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INHIBITORY PROTECTION OF LOW CARBON STEEL IN A FLOW OF PHOSPHORIC ACID SOLUTION CONTAINING IRON(III) PHOSPHATE

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Abstract. The corrosion of low carbon steel in a flow of H_3PO_4 solutions containing $FePO_4$, including media with additives of mixture of corrosion inhibitors consisting of a 3-substituted derivative of 1,2,4-triazole (IFKhAN-92) and KNCS, was studied. In the discussed medium, partial reactions of anodic ionization of iron, cathodic reduction of H^+ and Fe(III) cations are realized on steel. The first two reactions are characterized by kinetic control, and the last one is diffusion-controlled. The accelerating effect of $FePO_4$ on steel corrosion in a H_3PO_4 solution is mainly due to the reduction of Fe(III). In inhibited acid, the accelerating effect of Fe(III) cations affects all partial reactions of steel. Despite such an accelerating effect, the mixtures of IFKhAN-92 and KNCS retain a high inhibitory effect on the electrode reactions of steel, which is an important result. The data on corrosion of low carbon steel in the flow of the studied media, obtained from the mass loss of metal samples, are in satisfactory agreement with the results of the study of partial electrode reactions. The accelerating effect of $FePO_4$ on steel corrosion in the flow of H_3PO_4 solutions, including in the presence of inhibitors, is noted. In these media, steel corrosion is determined by the convective factor, which is typical of processes with diffusion control. Mixtures of inhibitors IFKhAN-92 + KNCS provide significant slowdown of steel corrosion in the flow of H_3PO_4 solution containing $FePO_4$, which is the result of its effective slowdown of all partial electrode reactions of the metal.

Keywords: *convection, diffusion kinetics, diffusion coefficient, acid corrosion, low carbon steel, phosphoric acid, iron (III) phosphate, corrosion inhibitors*

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INTRODUCTION

Phosphoric acid solutions are promising industrial media for cleaning the surfaces of products and processing equipment made of low carbon steels from thermal scale, rust and mineral deposits, which often include phases of Fe(III) oxides and oxyhydroxide. The relatively high dissolution rate of iron oxide phases (FeO, Fe_3O_4, Fe_2O_3) in these media is their important advantage compared to hydrochloric and sulfuric acid solutions traditionally used for acid purification of steels [1–3]. During operation, H_3PO_4 solutions, primarily due to their interaction with the surface phases of Fe(III) oxides and oxyhydroxide, accumulate Fe(III) phosphates. Phosphate Fe(III) is insoluble in water. The solubility of Fe(III) phosphate in H_3PO_4 solutions is the result of its chemical interaction with acid, leading to the formation of a mixture of acid phosphates of complex composition [4]. In the future, such systems will be formally considered as an H_3PO_4 solution containing $FePO_4$.

The accumulation of soluble Fe(III) salts in the media under consideration significantly increases their oxidizing ability, increases the aggressiveness of solutions against steel structures [5], and makes the use of corrosion inhibitors (**CIs**) ineffective in such solutions [6]. A specific feature of corrosion of steels in acid solutions containing Fe(III) salts is their sensitivity to the hydrodynamic parameter of the medium. In acid solutions, including inhibited media, corrosion of steel increases with an increase in the flow rate of the medium [7].

The practical significance of the presented research is determined by the need to create efficient low carbon steels in acid solutions for the needs of modern production [8]. At the same time, it is important to imagine how the developed CIs will protect steel in the flow of a corrosive medium when Fe(III) salts accumulate in it.

To understand the processes occurring in low carbon steel systems, H_3PO_4 solution containing $FePO_4$, it is important to analyze the influence of convection conditions of an aggressive environment both at individual stages and on the corrosion of steel as a whole. The effect of CI on the kinetic parameters of the system should be determined. The assessment of the influence of hydrodynamic parameters of acid solutions containing Fe(III) salts on steel corrosion is important not only theoretically, which makes it possible to identify the diffusion stages of the corrosion process and determine their kinetic parameters, but also in practice, since the industrial operation of these media is often carried out under conditions of liquid flow or is accompanied by significant natural convection as a result of the release on the metal surface of hydrogen gas formed due to the metal's reaction with acid.

