

Corrosion behavior and EIS study of steel in an alkaline medium containing chlorides with Catechol inhibitor

V.E. Kasatkin,^{ID} I.V. Kasatkina, I.G. Korosteleva,^{ID} L.P. Kornienko,
V.N. Dorofeeva and N.N. Andreev^{ID}

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation

*E-mail: vadim_kasatkin@mail.ru

Abstract

The study of the inhibitory effect of Catechol (*ortho*-dihydroxybenzene) for corrosion protection of steel in an alkaline environment was continued. Previously, we performed electrochemical studies of Catechol additives in a model electrolyte simulating the composition of the pore liquid of concrete. The principal possibility of the action of catechol as an inhibitor of steel corrosion in a certain range of concentrations has been shown. These studies were carried out by the linear polarization resistance (LPR) method, which allows monitoring the corrosion activity of the metal during its exposure in the electrolyte. However, this method is indirect (the corrosion rate is conditionally estimated in proportion to the polarization resistance of the system). Therefore, this publication presents the results of direct corrosion experiments on the mass loss of samples during monthly exposure in solutions with different concentrations of Catechol. It is established that effective protection of steel from corrosion is observed in the concentration range from 0.5 to 5 g/L of Catechol, which is in good agreement with the results of LPR monitoring. The results of EIS studies of changes in the state of the system over time at low (0.1 g/L) and optimal (1 g/L) Catechol concentrations are presented. Based on the results of previous and current studies, a conclusion is made about the possible mechanism of the protective action of Catechol, explaining the decrease in its effectiveness, both at low concentrations (<0.1 g/L) and with an increase in its content above 5 g/L. Being a strong antioxidant, Catechol is rapidly consumed, oxidized by oxygen at low concentrations. At a higher content, it permanently limits the concentration of oxygen in the electrolyte, preventing corrosion with oxygen depolarization. Also, being absorbed on the surface of the steel, it performs a certain blocking. An increase in the concentration of more than 5 g/L enhances the reducing effect of Catechol on surface iron oxides, leading to the predominance of Fe(II) compounds with less protective effect compared to Fe(III).

Received: October 17, 2023. Published: November 7, 2023

doi: [10.17675/2305-6894-2023-12-4-20](https://doi.org/10.17675/2305-6894-2023-12-4-20)

Keywords: steel, model concrete pore fluid, inhibitor, Catechol, corrosion, EIS.

1. Introduction

In the paper published earlier [1], the electrochemical behavior of Catechol (acronym CC) on platinum and steel electrodes in an alkaline medium was investigated. It was found that

CC at certain concentrations has an inhibitory effect on the corrosion of steel in the pore fluid of concrete. However, its addition does not expand the boundaries of the passive region in potentials, but leads to a decrease in current densities in the passive region. At the same time, the effectiveness of inhibition at different concentrations of the additive was evaluated by the method of linear polarization resistance and it has been found that the highest protective effect is observed at the concentration 1 g/L of CC and decreases markedly when its concentration in solution increases to 5 g/L of CC. This method of estimating the corrosion rate of steel is not direct. Therefore, in this publication we continued the research of CC inhibition for steel corrosion in model pores liquid solution using classical mass loss corrosion tests. In addition, we investigated the inhibitory properties of CC using the Electrochemical Impedance Spectroscopy method (EIS) to better understand the mechanism of its action.

2. Materials and Methods

2.1. Materials

Rolled carbon steel 08PS (an analog of A620 steel) 0.2 mm thick was 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 pore 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 a solution without additives). The experiments were carried out under conditions of natural aeration at room temperature.

2.2. Corrosion tests

The corrosion rate of steel samples in the model pores liquid solution and with CC additives was determined by mass loss. The test samples had a rectangular shape of 2×3 cm with 2 mm hole for mounting on a plastic retainer. Plastic 100 ml cells of were used. After surface preparation, as for other studies, the samples were attached in pairs in a cell with a certain concentration of the inhibitor. The upper edge of the sample was 10 mm below the solution level.

In the first group of experiments with natural aeration of solutions, the cells were closed with lids, in which there were holes for air access. At the same time, in the second group of experiments, the solution was poured into the cells “under the lid” and the vessel was tightly sealed with a polymer film to prevent air access. Unlike the experiments [2, 3], we did not

¹Using NaOH solution.

perform preliminary deaeration of solutions, and the degree of sealing was obviously low (any deformation of cells during exposure due to oxygen absorption from the solution was not observed).

After 30 days exposure, the samples were carefully removed from the solutions and the surface with sediment was photographed. Then they were rinsed with water from the resinous sediment and re-photographed. After that, corrosion products were mechanically removed from the samples to the metal, finally washed, dried, and corrosion losses were determined by the difference in weight before and after the experiment.

