

Application of the EIS method to study the mechanism of the inhibitory effect of catechol on steel corrosion in an alkaline medium containing chlorides

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Abstract

Various classes of compounds, including those from the phenol group, are used to inhibit steel corrosion. These include catechol, the structure of which is a benzene ring containing two hydroxyl groups in the *ortho* position. This compound has high antioxidant activity and reacts easily with reactive oxygen species present in electrolytes under conditions of natural aeration. In this case, catechol is oxidized, forming a brown resinous compound oxanthrene-2,3-dione. The latter is deposited on the solid phase of the system, including on the protected metal in the form of a viscous resinous mass. On the other hand, catechol can form adsorption chelate layers on steel, causing blocking of active centers. In previous publications in this journal, we presented the results of a study of catechol as an inhibitor of steel corrosion in alkaline, chloride-containing media. Its protective effect was found in concentrations from 1 to 5 g/L. Continuing this cycle of work, this publication is devoted to a comparative assessment of the effect of two possible mechanisms of catechol inhibition of steel corrosion: due to the formation of thin chelate films and due to the accumulation of a resinous precipitate on the surface, which can limit the diffusion of oxygen from the volume of the solution. Analysis of the results of 28-day experiments using the EIS method showed that the inhibitory effect of catechol is mainly determined by the formation of strong adsorption films on the surface of steel, which protect the metal even when it is transferred to a solution without an inhibitor. The optimal concentration according to the results of these experiments was 5 g/L of catechol.

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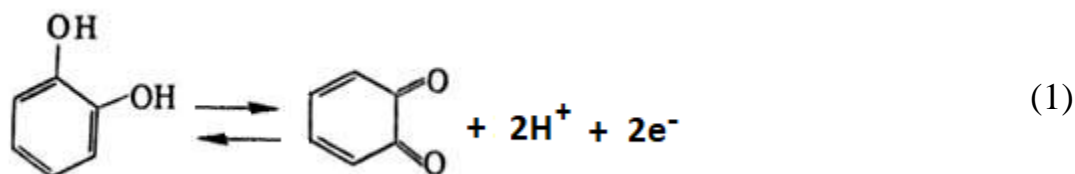
Keywords: *catechol, inhibitor, corrosion, electrochemical impedance spectra.*

1. Introduction

The possibility of using catechol (acronym CC) as an inhibitor of steel corrosion in alkaline environments, in particular, to protect reinforcement in reinforced concrete products, is due to several factors:

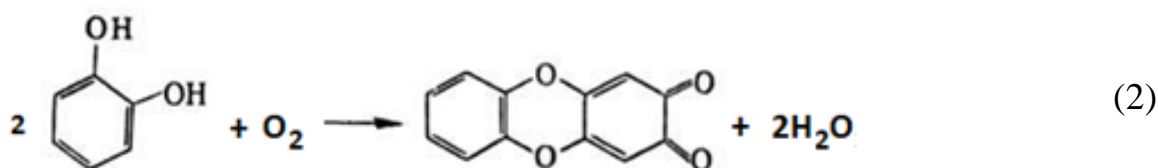
- On the one hand, catechol can form chelates with some metals, in particular with iron [1, 2]. The organic complexes formed on the surface of steel in the form of adsorption

films can contribute to the passivation of steel, *i.e.* enhance its corrosion resistance. The hydroxyl groups of catechol in the *ortho* position are responsible for the ability to form chelate forms with metal ions [3]. In the process of heterogeneous oxidation of catechol, 1,2-benzoquinone is formed at the first stage [4]:



The oxidation product no longer contains hydroxyl groups and, therefore, is not able to form chelate films on the metal surface, *i.e.*, the oxidized form of the inhibitor should not reduce the ability to form a strong bond with the metal surface and, therefore, should have less inhibitory ability.

- On the other hand, catechol, being a powerful antioxidant, has a reductive effect on reactive oxygen species in the pore liquid of concrete. Since corrosion of steel in an alkaline environment proceeds by the mechanism of oxygen depolarization, a decrease in oxygen concentration due to reaction with catechol should contribute to an increase in the corrosion resistance of steel. The homogeneous reaction of catechol with oxygen in the volume of the pore liquid proceeds with the formation of oxanthrene-2,3-dione [4]:



- The resulting product of reaction 2 is a dark brown slightly soluble resinous viscous compound deposited on the solid phase. Accumulating on the metal surface, this product can create a diffusion limitation of the supply of depolarizers to the metal and thus contribute to the inhibition of corrosion of steel.
- On the other hand, local acidification of the medium may occur under the sediment layer (for example, by reaction 1). The latter can increase the corrosion of steel and lead to the formation of local damage.

We observed the accumulation of dark brown resinous sediment on steel samples earlier in studies of the effect of catechol additives on corrosion in model solutions of concrete pore fluid [5, 6]. Figure 1 shows photos of samples after a month's exposure in a solution with catechol additives, which clearly show the formation of a resinous precipitate, easily washed off with a stream of water.