We studied a mixture of IFKhAN-92 (3-substituted 1,2,4-triazole) and KNCS as corrosion inhibitors for steel in an H_3PO_4 solution containing $FePO_4$. It was shown [9] that a mixture of 5 mM IFKhAN-92 + 0.5 mM KNCS effectively protects low carbon steels in static solutions of H_3PO_4. The protective effect of this CI is based on its ability to form a polymolecular layer from a solution of H_3PO_4 on the surface of steel, consisting of a polymer complex formed by Fe(II) cations, molecules of 3-substituted 1,2,4-triazole and rhodanide anions [10].

Corrosion of low carbon steels in solutions of mineral acids (so-called "non-oxidants") is described in a simplified form by the total reaction

$$2\,H^+ + Fe = Fe^{2+} + H_2, \qquad (1)$$

which is the result of the predominant course of partial reactions [11, 12]: cathodic hydrogen release

$$2\,H^+ + 2\,e = H_2 \qquad (2)$$

and anodic dissolution of iron

$$Fe - 2\,e = Fe^{2+}. \qquad (3)$$

The features of the reaction mechanism (2) realized on the surface of steels in acid solutions are discussed in [11–13]. The mechanisms of reaction (3) were studied by Heusler [11], Bockris [14], Kolotyrkin and Florianovich [15], and Reshetnikov [16]. Kolotyrkin and Florianovich showed [15] that the dissolution of iron in phosphate solutions is carried out with the participation of OH^- and $H_2PO_4^-$, while the participation of $H_2PO_4^-$ ions in the anodic process is observed only at pH > 4. Later, Reshetnikov [16], when studying solutions with a higher total content of phosphate anions, showed the participation of $H_2PO_4^-$ in the anodic reaction on steels at lower pH values.

We have shown [5] that in H_3PO_4 solutions containing Fe(III) phosphate, corrosion of low carbon steels occurs through three independent partial reactions: anodic ionization of iron (3), cathodic release of hydrogen (2), and reduction of Fe(III) cations:

$$Fe^{3+} + e = Fe^{2+}. \qquad (4)$$

In solutions with a high content of H_3PO_4, partial reactions (2) and (3) are carried out with kinetic control, and reaction (4) with diffusion control.

In our study, it seems appropriate to study the possibility of slowing down the partial reactions of steel (2)—(4) in H_3PO_4 solutions containing Fe(III) phosphate with IFKhAN-92 + KNCS mixed additives. We assume that the effective inhibition of reactions (2)—(4) by the studied mixed CIs should ensure a significant slowdown in steel corrosion not only in static but also in dynamic H_3PO_4 solutions containing Fe(III) phosphate.

EXPERIMENTAL PART

H_3PO_4 ("chemically pure" grade) and distilled water were used to prepare the solutions. H_3PO_4 solutions containing Fe(III) phosphate were obtained by the reaction of $Fe(OH)_3$ precipitated by NaOH ("chemically pure" grade) from a solution of $FeCl_3$ with an excess of H_3PO_4. To prepare a solution of Fe(III) chloride, $FeCl_3{\cdot}6H_2O$ ("pure" grade) was used. The inhibitor IFKhAN-92, which is a 3-substituted 1,2,4-triazole, and KNCS ("chemically pure" grade) were studied as corrosion inhibitors.

Electrochemical measurements of low carbon steel St3 (composition, in wt.%: C 0.14–0.22; P 0.04; Si 0.15–0.33; Mn 0.40–0.65; S 0.05; Cr 0.3; Ni 0.3; N 0.008; Cu 0.3; As 0.08; Fe the rest) was carried out on a rotating disk electrode (n = 460 rpm) in a solution of 2 M H_3PO_4 at t = 25 °C. The potential of the steel was measured relative to a silver chloride electrode filled with a saturated KCl solution. The steel electrode was cleaned with sandpaper (M20) and degreased with acetone. The polarization curves (**PC**) were taken using an EL-02.061 potentiostat at a polarization rate of 0.0005 V/s for the working electrode. Before applying polarization, the electrode was kept in the test solution for 30 minutes to establish the E_{cor} free corrosion potential, and then the curves of the anodic and cathodic polarization of the steel were taken. After removing them, the dependence of the cathode current, maintaining E = –0.30 V, on the speed of rotation of the electrode (n = 0, 460, 780, 1090 and 1400 rpm) was studied. In the case of steel corrosion in H_3PO_4 solutions containing Fe(III) salts, the cathode process includes reaction (2). The nature of its flow may depend on the pressure of hydrogen gas in the system. To obtain stable results of electrochemical measurements, the removal of dissolved oxygen from the studied media was carried out by deaeration with gaseous hydrogen. This made it possible to carry out electrochemical measurements at a constant pressure of hydrogen gas in the system. The solutions were deaerated for 30 minutes before

