in the general case, when a specimen is exposed in a *test* cell (beaker, desiccator, etc.) where the metal contacts with an electrolyte, the ions (metal corrosion products) can be accumulated on the metal surface, diffuse from the interface surface to the coating material, accumulate there, and then get transferred to the corrosive environment.

Coulometric determination of corrosion products (hereinafter, the CDCP method) was developed to determine corrosion products in ionic form.

According to the technology of the method, corrosion products (ions) from the *test cell* were placed into a *measuring coulometric cell*, where the *discharge current* of the ions on the indicator electrode

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[1)] In the papers cited, low frequencies (10^{-2} to 10^{-3} Hz) were used in order to minimize the distortion of electrode processes, but this required the researchers to decrease the coating resistance artificially, up to removal of the coating.

(IE) was measured. The desired mass loss Δm of corrosion products electrically converted in the electrochemical reaction on the IE was determined from Faraday's equation in the form convenient for coulometric measurements:

$$m = K_e \cdot q = \int I(t)\, dt \qquad (1),$$

where K_e is the electrochemical equivalent of the compound (electrolysis reactions); $q = \int I(t)\, dt$ is the total electrical charge of the ions of the electroactive compound (in this case, $Fe^{2+,3+}$ ions); $I(t)$ is the experimentally measured discharge current of the ions (corrosion products); and t is the running time of the analysis.

The experiment was controlled and the results processed using specialized software.

Taking into consideration that accumulation of the total mass m of ions (corrosion products) in a "*electrolyte-coating-metal*" system (ECM system) generally occurs in three zones:

I - on the metal surface under a coating layer - m_{surf};

II - in the coating layer - m_{cl};

III - in the electrolyte layer - m_{el},

expression (1) has the form:

$$m = m_{surf} + m_{cl} + m_{el} = K_{el}\left[\int_{surf} I(t)dt + \int_{cl} I(t)dt + \int_{el} I(t)dt\right] \qquad (2)$$

If we assume that the protective effect of a coating ceases because contact is established between the electrolyte and the metal (start of corrosion), the state of the coating over any exposure period can be characterized by a parameter such as the *rate of accumulation* of corrosion products in the corresponding zone of the ECM system:

$$v_i = \Delta m_i / \Delta t_i \qquad (3),$$

where the mass loss Δm_i is the amount of the compound obtained during exposure time period Δt_i (*i* being the sequential number). If the state of a coating that contacts a corrosive environment changes, the v_i value can change or remain constant, depending on the number of accumulated ions. Therefore, a *criterion of corrosion protection degradation* lies in the empirical relationship: $v_i \sim v_m$, where v_m is the rate of accumulation of ions from an unprotected metal during time interval Δt_i.

The conceptual scheme of the experiment is provided below.

3. Experimental

3.1. Specimens, instruments and equipment

Test samples were made of an epoxy compound used for the protection of storage tanks for demineralized water at nuclear plants.

The operation conditions of a storage tank are characterized by cyclic variation in the level of water as it is spent for process needs. Though the conductivity of demineralized water is low ($L \sim 10^{-6}$ S at $T = 20°C$), the operating environment is corrosive since a permanently moving intermittent wetting zone exists. Based on these conditions, the corrosion tests were carried out with free access of oxygen

at $T = 20°C$, in the "water-air" zone, without additional stirring.

A coating with a mean thickness of $\delta = 350$ μm in the *working area* was applied onto carbon steel cylinders (100×12 mm) with roughness $R_z = 80$ μm (similar to the condition of a metal support under industrial conditions). The geometrical surface area of the "water-air" test zone was $s = 7$ cm^2 for each specimen. The non-operational specimen surface was insulated with a chemically resistant material.

In these tests, we recorded the dependences of capacitance and resistance on the current frequency, $C(f)$ and $R(f)$, in order to estimate the effect of environment diffusion through the coating to the metal. The amount of the resulting corrosion products of steel, Fe^{2+} and Fe^{3+}, was determined by CDCP.

The study was carried out using an IPC-PRO electrochemical interface (made at A.N.Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences) with a control program, a magnetic thickness gage, and an AC bridge.

Glass beakers with a corrosive environment were used as the *test cells* for exposure of specimens and for impedance measurements. The coulometic *measurement cell* comprised an SU-2000 glass-carbon crucible with a volume of v=40 ml that served as the indicator electrode filled with a background electrolyte (background, see Table 2) also comprising a silver chloride reference electrode and glass fiber as the auxiliary electrode.