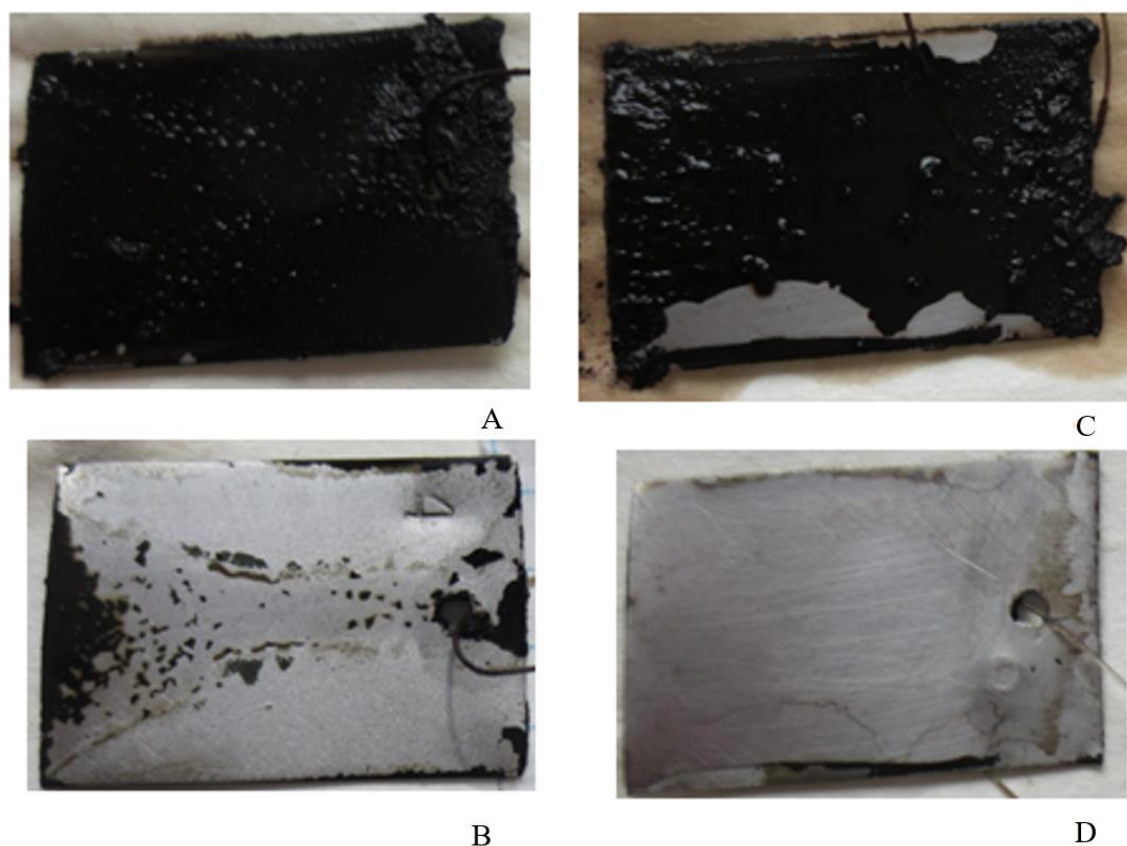


Figure 1. Photos of steel samples after a month's exposure in a solution of 1 g/L CaO+30 g/L NaCl with catechol additives. A, B–0.5 g/L of catechol. C, D–5 g/L of catechol. A, C—with a resinous precipitate after exposure in solution. B, D—after washing off the sediment.

Thus, the inhibitory effect of catechol on steel corrosion is determined by a number of factors, each of which will change over time. In this study, we performed a comparative assessment of the effect of two possible mechanisms of catechol inhibition of steel corrosion: due to the formation of thin chelate films that are firmly bonded to the metal surface and block the active centers on the metal surface and due to the accumulation of a layer of viscous resinous sediment on the surface, which can limit the diffusion of oxygen from the solution volume.

To assess the contribution of these factors, which have an inhibitory effect on steel corrosion, we measured the impedance spectra of steel samples during their long-term exposure in solutions with different concentrations of catechol. Periodically, with an interval of several days, the impedance of the sample was measured in a solution with the addition of catechol. Then the sample was removed from the solution with an inhibitor and the accumulated on the surface resinous precipitate was carefully washed off. The purified sample was transferred to a model solution without an inhibitor to re-obtain the impedance spectrum. Assuming that the chelated films formed on the surface are firmly bonded to the metal surface and will mainly persist after washing off the resinous sediment, we thus evaluated the possible “aftereffect of the inhibitor” after transferring the sample to the blank

solution. Since the fresh portion of the model solution is more saturated with oxygen compared to the “aged solution” with an inhibitor, it was also possible to assess the effect of this factor on metal corrosion. Chemisorbed catechol films on steel cannot significantly change the oxygen content in solution during measurement, therefore, the inhibitory effect estimated during repeated measurement in the blank solution will be mainly due to the blocking effect of strongly adsorbed catechol on the active centers of the metal surface. After the measurements were completed, the steel sample was returned from the “aged solution” with an inhibitor and the exposure was continued until the next cycle of comparative measurements of the impedance spectra.

2. Experimental

2.1. Materials

Rolled carbon steel 08PS (an analog of A620 steel) 0.2 mm thick has been used. The shape and design of the samples will be described below for each of the research methods. Before starting electrochemical measurements, the surface of the samples was sanded on abrasive paper (M40), degreased and washed with water.

The corrosion behavior of steel was studied in a model solution simulating a concrete pores liquid with high chloride content. A basic solution without an inhibitor (blank solution) had a composition: 1 g/L CaO+30 g/L NaCl (pH=12.2). Chemical grade reagents were used. Immediately before the start of the experiment, a calculated suspension of CC was added to it and thoroughly mixed and pH was adjusted¹ to 12.2 (as in the solution without additives). The experiments were carried out under conditions of natural aeration at room temperature.

2.2. Instruments and techniques

Electrochemical impedance spectra were obtained with IPC-FRA potentiostat (Russia). The measurements were carried out in a potentiostatic mode using a three-electrode circuit. The design of the measuring cell is described in detail in [7]. The steel samples serve as working electrode. It was in the form of disc clamped in a special cell attachment so that one-sided polarization of the working surface of the sample ($S=1\text{ cm}^2$) was provided. A saturated silver-chloride electrode connected to the cell via a salt bridge and a Luggin capillary was used as a reference electrode. The potentials in the article are given relative to this electrode. The auxiliary electrode was made of titanium wire. Electrochemical impedance spectra were recorded at an open circuit potential with a harmonic signal amplitude of 10 mV in the frequency range of 20 kHz–0.1 Hz.