2.3. Electrochemical Impedance Spectroscopy (EIS)

The EIS measurements were carried out with IPC series potentiostats² (Russia) [4]. The measurements were done in three-electrode cell at a potentiostatic control. The auxiliary electrode was made of titanium wire.³ A saturated chloride-silver 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 design of the samples and the measuring cell used for EIS is described in detail in [5]. Samples of steel in the shape of a disk with $D = 15$ mm were clamped into a special cell providing unilateral polarization of the working surface of the sample ($S = 1$ cm²). Before EIS tests, the samples were treated with sanding paper, degreased and washed with water, fixed in a cell and kept in contact with a solution without polarization for 40 min to stabilize the surface condition. Electrochemical impedance spectra were obtained in a potentiostatic mode at OCP with harmonic signal amplitude of 10 mV in the frequency range from 20 kHz to 0.1 Hz.

After recording the impedance spectrum, the steel sample was carefully removed from the cell and placed in a vessel filled with the test solution (100 ml) until the next measurement. After holding the sample in solution for 2 days, the impedance spectra were re-registered. To do this, the sample was carefully removed from the solution and, without wiping the working side, fixed in the cell with the studied “aged” solution. Prior to the start of EIS registration, the sample was kept for 30 min in the cell with a solution to stabilize the OCP value.

The specially developed software *ZMonitor* and *Dummy Circuit Solver* was used to process the EIS experiments results.

²The IPC-Pro and IPC-Micro models were used.

³We have previously checked that the titanium auxiliary electrode in the range of recorded currents is not inferior to a platinum electrode and does not disrupt the potentiostat operation. Unlike platinum, titanium electrode has no catalytic activity and does not change the properties of inhibitors.

3. Experimental Results

3.1. Corrosion tests

Our previous experiments based on the measurement of linear polarization resistance [1] provide information for evaluating the instantaneous inhibitory effect of CC at each moment of time. However, for practice it is more important to know the integral values of corrosion losses of metal over relatively long periods, measured by the classical gravimetric method. We chose 30-day exposure for the experiment.

Figure 1 shows the results of averaging two parallel corrosion experiments for each inhibitor concentration. Photos of the samples surface after a month's exposure are shown in Table 1.⁴

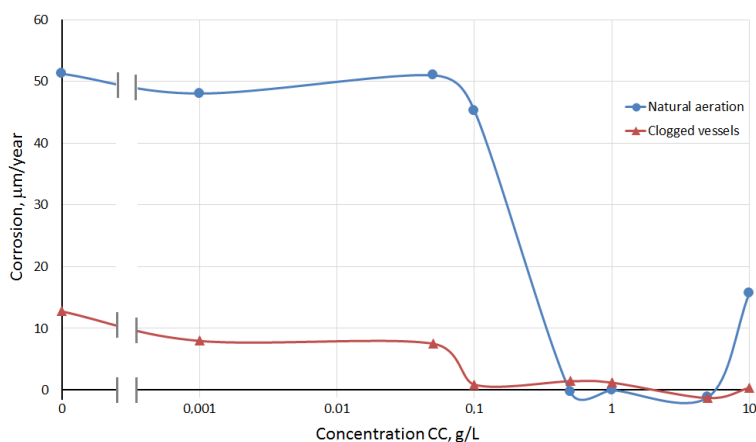


Figure 1. Corrosion rate of steel in the model solutions with CC additives. The blue line refers to the experiments with natural aeration of the solution. The red line shows the results in clogged vessels.

As is evident from the results, in a solution without additives (dots on the left axis of the log graph), the corrosion rate in a clogged vessel is approximately 5 times lower than with natural aeration of the solution. The same trend persists at low CC concentrations up to 0.05 g/L. Although the absolute tightness of the vessels was not achieved in our experiments (and the solutions were not previously deaerated with an inert gas), a decrease in oxygen access to the solution, as expected, contributes to the inhibition of the corrosion process of steel in an alkaline environment, proceeding with oxygen depolarization. The surface of the samples remained clean after a month's exposure, or with a slight coating of loose brownish, easily washed off sediment. At a higher concentration, corrosion losses decreased and at CC concentration above 0.05 g/L were practically absent. A resinous brown precipitate began to accumulate on the surface in the form of individual spots, and the solution in the vessel darkened to opacity with an increase in the concentration of the inhibitor. Obviously, in our





⁴The photo shows the condition of the samples immediately after extraction from the solution and after washing off the poorly bonded layer with a jet of water.

experiments, the complete tightness of the cells was not achieved and there was some influx of air that promotes the oxidation of CC. In experiments with concentrations of 1 g/L and 5 g/L of the inhibitor, after washing the samples from the resinous sediment, dark films with blue and purple colors were found on the surface. After exposure in the solution with 10 g/L CC, the flushing of the products from the surface of the samples after removal of the resinous sediment had a greenish tint, which is characteristic for CC in contact with iron ions [6]. In this case, no color films were observed on the surface of the samples. The surface looked dark gray.