3.2. Measurement procedure

Three specimens with an anti-corrosive coating were placed in a *test cell* for each time point of exposure in the test environment. In parallel, a blank experiment with unprotected steel specimens was carried out under similar conditions. The time interval of one exposure was $t_i = 168$ h, while the total test time was $t_{tot} = 1512$ h.

Impedance measurements were carried out at the start and end of exposure at frequencies of 20, 40, 60, and 90 kHz. The working area of a specimen was totally covered with demineralized water during each measurement.

After the specimens were removed from the test cell, the corrosive environment was *preserved by addition of hydrochloric acid* to a concentration of c = 1 M. The preservation was carried out in order to convert the corrosion products to a soluble state and preserve iron ions in the Fe^{2+} oxidation state. Using the control software, the "Faradaic" masses of Fe^{2+} and Fe^{3+} ions that passed into the electrolyte solution through the coating film were determined from Eq. (1).

To determine the corrosion products accumulated in the coating material, the coating film was mechanically removed from the working area of the specimen, crushed, and extracted with 2M HCl for 72 h at T = 20°C without stirring.

The corrosion products accumulated on the metal surface were removed and converted to dissolved state with an aqueous solution of the remover, namely, *ammonium sulfosalicylate*. The masses of Fe^{2+} and Fe^{3+} ions were determined in the solution of the remover. The background mass loss of the steel substrate on exposure to the remover was determined before the start of the tests for both types of ions.

4. Discussion of the results

The conditions of coulometric tests are presented in Table 1.

Table 1. Conditions of Fe^{2+} and Fe^{3+} determination in the background solution in case where both ions are present in the samples.

Ion	Sample composition	Potential, V	Background solution
Fe^{2+}	Hydrochloric aid solutions: Demineralized water and extract	0.77	Aqueous 0.1 M HCl solution + 4 mg/ml sulfosalicylic acid
	Ammonium sulfosalicylate solution	0.77	Aqueous 0.1 M HCl solution
Fe^{3+}	Hydrochloric aid solutions: Demineralized water and extract	0.13	Aqueous 0.1 M HCl solution + 4 mg/ml sulfosalicylic acid
	Ammonium sulfosalicylate solution	0.13	Aqueous 0.1 M HCl solution

Based on the results of coulometric measurements in each exposure interval, we determined the amount of corrosion products on the metal surface (m_{surf}), in the coating material (m_{cm}), and in the liquid environment (m_{el}), as well as the total amount M, for both types of iron types.

It was found that corrosion in the variable wetting zone gives Fe^{2+} compounds on the surface, which are transferred to the liquid corrosive environment after oxidation to Fe^{3+}. As one can see from Table 2, corrosion products of iron are formed and oxidized in different amounts during all exposure intervals. However, the total amount of Fe^{2+} + Fe^{3+} compounds in exposure intervals 2 to 9 is of the same order and amounts to $M_m \sim 12.8$ g/m^2 on average, indicating that the corrosion rate of the metal under the coating is uniform.

Table 2. Amount (mass) of corrosion products, Fe^{2+} (Δm_{Fe}^{2+}) and Fe^{3+} (Δm_{Fe}^{3+}) and total amount of corrosion products $v_m = \Delta m_{Fe}^{2+} + m_{Fe}^{3+}$, in each exposure interval in case of uncoated steel corrosion

| Exposure intervals, h	Interval number	Amount of Fe^{2+} compounds, g/m^2	Amount of Fe^{3+} compounds, g/m^2	Total amount of corrosion products, g/m^2
168	1	8.3	12.0	20,3
336	2	-2.1	15.7	13,6
504	3	4.7	6.9	11,6
672	4	-2.9	15.4	12,5
840	5	-0.9	13.3	12,4
1008	6	5.0	6.8	11,8
1172	7	1.7	12.8	14,5
1344	8	-4.1	17.6	13,5
1512	9	-1.4	14.2	12,8
Mean value over 8 intervals (2- 9)		0	12.8	12.8

The mean amount of corrosion products in the Fe^{2+} form during intervals 2 to 9 is $\Delta m_{Fe}^{2+} = 0$, while that in the Fe^{3+} form equals the mean total value, $\Delta m_{Fe}^{3+} = M_m$. In other words, all iron compounds are eventually oxidized to Fe^{3+} in demineralized water with free access of oxygen. Therefore, the anti-corrosive efficiency of a coating should be estimated on the basis of the yield and accumulation .

of trivalent iron.