At the beginning of the experiment, the samples were treated with sanding paper, degreased and washed with water and fixed in a cell. Before recording the impedance spectrum, the sample was kept in contact with a solution of the studied composition without polarization for 40 minutes to stabilize the surface condition. Then EIS measurements were

¹Using NaOH solution.

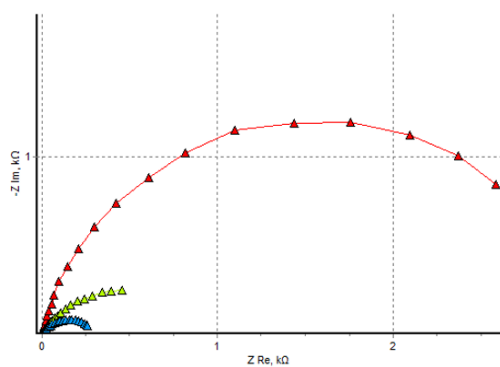
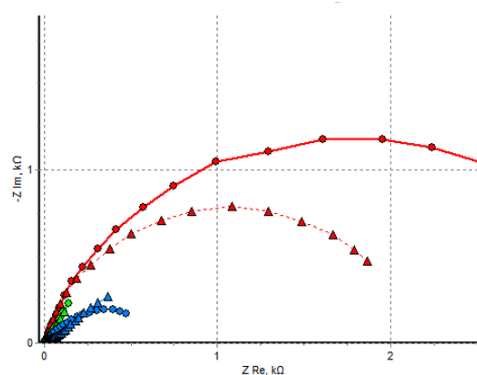
performed and the steel sample was left in this solution for several days to interact during the “aging of the solution”. After a certain time (several days), the measurement of the impedance spectrum was repeated in an “aged solution” with an inhibitor. Then, the accumulated resinous precipitate was carefully washed off the surface of the steel with a model solution without an inhibitor, trying to avoid without mechanical action. After that, the cell was filled with a fresh blank solution and kept without polarization for 40 minutes to achieve a quasi-stationary value of the open circuit potential. After repeated EIS measurement, the residual inhibitory effect of an indelible dense adsorption film of catechol interaction products with the steel surface was evaluated.

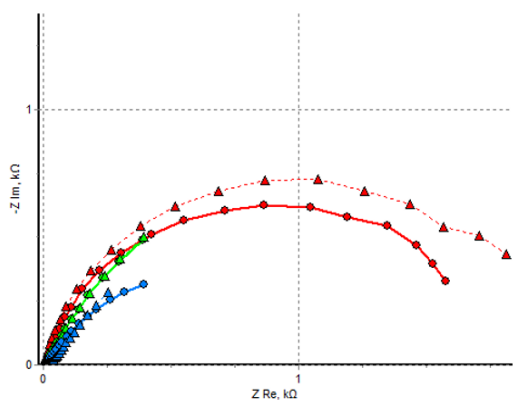
The design of the clamping cell could not ensure the tightness of the sealing of the steel sample during prolonged contact with the solution (more than 2 days). Therefore, after repeated EIS, the sample was removed from the cell, replaced in a vessel with an “aged solution” with an inhibitor until the next cycle of measurement. Experiments with all catechol concentrations were started simultaneously and completed after 28 days.

A specially developed ZMonitor software was used to graphically represent the obtained impedance spectra. The interpretation of the EIS results in terms of equivalent circuits was performed using the Dummy Circuit Solver software.

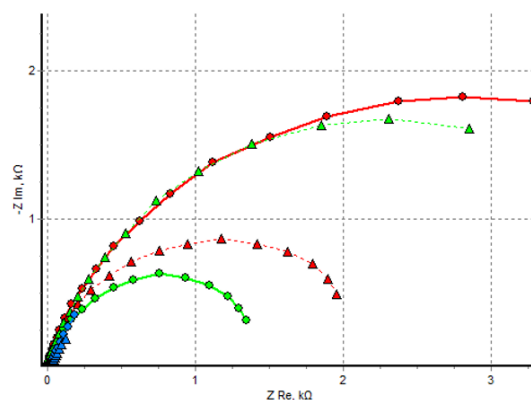
3. Results and Discussion

It can be seen from Figure 2 that, although low-frequency capacitive arcs are most pronounced in Nyquist diagrams, some change in the shape of the spectra in the high-frequency region is also observed, especially at high concentrations of catechol. These changes are most noticeable in the phase Bode diagrams in the frequency range from 20 kHz to 100 Hz, shown in Figure 3. It is evident that in blank solution, at all exposure times, the spectra are characterized by a single time constant. On the contrary, in experiments with catechol additives, especially at 28-day exposure, the appearance of a second time constant (at a frequency of about 1 kHz) becomes clearly noticeable, which may indicate the appearance of a resistive film on the surface that affects charge transfer.