In experiments with natural aeration of solutions up to 0.05 g/L CC, the corrosion rate practically did not differ from the value in the blank solution without additives. Then the mass losses of samples were reduced to almost zero. At a concentration of 0.1 g/L of CC, a loose brown precipitate formed on the surface, after washing off which the surface looked gray with separate brown corrosion lesions mainly along the edges of the sample. At concentrations from 1 g/L to 5 g/L of CC, although a large amount of resinous sediment was formed in the volume of solutions, it accumulated little on the surface of the samples. But these samples clearly show colored blue-violet films, especially at 1 g/L of CC. Just for this sample, a complete absence of mass loss was found during the experiment. Such films proved to be well bonded to the metal surface and persist even after mechanical action when removing corrosion products. So, for the sample with 5 g/L CC, even a small gain ($\sim 0.1 \text{ mg/cm}^2$) was obtained, probably due to incomplete removal of corrosion products.

However, at 10 g/L CC the corrosion of steel increased again, although its rate was approximately 3 times lower than in the blank solution. After a month's exposure in a solution with 10 g/L CC, a solid layer of resinous sediment accumulates on the metal surface. It is also formed in the volume of the solution and at the walls of the cell. This is due to the oxidation of CC with the formation of oxanthrene-2,3-dione [6]. After removal of this sediment, colored films are not visible on the surface of the samples and there are many individual pitting corrosion lesions.

Table 1. Photos of samples after 30 days of exposure in the model solution with CC.

	In clogged vessels			With natural aeration of the solution		
	Directly from the cell	After washing	Corrosion, $\mu\text{m}/\text{year}^5$	Directly from the cell	After washing	Corrosion, $\mu\text{m}/\text{year}$
Blank solution			12.7			51.2

⁵Negative values indicate incomplete removal of corrosion products that have good adhesion to the metal surface.

















	In clogged vessels			With natural aeration of the solution		
	Directly from the cell	After washing	Corrosion, $\mu\text{m}/\text{year}^5$	Directly from the cell	After washing	Corrosion, $\mu\text{m}/\text{year}$
+0.1 g/L CC			0.89			45.3
+1 g/L CC			1.2			0
+5 g/L CC			-1.2			-1.1
+10 g/L CC			0.38			15.7

Table 2a. Inhibitory properties of CC in a model solution in clogged vessels during natural aeration.

Concentration of CC, g/L	Corrosion rate		γ	Z%
	h , $\mu\text{m}/\text{year}$	K , $\text{g}/\text{m}^2\cdot\text{day}$		
0	12.756	0.260	1.00	0.00
0.01	7.981	0.162	1.60	37.44
0.05	7.532	0.153	1.69	40.95
0.1	0.897	0.018	14.21	92.96
0.5	1.442	0.029	8.84	88.69
1	1.218	0.025	10.47	90.45
5	-1.282	-0.026	∞	>100
10	0.385	0.008	33.17	96.98

Table 2b. Inhibitory properties of CC in a model solution with natural aeration.

Concentration of CC, g/L	Corrosion rate		γ	Z%
	h , $\mu\text{m}/\text{year}$	K , $\text{g}/\text{m}^2\cdot\text{day}$		
0	51.250	1.043	1.00	0.00
0.01	48.045	0.978	1.07	6.25
0.05	50.994	1.038	1.01	0.50
0.1	45.289	0.921	1.13	11.63
0.5	-0.321	-0.007	∞	>100
1	0.000	0.000	∞	100
5	-1.154	-0.023	∞	>100
10	15.737	0.320	3.26	69.29

Tables 2a and 2b summarizes the numerical results of gravimetric experiments. Based on these data, it is possible to estimate the coefficients of corrosion inhibition γ under the action of an inhibitor by the formula:

$$\gamma = K_0 / K_{\text{inh}} \quad (1)$$

where K_0 and K_{inh} are, respectively, the corrosion rates in a blank solution and with an inhibitor.