4.1. Estimation of the anti-corrosive efficiency of a coating

The results of impedance measurements in the "metal-coating-environment" system (Figs. 1, 2) have shown that the frequency plots were within approximately the same order of magnitude during the entire test period: C(f) ~10^2 pF, R(f) ~ ($10^3 \div 10$) kOhm. The system capacitance increased ~1.5-fold and the resistance decreased ~2.6-fold.
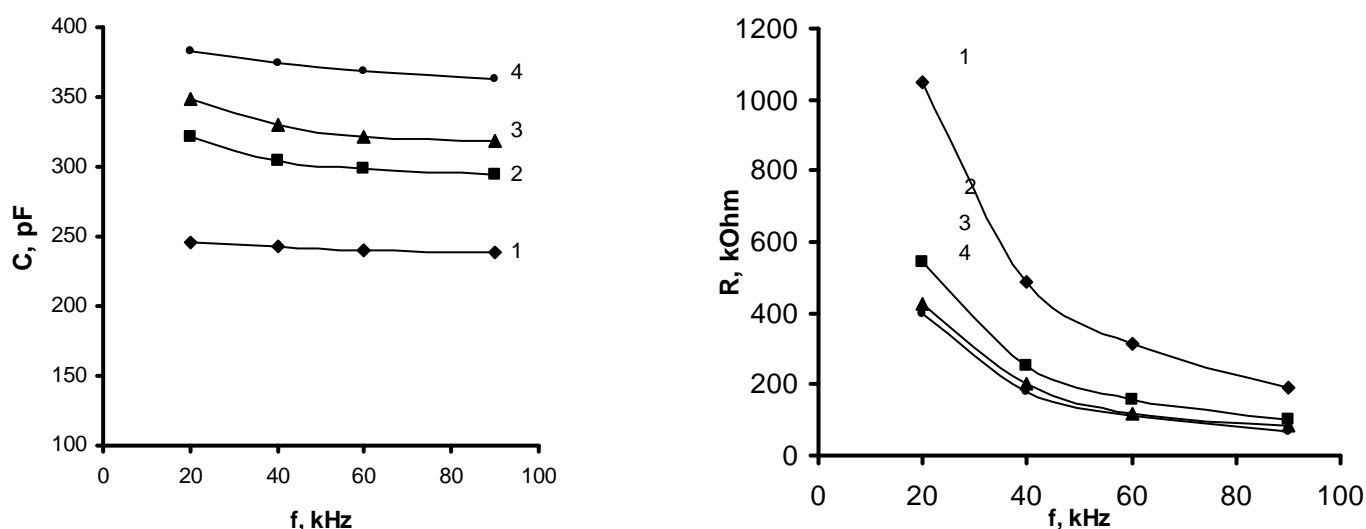

Fig. 1. Frequency plots C(f) in the "metal-coating-environment" system: 1. t = 0 h; 2. t = 504 h; 3. t = 1008 h; 4. t = 1512 h.

Fig. 2. Frequency plots R(f) in the "metal-coating-environment" system: 1. t = 0 h; 2. t = 504 h; 3. t = 1008 h; 4. t = 1512 h.

Obviously, the results obtained do not allow us to conclude if direct contact of the metal with the corrosive environment is established in the test system. On the other hand, a decrease in resistance and increase in capacitance may indicate that the corrosive environment diffuses into the coating. This uncertainty is probably due to the low conductivity of the environment and the insoluble state of iron corrosion products accumulated in the coating.

The results of coulometric determination of Fe^{2+} and Fe^{3+} in environment samples, in the corrosion product eliminating agent, and in the extract have shown that iron corrosion products are accumulated in the coating film only. No iron ions were found on the metallic substrate and in the bulk of the corrosive environment. Therefore, we accepted v_{cm}, *i.e.*, *accumulation rate* of iron ions in the coating layer, as the parameter determining the protective effect of the coating.