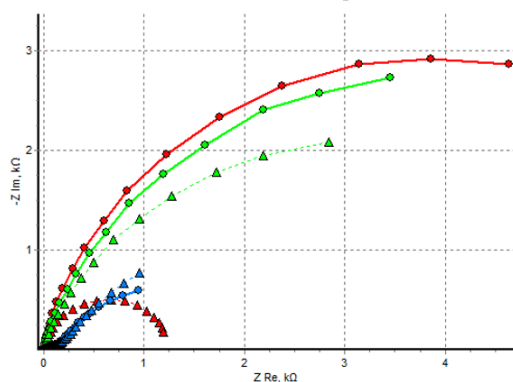
**A****B**



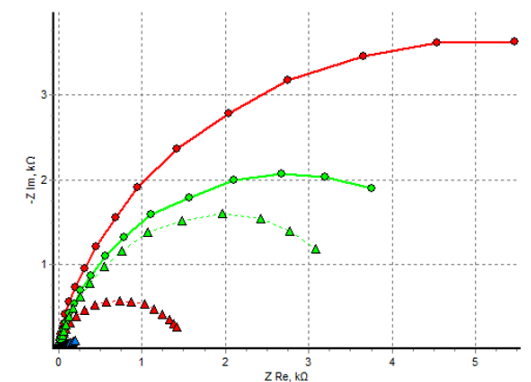
C



D

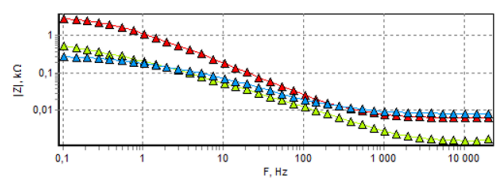


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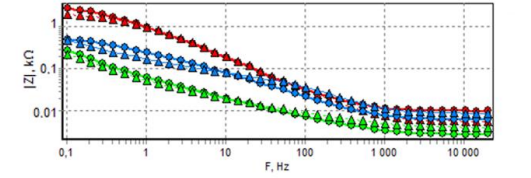


D

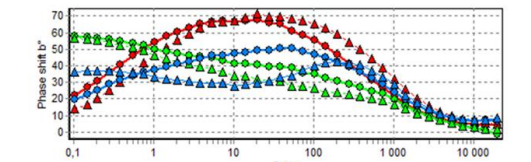
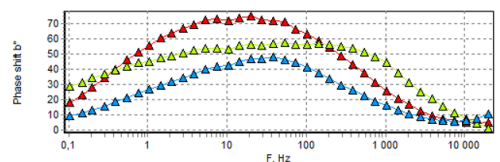
Figure 2. Nyquist diagrams in a model solution without an inhibitor (A) and with catechol additives: 0.1 g/L (B); 0.5 g/L (C); 1 g/L (D); 5 g/L (E); 10 g/L (F). Solid lines and triangular markers refer to the first EIS measurement in solution with an inhibitor. The dotted lines and round markers refer to the second EIS measurement in the blank solution after flushing the resinous sediment. The hodographs are indicated in red at the beginning of the experiment, in green after 14 days and in blue after 28 days of exposure.