The degree of protection of steel under the action of the Z inhibitor can be calculated by the formula:

$$Z = (K_0 - K_{\text{inh}}) / K_0 \cdot 100\% \quad (2)$$

Summarizing the results of gravimetric experiments, it can be concluded that CC, both in aerated solutions and with restricted air access, provides high protective effect for at least 1 month at concentrations from 0.5 to 5 g/L, and at a higher content it becomes less effective. This does not contradict the previously obtained results based on the measurement of linear polarization resistance. A slightly wider range of effective inhibitor concentrations established in mass loss experiments is probably due to their longer duration and the absence of any effect of polarizing current on the sample during mass lost corrosion test. However, these experiments also showed that the concentration of CC should not exceed a certain limit when it begins to react intensively with surface oxides, violating their protective properties. It is interesting to note that the decrease in protective properties at 10 g/L CC was manifested only in experiments with natural aeration. There were no corrosion losses in closed cells without oxygen access, although the green staining of the solution washed off the surface when the sediment was removed indicated the reaction of CC with iron ions in the solution.

3.2. Electrochemical Impedance Spectroscopy

Unlike the linear polarization resistance method that we used earlier [1], where the polarization of the sample is carried out by direct current, the EIS method uses a low-amplitude, variable-frequency harmonic signal superimposed on the open circuit potential. This makes it possible to determine the impedance of the system by the current response and Nyquist diagrams on the complex plane provide a key to understanding not only the kinetics of the electrochemical reaction, but its possible mechanism. In this paper, we limited ourselves to studying the effect of two concentrations of CC: at its low content of 0.1 g/L, which does not cause a long-term inhibitory effect, and at a higher concentration of 1 g/L, when its protective effect against corrosion is manifested. At these concentrations, we investigated the impedance spectra during the aging process of the solutions with an inhibitor and compared them with the results obtained in solutions without additives.

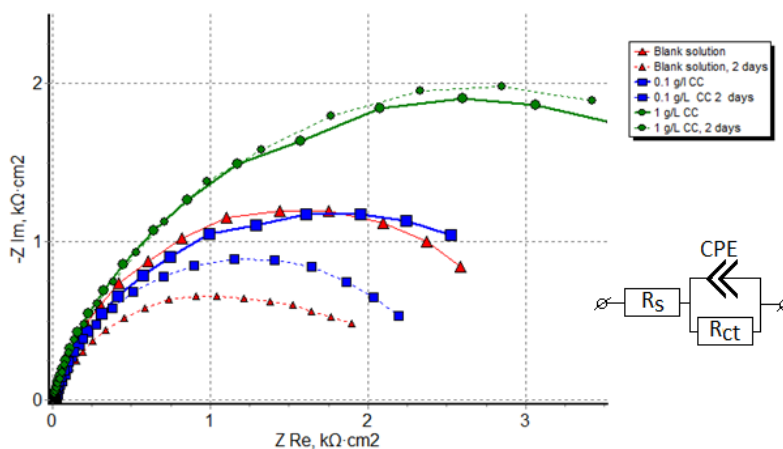


Figure 2. Nyquist diagrams for steel samples in the model solutions with CC additives and the equivalent circuit for fitting EIS results.

For comparison, Figure 2 shows Nyquist diagrams obtained in a blank solution without additives at the beginning of the experiment (after 40 min, when the system has already stabilized, but the corrosion process still slightly affected the surface condition) and after 2 days of exposure in solution (when the sample was subjected to corrosion damage).

All the obtained Nyquist diagrams in the studied frequency boundaries, both in blank solutions and with CC additives, have the shape of a single semicircle arc. This indicates the predominance of the only electrochemical process associated with corrosion reaction. Usually, to quantify the EIS results, an equivalent circuit is used that adequately models the experimental frequency dependences of the impedance and calculates the values of its elements. This form of Nyquist diagrams can be modeled by Randles's circuit without Warburg diffusion element [7]. We have modified this circuit, using the Constant Phase Element (*CPE*) instead capacity. This allows us to take into account the imperfect structure of the This allows us to take into account the imperfect structure of the capacitor. The values of the circuit elements after fitting are shown in Table 3.

In this equivalent circuit, R_s represents the resistance of the electrolyte in the space between the sample surface and the Luggin capillary. This strongly depends on the distance of the capillary from the electrode, and in this case this parameter is not informative.

The charge transfer resistance R_{ct} is proportional to the arc radius of the Nyquist diagram and inversely proportional to the rate of electrochemical reaction at the electrode. In our case, it can be used to judge the change in the corrosion rate over time: an increase in R_{ct} indicates a decrease in the corrosion rate [8].

The module Q_0 of CPE element with a phase factor n close to 1 can be considered as the capacity of the EDL. At the same time, the phase factor n is less than 1, the more inhomogeneous and/or diffuse the structure has a near-electrode layer. With regard to the results obtained, it was found that for all measurements the phase factor turned out to be about 0.8, which indicates some imperfection of EDL structure. The presence of CC in the solution does not cause noticeable changes in the capacitance characteristics of the system. On the contrary, the changes are manifested in the magnitude of the resistance to charge transfer, which is clearly noticeable by the change in the radii of the arcs on the Nyquist diagram.