Prior to the test, we estimated the starting amount of Fe^{2+} and Fe^{3+} ions (background) in the coating access to the system into account, it is logical that the amount of Fe^{2+} ions in the film decreased during the test whereas that of Fe^{3+} ions increased (Figs. 3, 4).   Regression analysis of experimental results has shown that both kinetics, *i.e.*, the decrease in Fe^{2+} amount and increase in Fe^{3+} amount, demonstrate a linear trend. The *oxidation rate* of Fe^{2+} ions in the coating film (slope of the calculated dependence), $v_{Fe^{2+}}$, is smaller than the rate of Fe^{3+} accumulation, $v_{Fe^{3+}}$. It follows from Figs. 3 and 4

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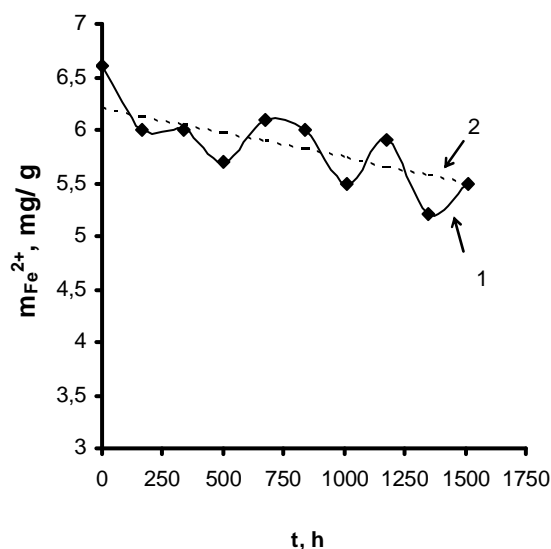
Fig. 3. Kinetics of the amount of m_{Fe2+} ions in the coating: 1-experiment; 2- calculation (regression analysis).
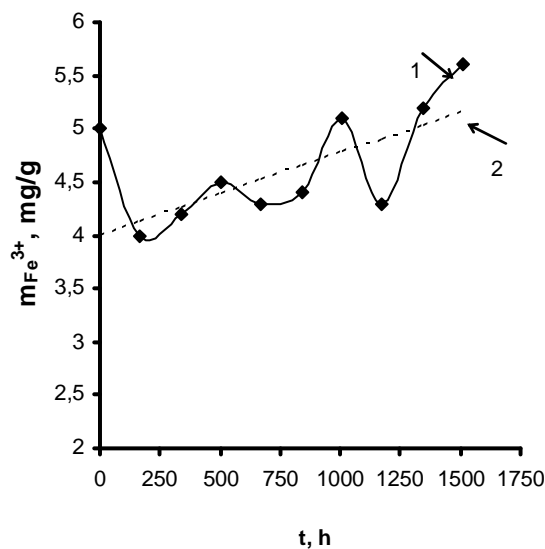
Fig 4. Kinetics of the amount of m_{Fe3+} ions in the coating: 1-experiment; 2- calculation (regression analysis).

that $v_{Fe}^{2+} = 4.7 \cdot 10^{-4}$ mg/g per hour and $v_{Fe}^{3+} = 7{,}6 \cdot 10^{-4}$ mg/g per hour. The result obtained, namely, the increase in the amount of Fe^{3+} ions in the coating material, is due to two simultaneous processes:

- oxidation of the original (background) amount of Fe^{2+} ions contained in the coating layer to Fe^{3+} ions[2];
- corrosion of the metallic support itself by the mechanism $Fe^0 \rightarrow Fe^{2+} \rightarrow Fe^{3+}$, where Fe^{3+} is the end product.

The reason of both processes lies in the swelling of the coating layer in the electrolyte, which is conformed by impedance measurements.

Based on the value $\Delta v = v_{Fe}^{3+} - v_{Fe}^{2+} = 2.9 \cdot 10^{-4}$ (mg/g) $\cdot$ h and taking into consideration the interval duration, the geometrical surface area of the test zone, and the coating thickness and density, we can determine the amount of iron resulting from corrosion, v_{sm}, accumulated in the form of Fe^{3+} in the film during each exposure interval. Calculation has shown that $v_{sm} = 1.25 \cdot 10^{-2}$ (g/m^2) / h.

If we assume that the coating working conditions remain unchanged during the entire operation period and that the corrosion rate remains constant, then, based on the criterion $v_i \sim v_m$, one can estimate the time t of the loss of the coating protective ability:

$$t = v_m \cdot t_\Delta / v_i \qquad (6).$$

If $v_i = v_{sm}$, then the service life of a coating based on the epoxide tested in demineralized water under variable surface wetting is ~ 170,000 hours.

Conclusions

1. A technique has been developed for quantitative estimation of the anti-corrosion efficiency of coatings in low conductivity environments by coulometric determination of corrosion products (CDCP).

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2. The use of the methodological approach that we developed for estimation of the protective and efficiency of measurements.

3. The results obtained have made it possible to assess the service life of an anti-corrosion coating for protection of storage tanks for demineralized water at nuclear plants.

ANOWLEGEMENT

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