A



B



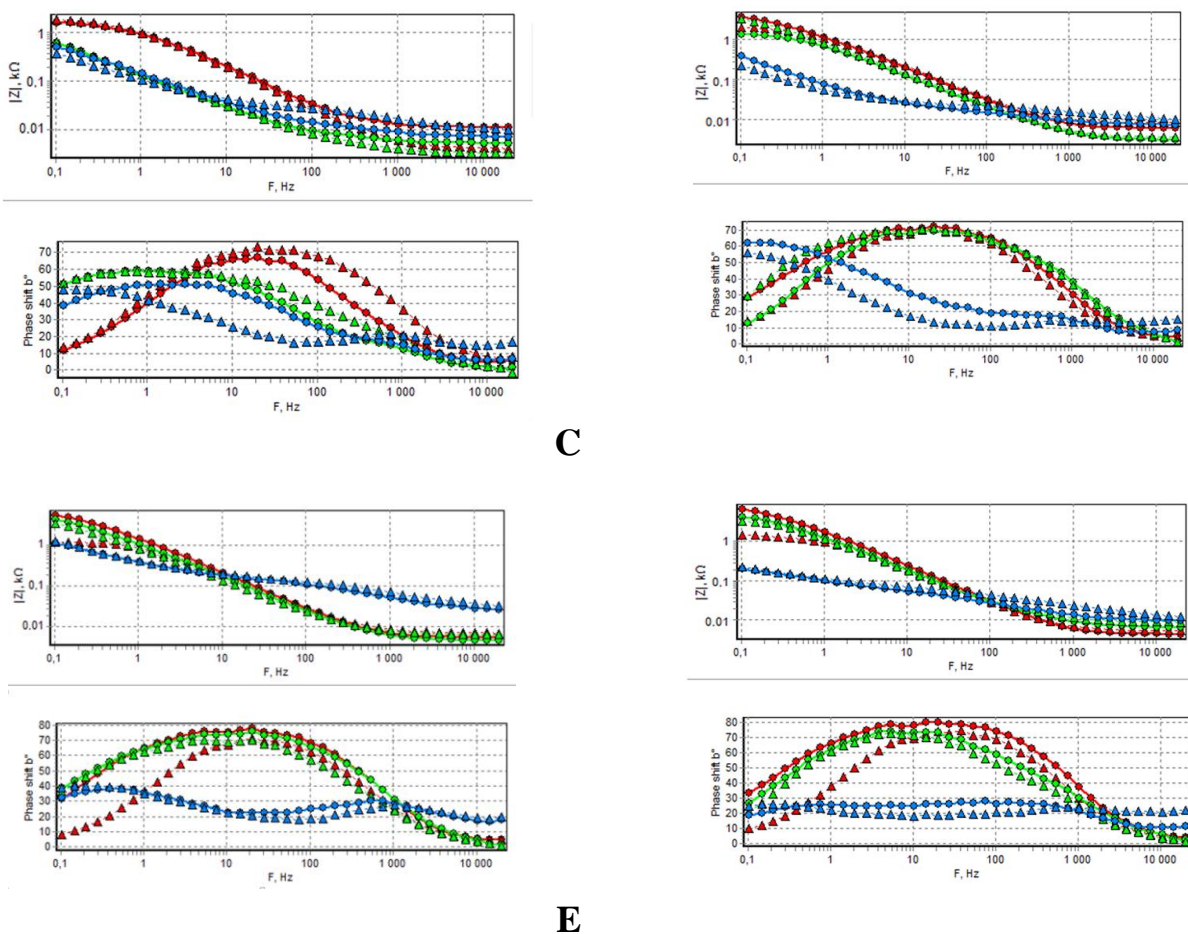


Figure 3. Bode diagrams in a model solution without an inhibitor (A) and with catechol additives: 0.1 g/L (B); 0.5 g/L (C); 1 g/L (D); 5 g/L (E); 10 g/L (F). Solid lines and triangular markers refer to the first EIS measurement in solution with an inhibitor. The dotted lines and round markers refer to the second EIS measurement in the blank solution after flushing the resinous sediment. The hodographs are indicated in red at the beginning of the experiment, in green after 14 days and in blue after 28 days of exposure.

To quantify the results of EIS measurements, the experimental EIS spectra were interpreted in terms the equivalent circuit proposed by F. Mansfeld [8]. Such equivalent circuit is usually used to describe processes on a metal whose surface has a film layer with ohmic resistance [9].

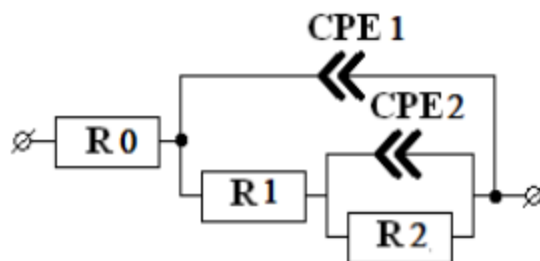


Figure 4. The equivalent Mansfeld circuit.

In this equivalent circuit, R_0 represents the resistance of the electrolyte layer between the reference electrode and the outer surface of the steel. Resistor R_1 refers to the ionic resistance of the surface film, and resistor R_2 refers to the resistance of the Faraday process under the film on the surface of the steel. The capacitance properties of the system are determined by two constant phase elements (CPE), which replace the capacitors in the original Mansfeld model. The use of CPE makes it possible to take into account the imperfection and/or heterogeneity of the capacitive characteristics of the system. Since the impedance Z of the CPE element is expressed by the equation:

$$Z_{\text{CPE}} = Q^{-1}(j\omega)^{-n} \quad (3)$$

where: Q is the proportionality factor; j is the imaginary unit; ω is the cyclic frequency of the alternating current signal; n is the phase factor, whose values range from 0 to 1. The magnitude of n can be used to judge the nature of the CPE element. If the value of n approaches 1, the element exhibits the properties of a capacitor. A decrease in this value characterizes an increase in the diffusivity and/or heterogeneity of the structure of the capacitor plates. In the employed equivalent circuit, CPE_1 represents the overall capacitance of the electrode, and CPE_2 represents the pseudo-capacity of the Faraday process.

The fitting results in terms of this model are given in Tables 1–6. Tables with index “a” refer to experiments in an “aged solution” with an inhibitor and an accumulating resinous precipitate of its oxidation products on the metal surface. Index “b” refers to experiments after rinsing the sediment and impedance measurements in fresh blank solution.

Table 1. Elements of the equivalent circuit. The model blank solution without additives.

Exposure, days	R_0 , Ω	R_1 , $\text{k}\Omega$	R_2 , $\text{k}\Omega$	$\text{CPE}_1 Q$, $\mu\text{S}\cdot\text{s}^n$	CPE_1 , n	$\text{CPE}_2 Q$, $\mu\text{S}\cdot\text{s}^n$	CPE_2 , n	Error, %
0	6.3	2.543	0.540	148.3	0.872	663.2	0.903	1.24
14	1.4	0.053	0.967	547.9	0.770	111.8	0.807	2.22
28	6.8	0.005	0.302	107	0.570	39.2	1.000	1.63

Table 2a. Elements of the equivalent circuit. The model solution +0.1 g/L of catechol.

Exposure, days	R_0 , Ω	R_1 , $\text{k}\Omega$	R_2 , $\text{k}\Omega$	$\text{CPE}_1 Q$, $\mu\text{S}\cdot\text{s}^n$	CPE_1 , n	$\text{CPE}_2 Q$, $\mu\text{S}\cdot\text{s}^n$	CPE_2 , n	Error, %
0	9.5	2.811	0.505	184.0	0.817	967.6	0.936	1.31
14	2.5	0.068	3.114	3442	0.617	1659	0.769	1.71
28	5.0	0.003	0.768	1090	0.564	22.7	1.000	1.01

Table 2b. Elements of the equivalent circuit. The aftereffect of 0.1 g/L of catechol after washing and transfer to the blank solution.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	5.3	1.834	0.316	153.9	0.837	1243	0.742	1.03
14	3.8	0.030	3.334	3001	0.610	3419	0.711	1.70
28	8.2	0.058	1.871	106	0.843	2610	0.559	1.26

Table 3a. Elements of the equivalent circuit. The model solution + 0.5 g/L of catechol.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	4.6	2.654	0.273	147.7	0.846	1.16	0.916	0.94
14	5.6	0.220	2.478	1880	0.704	73.24	0.971	2.46
28	6.8	0.012	1.257	1210	0.618	784	0.718	1.04

Table 3b. Elements of the equivalent circuit. The aftereffect of 0.5 g/L of catechol after washing and transfer to the blank solution.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	4.2	1.765	0.272	146.5	0.854	2.812	0.866	0.86
14	3.4	0.848	2.046	1804	0.696	172.6	1.000	1.91
28	8.0	0.025	2.719	553	0.563	2870	0.652	1.55