Table 3. Nominal values of equivalent circuit elements.

Model solution	Exposure, days	$R_s, \Omega \cdot \text{cm}^2$	$R_{ct}, \Omega \cdot \text{cm}^2$	CPE $Q_0,$ $\mu\text{F}/(\text{cm}^2 \cdot \text{s}^{1-n})$	CPE n	Model error
Blank	0	5.9	3089	165	0.846	2.53%
	2	3.9	2456	253	0.732	4.22%
+0.1 g/L CC	0	9.1	3330	202	0.795	2.27%
	2	4.6	2547	162	0.815	2.04%
+1 g/L CC	0	5.2	5023	176	0.794	5.81%
	2	4.9	5042	159	0.820	3.99%

From Nyquist diagrams and R_{ct} values in the blank solution, it can be seen that the corrosion rate of steel increases markedly over time. So, after 2 days of exposure, the charge transfer resistance decreased by ~20% due to the occurrence of corrosion of steel in a chloride-containing electrolyte. When comparing the Nyquist diagrams obtained for a blank solution and with a low concentration 0.1 g/L of CC, it can be seen that their arc radii and R_{ct} values are almost the same at the beginning of the experiment. Although when using an inhibitor, a slight increase in R_{ct} is still noticeable, *i.e.* a weak inhibitory effect was manifested. This is in good agreement with previously performed experiments with a linear resistance polarization method, where Figure 6a [1] shows that at such CC concentration, the corrosion rate in the first hours is slight lower than in blank model solution. However, after two days of exposure in the model solution, the radius of the hodograph in a solution with a low CC concentration decreased, although it remained slightly higher than in a

solution without an additive to the same exposure period. In other words, such concentration of the additive does not provide any lasting inhibitory effect.

In a solution with a higher CC content (1 g/L), on the contrary, the radius of the Nyquist diagrams and the R_{ct} value increased by more than 1.5 times compared with the blank solution at the beginning of the experiment. These parameters did not change after 2 days, which indicates a long-term protective effect. Such results are fully consistent with both the corrosion test data by the classical weight method and with previously obtained measurements based on DC polarization.

By comparing the charge transfer resistances in the blank solution R_{ct0} and with the addition of an inhibitor R_{ctI} , measured at the same exposure time in solution, it is possible to numerically evaluate the inhibitory properties of CC.

$$\gamma = \frac{R_{ctI}}{R_{ct0}} \quad (3)$$

$$Z = \frac{(R_{ctI} - R_{ct0})}{R_{ct0}} \cdot 100\% \quad (4)$$

These calculation results are shown in Table 4.

Table 4. Inhibitory properties of CC in a model solution according to EIS experiments.

Concentration of CC, g/L	Exposure, days	γ	Z%
0.1	0	1.08	7.8
	2	1.04	3.7
1	0	1.63	62.6
	2	1.98	98.0

These data show that with a low concentration of CC, weak inhibition in the initial period weakens even more over time and the corrosion rate of the sample practically does not differ from the experiment in a solution without an inhibitor. And at a higher concentration of CC (1 g/L), its inhibitory effect is noticeably enhanced, which is especially well manifested after two days against the background of increasing corrosion in a solution without additives.

4. Discussion of the Results

Earlier studies using a complex of electrochemical methods [1], as well as the results of classical gravimetry and the EIS spectra given in this article, confirmed the possibility of CC I to provide protection against corrosion of steel in an alkaline environment containing chlorides.

Earlier we have shown [1] that the addition of Catechol to the solution without correcting its pH leads to acidification of the solution and a decrease in the potential of pitting

formation on steel (E_p), after which there is a sharp increase in the anode current on the steel. If the pH of the solution with CC is adjusted at the level of the blank electrolyte, there is no increase in the potential of steel depassivation (E_p). Since this potential turns out to be 100 mV lower than the oxidation potential of Catechol on an inert metal (Pt) [1], the previously stated assumption is not confirmed that a sharp increase in the anodic current may be associated with the oxidation of CC, and not the beginning of metal pitting [2]. Although the potentials boundaries of the passive region do not expand according when using CC with pH control, a decrease in current densities in this passive zone was found in comparison with experiments in pure solution, *i.e.* the inhibitory effect of the additive on steel corrosion is manifested.

