CORROSION INHIBITION OF CARBON STEEL IN A MILDLY ALKALINE ENVIRONMENT BY COMPOSITION OF BIOPOLYMER AND CARBOXYLATE

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The corrosion behavior of St3sp steel was studied in a mildly alkaline environment inhibited by starch and a starch-based composition. The optimal concentration of the inhibitor composition "starch and sodium glutamate" was determined for use in the corrosive medium. A twentyfold increase in charge transfer resistance and a significant decrease in the double-layer capacitance on the carbon steel surface were observed after 120 hours of exposure. The composition demonstrated high efficiency in protecting carbon steel under mildly alkaline corrosive conditions.

Keywords: steel, corrosion inhibitors, starch, sodium glutamate, reinforced concrete, rebar corrosion, electrochemical impedance spectroscopy

Introduction. Carbon steel reinforcement of the St3sp type is widely used for the production of welded and non-welded elements as well as reinforcement bars in load-bearing building structures due to its excellent operational properties [1]. It is used in the production of reinforced concrete – a composite construction material formed as a result of the monolithic combination of concrete and steel reinforcement [2]. However, reinforcing steel is susceptible to corrosion damage during exposure to corrosive environments in service conditions [1]. Freshly prepared concrete mixtures have high alkalinity, which decreases after hardening, thereby contributing to the corrosion of steel [1]. Additionally, under the influence of environmental factors and internal chemical processes, the physical and mechanical properties of concrete deteriorate over time, which leads to concrete corrosion. In practice, certain corrosion inhibitors have been developed and tested that enhance the protective properties of concrete with respect to reinforcing steel — one such inhibitor is calcium nitrate [3]. Currently, the use of environmentally friendly substances with corrosion-inhibiting potential is a priority [4–5]. Among them is starch, a natural biopolymer. It is a widely available, biodegradable polysaccharide obtained from agricultural raw materials. Starch is a high-molecular-weight carbohydrate compound with glycosidic bonds that chemically link numerous glucose units [5].

Most experimental studies of this polysaccharide have been conducted in acidic media [5]. However, there is a study [6] describing the use of cassava-derived starch in an alkaline medium, which demonstrated good anticorrosion performance on steel. Therefore, the aim of this work was to investigate the potential anticorrosion effect of starch and a starch-based composition on steel corrosion under conditions of reduced alkalinity. A majority of experimental investigations on this polysaccharide have focused on acidic environments [5]. At the same time, a publication [6] reports the application of cassava starch in an alkaline medium, where it exhibited effective corrosion-inhibiting properties for steel. In this regard, the present study aimed to explore the potential anticorrosion performance of starch and its composition for protecting carbon steel in a mildly alkaline medium.

Materials and methods. The corrosion behavior of carbon steel St3sp was studied in a mildly alkaline $Ca(OH)_2$ solution with pH = 10. The corrosive medium was inhibited using starch (ST), monosodium glutamate (MSG), calcium nitrate (CN), and a composition of ST + MSG. Each inhibitor was added at a concentration of 2 g/L, and the total content of the ST + MSG composition was also 2 g/L. The characteristics of corrosion processes were examined in potentiodynamic mode using a Gill AC potentiostat. A silver/silver chloride reference electrode (EVL-1M1 type) was used, with carbon steel St3sp as the working electrode and a platinum electrode as the counter electrode. The potential scan rate was 2 mV/s. The corrosion inhibition efficiency was evaluated by electrochemical impedance spectroscopy (EIS) at open circuit potential over the frequency range of 10000 to 0.01 Hz using the Gill AC instrument. The amplitude of the applied signal was 10 mV. The working electrode surface area was 1 cm². Prior to immersion, steel samples were polished with P320-grade abrasive paper and degreased with acetone. The obtained impedance spectra were modeled using the equivalent electrical circuit $R_s(Q_{dl}R_{ct})$, where R_s and R_{ct} represent the solution resistance and the charge transfer resistance of the metal, respectively, and Q_{dl} is the double-layer capacitance of the metal, expressed through a constant phase element.

The inhibition efficiency was determined based on electrochemical impedance spectroscopy data using the following formula:

$$\eta = \frac{R_{ct} - R_{ct0}}{R_{ct}} \cdot 100\ \%$$

де R_{ct}, R_{ct0} – the charge transfer resistances of the metal in the solutioncontaining the biopolymer-based composition and in the uninhibited solution, respectively.

Results and discussion. Electrochemical tests (Fig. 1) showed that after 24 hours of exposure, starch (ST) used alone did not demonstrate an inhibiting effect, as visible corrosion products were observed on the steel surface. The impedance modulus at a frequency of 0.1 Hz ($Z_{0.1}$) was $5.4 \cdot 10^2$ Ohms·cm^2 (Fig. 1a), and the charge transfer resistance (R_{ct}) was $5.6 \cdot 10^2$ Ohms·cm^2 (Table 1). Upon the addition of monosodium glutamate (MSG) and the ST + MSG composition at a concentration of 2 g/L to the corrosive solution under the same exposure time, significant corrosion suppression of steel was observed (Fig. 1a). In these cases, the charge transfer resistance (R_{ct}) of the steel reached $1.3 \cdot 10^4$ and $1.1 \cdot 10^4$ $\Omega \cdot$cm², respectively (Table 1). However, after prolonged exposure of 120 hours, the composition ST + MSG exhibited better inhibiting properties, as the R_{ct} value reached $6.2 \cdot 10^3$ Ohms·cm^2, compared to $4.1 \cdot 10^3$ Ohms·cm^2 for MSG alone (Fig. 1b, Table 1).