Table 4a. Elements of the equivalent circuit. The model solution + 1 g/L of catechol.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	5.8	4.061	1.038	155.8	0.827	867.7	1.000	2.17
14	3.2	0.588	0.954	218.1	0.840	36.4	0.936	1.64
28	7.3	0.019	–	1140	0.642	2460	0.760	1.61

Table 4b. Elements of the equivalent circuit. The aftereffect of 1 g/L of catechol after washing and transfer to the blank solution.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	8.5	2.058	0.274	137.2	0.843	2541	0.872	1.15
14	3.7	2.866	1.492	217.2	0.830	110.2	1.000	2.12
28	7.3	0.022	–	1270	0.454	5150	0.738	1.35

Table 5a. Elements of the equivalent circuit. The model solution + 5 g/L of catechol.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	5.2	6.561	1.098	1.5.2	0.872	1243	1.000	2.19
14	4.4	5.183	1.929	175.2	0.847	454.6	1.000	1.46
28	6.8	0.599	9.402	928	0.347	183	1.000	3.74

Table 5b. Elements of the equivalent circuit. The aftereffect of 5 g/L of catechol after washing and transfer to the blank solution.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	6.9	1.177	0.098	136.9	0.873	2751	0.885	1.21
14	6.3	4.057	1.267	235.5	0.823	373.7	1.000	1.41
28	22.5	0.160	4.234	116	0.555	881	0.632	1.49

Table 6a. Elements of the equivalent circuit. The model solution + 10 g/L of catechol.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	4.0	7.488	2.060	102.4	0.893	689.1	1.000	2.21
14	6.7	5.119	0.237	150.6	0.854	5238	1.000	3.83
28	6.2	0.016	0.563	4590	0.349	5.91	1.000	1.49

Table 6b. Elements of the equivalent circuit. The aftereffect of 10 g/L of catechol after washing and transfer to the blank solution.

Exposure, days	R_0 , Ω	R_1 , $k\Omega$	R_2 , $k\Omega$	$CPE_1 Q$, $\mu S \cdot s^n$	CPE_1 , n	$CPE_2 Q$, $\mu S \cdot s^n$	CPE_2 , n	Error, %
0	5.1	1.355	0.173	122.5	0.885	3423	1.000	1.26
14	8.6	0.107	3.842	138.7	0.837	22.45	1.000	1.28
28	3.4	0.140	0.440	2190	0.339	3490	0.711	0.99

The obtained fitting results according to Mansfeld equivalent circuit provided good agreement with the experimental EIS data in the frequency range from 20 kHz to 0.1 Hz. The calculation error did not exceed 4%.

Since in this model the resistance R_1 refers to the surface resistive layer, by changing its value after rinsing the electrode, one can judge the effect of resinous sediment accumulating on the surface during exposure. Obviously, there is no any resinous precipitate

in the blank solution. Consequently, the decrease in R_1 with time for the sample in the blank solution can be explained by the destruction of the surface oxide layer formed in air during prolonged contact with the solution. A similar trend can be observed at a minimum concentration 0.1 g/L of catechol, when the formation of a resinous precipitate is still slightly.

At higher concentrations of the inhibitor, the resinous precipitate begins to accumulate more strongly, which is noticeable by the increase in resistance R_1 and its change after rinsing. Unfortunately, the results of the experiments do not show systematic patterns of the effect of the CC concentration on the surface resistance R_1 when rinsing off the resinous sediment². It is also difficult to unambiguously interpret the change in the ratio of surface R_1 and Faraday R_2 resistances during exposure in solutions with an inhibitor.

A noticeable increase in the capacitance factor in systems containing an inhibitor is noteworthy. Thus, at the values of $n \approx 1$ the high values of Q CPE₂ modules can be explained by the pseudo-capacity effect due to the reactions of metal interaction with an organic inhibitor. A noticeable decrease in the phase factor n during prolonged contact of steel with the solutions with an inhibitor indicates an increase in diffusion factors and/or inhomogeneity of the metal surface in these systems.

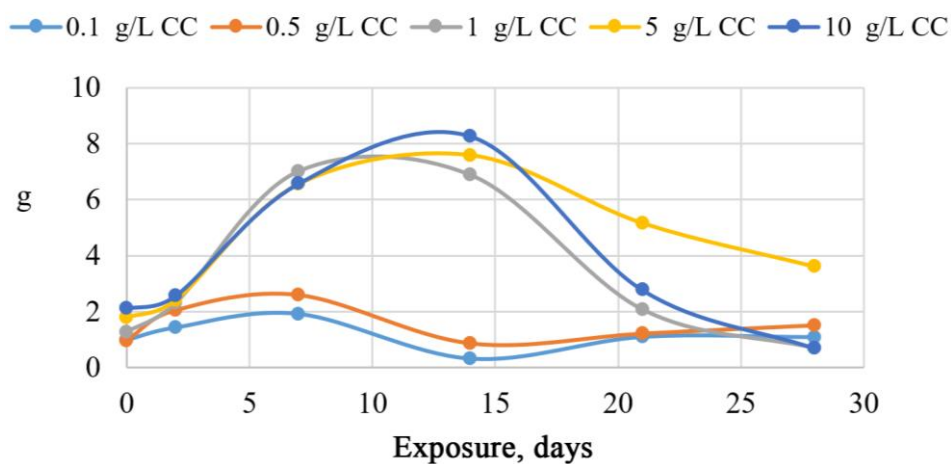
Thus, processing the EIS results in terms of the equivalent Mansfeld circuit leads to multifactoriality, which makes it difficult to analyze the situation. More visual results can be obtained by comparing the impedance of the samples at the lowest frequency (0.1 Hz), which most closely approximate the conditions of DC polarization (*i.e.*, a quasi-stationary state). For this frequency, the actual component of the impedance vector must correlate with the total charge transfer inhibition caused by both the ionic resistance of the surface layers and the resistance of the Faraday metal oxidation reaction, together determining the rate of corrosion. The Z_{Re} component of the impedance vector at a single frequency no longer depends on the structure of the equivalent circuit and the results of its fitting.