Based on the results obtained, it can be imagined that CC, as a corrosion inhibitor, acts by two mechanisms:

- On the one hand, being a very strong antioxidant, it reacts with active oxygen forms in solution, maintaining the concentration of the latter at a low level, while the residual concentration of the non-oxidized form of CC remains. Low oxygen concentration slows down the electrochemical process of corrosion of steel with oxygen depolarization. This effect alone can provide some protection for steel until the antioxidant supply runs out in the solution.
- On the other hand, CC must inevitably have a reducing effect on oxidized forms of iron in the surface layers of steel undergoing corrosion. Therefore, it is expected that the surface will be enriched with reduced forms of Fe(II), the oxides and hydroxides of which have less protective effect compared to Fe(III) compounds [9]. The speed of this reduction process will increase with increasing concentration of the antioxidant (according to the law of mass action). Therefore, an increase in the concentration of CC in solution may reduce the protective effect of surface iron oxides. It should also be taken into account that CC, when interacting with iron ions, forms organometallic compounds – chelates [10, 11]. The formation of chelates with iron ions occurs due to hydroxyl groups in the *ortho* position during their deprotonization. These chelates with iron ions can form a conversion layer on the metal surface [10] (Figure 3).

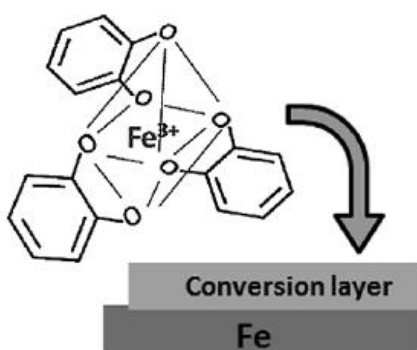


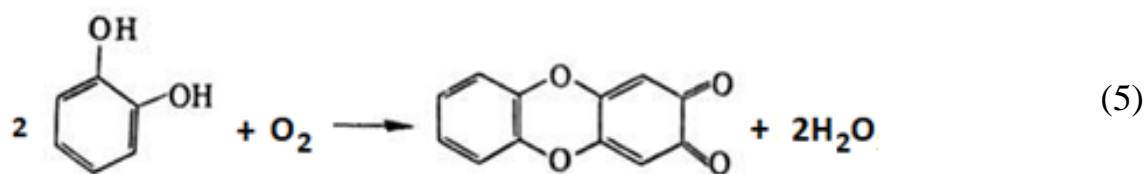
Figure 3. Structure of iron chelate.

In turn, this conversion layer can have an additional protective effect on the metal, provided its solubility is low. In studies on the inhibitory effect of ascorbic acid, which also has antioxidant properties and has hydroxyl groups in the *ortho* position of the lactone ring, providing the ability to form chelates with iron ions. It was shown [12] that the solubility of the chelate with Fe(II) ion is significantly higher than with Fe(III), therefore, an increase in the concentration of ascorbic acid above a certain limit is not desirable, due to its increased reducing effect on iron compounds.

When studying the kinetics of CC interaction with Fe(III), it was found [13] that behind the rapid reaction of the formation of a chelate complex $[\text{Fe}(\text{CC})]^+$ its slower disappearance follows due to the redox reaction with the formation of Fe(II) and o-benzoquinone as an oxidation product of CC. Kinetic analysis showed that the formation of Fe(II) and o-benzoquinone occurs at the same rate. The chelate is destroyed in time, and the resulting o-benzoquinone is no longer capable of chelation. In other words, the chelate formed on the surface is destroyed over time and its protective effect will weaken. Consequently, the same patterns of behavior can be expected for CC as for ascorbic acid in terms of the protective effect of the conversion layers.

After a month's exposure in a solution with CC, we observed the formation of the thinnest colored films directly on the surface of steel at the concentrations above 0.1 g/L of CC, *i.e.* when the strongest protective effect is manifested. At the same time, in the solution with the highest studied concentration 10 g/L of CC, these films are least noticeable, and the protective effect is reduced. Probably, these color films can be identified with chelated conversion layers that provide protection against corrosion.

Another factor that has to be taken into account when using CC is the accumulation in the solution of resinous viscous oxidation products of the reaction:



This effect increases with an increase in the concentration of the inhibitor, especially at natural aeration of the solution. So, at the content above 0.5 g/L of CC, the solution becomes completely opaque. This resinous precipitate adheres to the metal surface, but probably does not have a noticeable blocking effect, which could manifest itself in the form of additional high frequency arcs in the EIS spectra. The accumulation of resinous sediment on the surface of steel samples during prolonged exposure causes in some cases the formation of corrosion lesions under it (Figure 4). Obviously, in this case, a kind of slit effect occurs on these areas of the surface blocked by resinous sediment, which enhances local corrosion.

Thus, when using CC as a steel corrosion inhibitor, these features should be taken into account and used in an optimal concentration range, which is a compromise between maintaining a low oxygen level in solution and the absence of a strong reducing effect on iron surface compounds. According to the results of our research, both from experiments on

polarization resistance and on the classical corrosion test with monthly exposure in solution, 1 g/L CC can be considered this optimum concentration.