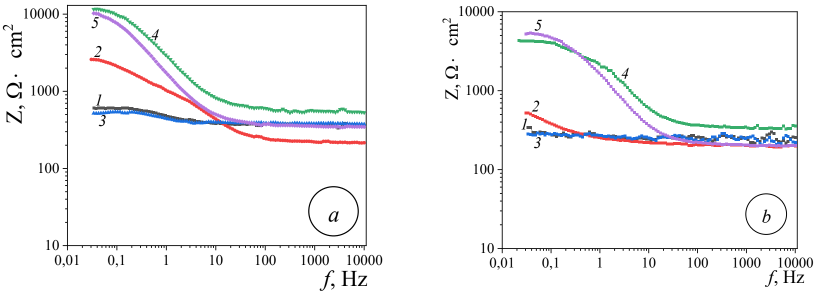

Fig. 1. Impedance spectra of carbon steel after 24 h (a) and 120 h (b) exposure in alkaline medium inhibited with: 1 – $Ca(OH)_2$; 2 – 2.0 g/L CN; 3 – 2.0 g/L ST; 4 – 2.0 g/L MSG; 5 – 2.0 g/L ST + MSG.

Table 1. Parameters of the equivalent electrical circuit $R_s(Q_{dl}R_{ct})$ calculated from the impedance spectra of steel in control and inhibited solutions.

Curve number according to fig.1	R_{ct}, Ohms·cm^2	$Y_0(Q_{dl})$, s^n/ Ohms·cm^2	$n(Q_{dl})$	R_s, Ohms·cm^2	η, %
24 h					
1	616	$7.9 \cdot 10^{-3}$	0,63	370	–
2	2681	$1.5 \cdot 10^{-4}$	0,75	230	77
3	510	$8.0 \cdot 10^{-3}$	0,60	360	–
4	13892	$8.4 \cdot 10^{-5}$	0,79	554	96
5	10836	$1.6 \cdot 10^{-5}$	0,77	591	94
120 h					
1	310	$1.58 \cdot 10^{-3}$	0,46	220	–
2	541	$6.0 \cdot 10^{-3}$	0,49	190	43
3	290	$1.1 \cdot 10^{-3}$	0,75	210	–
4	4100	$1.2 \cdot 10^{-4}$	0,91	354	92
5	6254	$3.1 \cdot 10^{-5}$	0,80	200	95

Note: $Y_0(Q_{dl})$, $n(Q_{dl})$ – conductivity and degree index of the constant phase element Q_{dl}, accordingly; R_s – resistance to the corrosive environment.

A decrease in the conductivity Y_0 (Q_{dl}) by two orders of magnitude (Table 1) was observed in solutions inhibited with 2 g/L of the ST + MSG (1:1) composition and 2 g/L MSG compared to the uninhibited alkaline solution. This indicates the formation of a relatively stable protective organic film on the steel surface, which prevents the ionization of iron and its dissolution into the solution.

No inhibition effect of calcium nitrate was observed. In mildly alkaline solutions at pH 10, in the presence of calcium nitrate, a thick layer of corrosion products formed on the steel surface, which was reflected in a relatively low charge transfer resistance R_{ct} of $2{,}9\cdot10^2$ $\Omega\cdot cm^2$ and a high conductivity Y_0 of $1{,}1\cdot10^{-3}$ $s^n/\Omega\cdot cm^2$ (Table 1).

The inhibition ability of starch is attributed to its molecular structure, which contains electron-rich hydroxyl groups that facilitate the adsorption of the polysaccharide onto the steel and the formation of surface complexes with Fe^{3+} [5]. MSG exhibits high inhibitory properties, but this ability is significantly enhanced when combined with starch. This may be due to the fact that, in neutral environments, MSG can ionize and interact through chemical adsorption, operating via a donor–acceptor mechanism. It is likely that ionized glutamate ions densify the surface film formed by the interaction of starch hydroxyl groups with iron, which ensures an inhibition efficiency of 95% when using the ST + MSG composition.

Conclusions. A high inhibition efficiency of the biopolymer-based composition consisting of starch and sodium glutamate was established based on electrochemical impedance spectroscopy data. A synergistic protective effect of the composition was observed, providing 95% steel protection during prolonged exposure in a corrosive environment. The ST + MSG composition (1:1) at a concentration of 2 g/L effectively inhibits the corrosion of carbon steel in a mildly alkaline medium and may contribute to improving the anticorrosion protection of aged reinforced concrete.

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