As a criterion for the analysis, we took the coefficients of corrosion inhibition γ under the action of an inhibitor calculated by the formula:

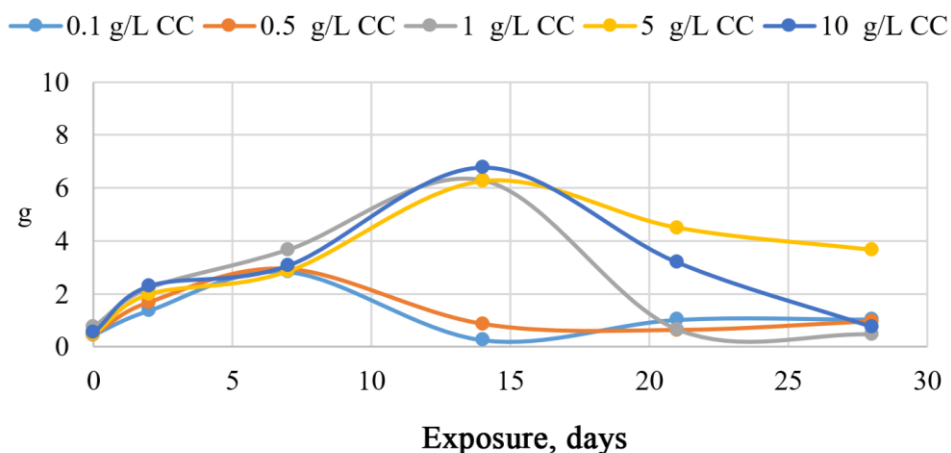
$$\gamma = Z_{Re,inh} / Z_{Re,0} \quad (6)$$

where: $Z_{Re,0}$ and $Z_{Re,inh}$ are, respectively, the actual components of the impedance vector in the blank solution and in the solution with an inhibitor, measured at the same frequency 0.1 Hz at the same time since the beginning of the experiment. These results are shown in Figure 5.

² When analyzing the results, it should be borne in mind that the sediment did not accumulate continuously from the beginning of the experiment, but was periodically rinsed off in each measurement cycle.



A



B

Figure 5. Corrosion inhibition coefficients γ under the action of CC inhibitor. A – in solution with CC inhibitor. B – after rinsing off the resinous sediment in the blank solution.

It can be seen from Tables 1 and 2 that the active elements of impedance (R_1+R_2) decrease rapidly over time due to increased corrosion of steel in a solution without additives. At the same time, for samples with an inhibitor, they decrease more slowly, at least from the first weeks of exposure. Therefore, the characteristic type of dependence with a maximum is observed. That is, the relative protective effect is due to a combination of a delay in the onset of intense corrosion in solutions with catechol compared with a blank solution.

As has been noted earlier, from Figure 5(A) it is obvious that at low catechol concentrations of 0.1 and 0.5 g/L, moderate inhibition of steel corrosion occurs, not exceeding $\gamma=3$ and reaching a maximum after a week. Further, γ decreases to a level from 0.5 to 1. That is, at low concentrations of catechol, long-term corrosion protection cannot be provided and from the second week the corrosion rate approaches that observed in the blank solution or even more. At concentrations from 1 to 10 g/L of catechol, at first two weeks there is a sharp increase in the inhibitory ability to $\gamma=7-8$, *i.e.* the corrosion rate in solutions

with an inhibitor turns out to be almost an order of magnitude lower compared to the background solution at the same time. However, after two weeks of exposure in solution, there is a decrease in protective ability. By the end of the experiment, the protective effect decrease to $\gamma \approx 1$ (no inhibition) at concentrations of 1 and 10 g/L of catechol. At an intermediate concentration of 5 g/L of catechol, the protective effect decreases more slowly and reaches $\gamma \approx 4$ by the end of the fourth week. In other words, a simple increase in the concentration of the inhibitor cannot provide long-term protection of steel from corrosion, but there is an optimum. According to the results of this series of experiments, the concentration of 5 g/L of catechol turned out to be the most effective. This concentration falls within the effective protection range that we established earlier in corrosion experiments on weight loss of steel samples [7].

Comparing Figures 5(A) and 5(B), it is possible to evaluate the effect of the resinous sediment rinsed off the surface on the change in impedance when measured in a fresh blank solution. It can be seen that in this series of experiments, the same patterns remain as at the exposure in an “aging solution” with an inhibitor (Figure 5(A)). This means that when the resinous sediment is removed and the sample is transferred to a blank solution, the inhibitory effect remains, although it may be slightly lower. *I.e.*, the presence of resinous sediment on the surface obviously does not significantly contribute to the inhibitory effect. On the contrary, catechol protects steel mainly by forming a dense indelible adsorption layer of chelates when interacting with metal.

It can be assumed that during the initial period of exposure in solution (the first days), the increase in the protective effect of the inhibitor is due to both a sharp decrease in the oxygen content in the solution (due to the antioxidant properties of catechol) and the adsorption of the inhibitor on the surface of steel, blocking the active centers on the metal. After rinsing the surface from the resinous sediment and placing the sample in a fresh blank solution, the oxygen concentration in it increases. If corrosion inhibition occurred mainly due to the accumulation of resinous sediment, after washing it off, one would expect increased corrosion of the metal in a fresh blank solution. Nevertheless, the protective effect changes little when the sample is transferred to a fresh solution with a higher oxygen concentration, although it turns out to be slightly lower. Consequently, it is provided by a dense adsorption film of chelates formed during pre-exposure in solution with catechol.