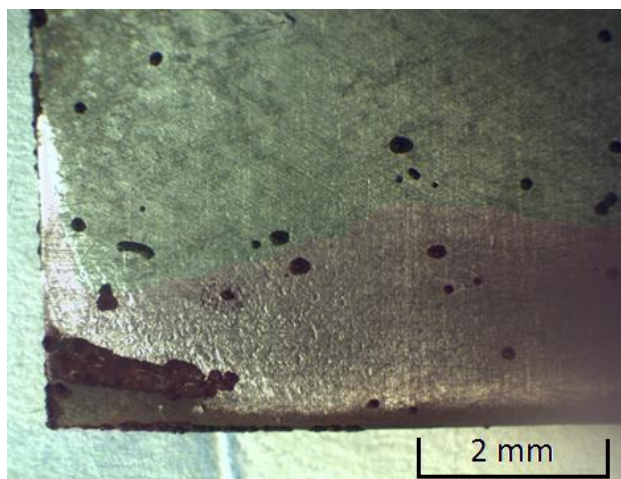


Figure 4. Microphoto of the steel surface after partial removal of corrosion products. Model solution +0.1 g/L CC. Exposure 7 days. The pink tone marks the area covered with a viscous resinous sediment removed before shooting.

In addition, it should be taken into account that, although CC has a natural origin and is found in some plants [13], it cannot be considered environmentally safe. Being an allergen, CC also has mutagenic and carcinogenic properties, causes severe skin irritation and dermatitis [14]. The maximum permissible concentration (MPC) of CC in water is 0.1 mg/L, which is significantly lower than for such an effective inhibitor as sodium nitrite (MPC in water 3.3 mg/L).

5. Conclusions

1. In the presence of CC, the concentration of dissolved oxygen decreases due to the reducing action of C. At the same time, CC is consumed and its oxidation products do not have an inhibitory effect.
2. The potential at which a sharp increase in anodic currents occurs on steel practically does not depend on the concentration of CC in solution and is 100 mV lower than the oxidation potential of CC on platinum electrode. Therefore, this potential should be considered the potential of steel depassivation.
3. In the presence of CC, the depassivation potential of steel does not depend on its concentration, provided that the pH of the solution with additives is maintained at the level of the background solution. It is shown that the inhibitory effect of CC is not associated with the expansion of the passivation region by potentials, but is caused by a decrease in currents in the passive region.
4. After holding the steel in solutions with different concentrations of the inhibitor for a month, it was found that under conditions of natural aeration, the concentration less than 0.1 g/L CC did not reduce the rate of corrosion. However, at concentrations from 0.5 to

- 5 g/L CC, the corrosion losses are practically absent, but at 10 g/L they begin to increase, although they remain three times lower than in the blank solution.
5. With limited oxygen access to the solution, the corrosion rate is expected to decrease, and the area of almost complete inhibition lies in the range from 0.1 to 10 g/L of CC.
 6. The boundary concentrations of CC, where the inhibitory effect is manifested, obtained by the methods of classical gravimetry and linear polarization resistance are in good agreement.
 7. Measurements of the EIS spectra on steel samples in the model pores liquid solution showed that the addition 0.1 g/L CC slightly increases the corrosion resistance of the metal and this effect decreases markedly after two days. At the same time, the addition of 1 g/L CC immediately provides significant inhibition and maintenance of protection over time.
 8. The observed features of the behavior of CC are explained by the inhibition of the oxygen depolarization reaction due to the antioxidant properties of the additive. At the same time, with an increase in the concentration of CC, its reduction effect on surface oxides and iron hydroxides increases, causing a decrease in their protective properties. Therefore, to ensure an optimal protective effect, the concentration of CC should not exceed a certain limit. According to the results of our research, it is shown that the optimal concentration is 1 g/L CC in short-term experiments based on linear polarization resistance (1 week) and from 0.5 to 5 g/L CC according to the results of monthly gravimetric studies.

Declarations of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. V.E. Kasatkin, I.V. Kasatkina, L.P. Kornienko, I.G. Korosteleva, V.N. Dorofeeva and N.N. Andreev, Catechol as a corrosion inhibitor of steel in an alkaline medium containing chlorides, *Int. J. Corros. Scale Inhib.*, 2023, **3**, no. 3, 995–1012. doi: [10.17675/2305-6894-2023-12-3-12](https://doi.org/10.17675/2305-6894-2023-12-3-12)
2. I.A. Gedvillo, A.S. Zhmakina, N.N. Andreev and S.S. Vesely, Effect of hydroquinone and catechol on the corrosion and electrochemical behavior of steel in a model concrete pores liquid, *Int. J. Corros. Scale Inhib.*, 2019, **8**, no. 3, 560–572. doi: [10.17675/2305-6894-2019-8-3-7](https://doi.org/10.17675/2305-6894-2019-8-3-7)
3. I.A. Gedvillo, A.S. Zhmakina and N.N. Andreev, Effect of pyrocatechol on the electrochemical behavior of rusty reinforcing steel in chloride-containing concrete, *Korroziya: Mater., Zashch. (Corrosion: Materials, Protection)*, 2020, **9**, 25–29 (in Russian). doi: [10.31044/1813-7016-2020-0-9-25-29](https://doi.org/10.31044/1813-7016-2020-0-9-25-29)
4. V.E. Kasatkin, L.N. Solodkova and Yu.V. Kondrashov, IPC series potentiostats: Application practice in Electrochemical research methods. Part 1, *Gal'vanotekhnika i obrabotka poverkhnosti (Electroplating and Surface Treatment)*, 2011, **19**, 27–34 (in Russian).

5. V.E. Kasatkin, V.N. Dorofeeva, I.V. Kasatkinaet, I.G. Korosteleva and L.P. Kornienko, Monitoring the effectiveness of corrosion inhibitors by electrochemical methods. Sodium nitrite as an inhibitor for the protection of steel in a model solution of the concrete pores fluid, *Int. J. Corros. Scale Inhib.*, 2022, **11**, no. 1, 198–220. doi: [10.17675/2305-6894-2022-11-1-11](https://doi.org/10.17675/2305-6894-2022-11-1-11)
6. G.I. Putsa, *Catechol*, in *Chimicheskaya Encyclopedia*, 3rd edn., Bolshaya Rossiyskaya Encyclopedia, Moscow, Russia, 1992, 1056 pp. (in Russian).
7. H.H. Hernández, A.M.R. Reynoso, J.C.T. González, C.O.G. Morán, J.G.M. Hernández, A.M. Ruiz, J.M. Hernández and R.O. Cruz, *Electrochemical Impedance Spectroscopy (EIS): A Review Study of Basic Aspects of the Corrosion Mechanism Applied to Steels*, Ed. M. El-Azazy, M. Min and P. Annus, 2020, 36 pp. doi: [10.5772/intechopen.94470](https://doi.org/10.5772/intechopen.94470)
8. S.S. Vinogradova, I.O. Iskhakova, R.A. Kaidrikov and B.L. Zhuravlev, *Method of impedance spectroscopy in corrosion research*, Publishing house of KNITU, Kazan, Russia, 2012, 96 pp. (in Russian).
9. I.L. Rozenfeld, *Corrosion Inhibition*, McGraw Hill Inc, New York, USA, 1982, 327 pp.
10. D. Veys-Renaux, S. Reguer, L. Bellot-Gurletet, F. Mirambet and E. Rocca, Conversion of steel by polyphenolic model molecules: Corrosion inhibition mechanism by rutin, esculin, esculetol, *Corros. Sci.*, 2018, **136**, 1–8. doi: [10.1016/j.corsci.2018.02.015](https://doi.org/10.1016/j.corsci.2018.02.015)
11. E. Mentasti and E. Pelizzetti, Reactions between Iron(III) and Catechol (o-Dihydroxybenzene). Part I. Equilibria and Kinetics of Complex Formation in Aqueous Acid Solution, *J. Chem. Soc., Dalton Trans.*, 1973, **23**, 2605–2608. doi: [10.1039/DT9730002605](https://doi.org/10.1039/DT9730002605)
12. V.A. Timoshnikov, T.V. Kobzeva, N.E. Polyakov and G.J. Kontoghiorghes, Redox Interactions of Vitamin C and Iron: Inhibition of the Pro-Oxidant Activity by Deferiprone, *Int. J. Mol. Sci.*, 2020, **21**, 3967. doi: [10.3390/ijms21113967](https://doi.org/10.3390/ijms21113967)
13. Y. Zhang, Y. Yu, X. Li, Sh. Meguro, S. Hayashi, Effects of catechin-enriched green tea beverage on visceral fat loss in adults with a high proportion of visceral fat: A double-blind, placebo-controlled, randomized trial, *J. Funct. Foods*, 2012, **4**, 315–322. doi: [10.1016/j.jff.2011.12.010](https://doi.org/10.1016/j.jff.2011.12.010)
14. A.V. Moskvina et al. *New Handbook of Chemistry and Technologist. Radioactive substances. Harmful substances. Hygienic standards*, ANO NPO “Professional”, St. Petersburg, Russia, 2004, 1142 pp. (in Russian).