The noticeable difference observed in the first week between the data in Figure 5(A) and 5(B) are probably due to insufficient blocking of active centers by catechol, on which a depolarizing reaction can take place in a “fresh” blank solution saturated with oxygen. It is interesting to note that the greatest difference after a week is manifested in solutions with a high concentration of the inhibitor.

During two weeks of exposure, a larger amount of the inhibitor and its oxidation products accumulate on the surface of the steel in a solution with catechol, sufficient to continue protecting the metal even after rinsing the surface and replacing it with an oxygen-enriched background solution. The “residual inhibition efficiency” turns out to be different depending on the initial concentration of catechol. Thus, in solutions with a low

concentration 0.1 and 0.5 g/L of catechol, the protective effect practically disappears after two weeks, and at higher concentrations reaches a maximum ($\gamma \approx 6-7$). During further exposure in the solution, the protective ability decreases, both in “aging solutions” with an inhibitor, and when transferring metal to a fresh background solution. It is worth noting that the greatest difference in curves is shown in Figure 5(A) and 5(B) are observed at a concentration of 1 g/L of catechol. After removing the resinous sediment and replacing the solution, the protective effect is halved. At higher concentrations, flushing of the resinous sediment practically has no effect. The strongest protective effect after replacement of the solution remains at a concentration of 5 g/L of catechol. Obviously, in this case, the most durable adsorption film is formed, protecting against corrosion. Such a film works both in the presence and in the absence of a resinous layer on the surface. The natural decrease in the protective effect by the fourth week at all concentrations and the small difference in γ when replacing the “aged” solution with an inhibitor with a fresh background solution can probably be explained by the depletion of a non-oxidized form of catechol in solution, which prevents oxygen entering from the atmosphere. That is, the observed level of protection can only be due to the influence of the previously formed adsorption film of catechol in the absence of its non-oxidized form in solution.

Discussing the possible contribution of resinous sediment on the surface at high concentrations of catechol, it can be noted that in the Bode impedance diagrams it manifests itself as an additional wave precisely by the fourth week of exposure, which indicates a change in the charge transfer mechanism due to the formation of a resistive layer on the surface. However, the effect of this layer is manifested only in the high-frequency region and practically does not affect the degree of corrosion inhibition estimated at a frequency of 0.1 Hz.

It is interesting to note that in this series of experiments, as previously in experiments on assessing the corrosion rate by casting polarization resistance [6], and during monthly corrosion tests for mass losses [7], the concentration dependence of the degree of inhibition passes through a maximum. We observed the strongest and longest-lasting protective effect at a concentration of 5 g/L of catechol. Obviously, at low concentrations of the inhibitor, it is not enough for long-term protection, since it is quickly completely consumed to oxygen reduction in the volume of the solution. Previously, we showed that at a concentration 0.05 g/L of catechol, the stoichiometry of the ratio of components according to reaction (2) is approximately achieved and thus the complete oxidation of catechol into oxanthrene-2,3-dione occurs [6].

Thus, at low concentrations of 0.1 g/L and 0.5 g/L, catechol is fully consumed in the first days after injection into the solution and does not provide long-term “containment” of oxygen intake from the atmosphere. At higher concentrations (1–10 g/L), catechol can permanently limit the oxygen content in the solution, which helps to inhibit the rate of corrosion. However, with increasing concentration, its reducing effect on surface Fe (III) oxides, which have a greater protective effect compared to Fe (II) oxides, will increase [7]. When choosing the concentration of the inhibitor, it is necessary to choose a compromise

between reducing the oxygen content in the solution due to the reaction with catechol and its reducing effect on surface oxides on metal, leading to a decrease in their corrosion resistance.

Experiments have shown that catechol has a protective effect on steel in an alkaline solution mainly by limiting the concentration of oxygen in the solution and forming a dense (indelible) adsorption film on the metal surface. The resinous precipitate of the inhibitor's oxidation products has a much lesser effect, since after washing it off, the aftereffect of the inhibitor persists. These conclusions are valid for experiments performed on steel samples in a model pore liquid. However, the formation of resinous sediment when using catechol as a corrosion inhibitor for real reinforced concrete systems can have a blocking effect on the pores of concrete, which requires special research.

4. Conclusions

1. The study of the protective ability of catechol additives to corrosion of steel in model chloride-containing solutions of concrete pore liquid by means of electrochemical impedance spectroscopy showed its effectiveness at concentrations above 1 g/L.
2. It has been established that the accumulation of a resinous precipitate of catechol oxidation products on the metal surface as a result of a homogeneous reaction with oxygen is not an essential factor determining the magnitude of corrosion inhibition.
3. Steel samples, after exposure in solution with an inhibitor and after rinsing and transferring to a fresh blank solution, largely retain the “aftereffect” of inhibition.
4. The “aftereffect” effect can be caused by the formation of a strong adsorption layer of chelates on the surface during the interaction of catechol with steel.
5. The effectiveness and long-term protective effect of catechol is determined by a combination of its “restraining” effect on the supply of oxygen (corrosion depolarizer) from the atmosphere into the solution and the formation of strong adsorption films on the metal surface blocking the active centers.
6. The most effective concentration of the inhibitor, providing the highest degree of protection, its duration and “aftereffect” according to the results of 28 daily tests, was the concentration 5 g/L of catechol.

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