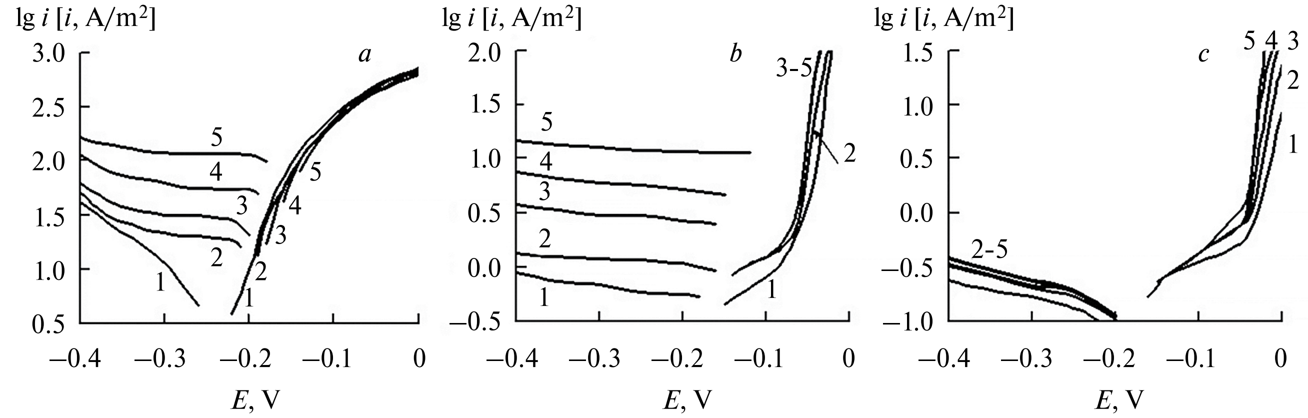

Fig. 1. Polarization curves of St3 steel in 2 M M H_3PO_4 (*a*) with additions of 0.5 mM IFKhAN-92 + 0.5 mM KNCS (*b*) and 5 mM IFKhAN-92 + 0.5 mM KNCS (*c*) containing $FePO_4$, M: *1*—0; *2*—0.01; *3*—0.02; *4*—0.05; *5*—0.10. The value of $n = 460$ rpm; $t = 25$ °C.

the start of the studies. Hydrogen was obtained in an electrolyzer from a solution of NaOH. The average gas supply rate was 1 mL/s. During the electrochemical measurements, the transmission of hydrogen directly through the acid solution was stopped.

The lowest of the discussed values, 460 rpm, was chosen as the base rotation speed of the steel disc electrode during electrochemical studies. At such a rotational frequency, the densities of kinetic and diffusion currents characterizing the cathode reaction occurring on the electrode under experimental conditions are the closest. This situation allows us to hope for a more correct assessment of the effect of Fe(III) phosphate additives on the partial cathode reactions of steel.

The effect of inhibitors on electrode processes was assessed by the values of the cathode inhibition coefficient.

$$\gamma_c = i_{c,0}\, i_{c,in}^{-1} \tag{5}$$

and anodic reactions:

$$\gamma_a = i_{a,0}\, i_{a,in}^{-1}, \tag{6}$$

where $i_{c,0}$ and $i_{a,0}$ are the densities of the cathode and anode currents in the background solution, $i_{c,in}$ and $i_{a,in}$ are the densities of the cathode and anode currents in the solution with the additive under study at potentials of –0.30 and –0.10 V, respectively. When calculating the values of γ_c and γ_a, a solution containing only Fe(III) cations of the appropriate concentration as additives was taken as the background solution.

The values of the electrode potentials are given according to the standard hydrogen scale.

The corrosion rate of steel 08PS (composition, in wt.%: C 0.08; Mn 0.5; Si 0.11; P 0.035; S 0.04; Cr 0.1; Ni 0.25; Cu 0.25; As 0.08; Fe the rest) in 2 M H_3PO_4 at a temperature of 20±2 °C was determined by the mass loss of samples (⩾ 5 per point) measuring 50 mm × 20 mm × 0.5 mm, based on the calculation of 50 mL of acid solution per sample:

$$k = \Delta m\, S^{-1}\, \tau^{-1}, \tag{7}$$

In this case, Δm is the change in the mass of the sample, g; S is the sample area, m^2; τ is the duration of corrosion tests, 1 hour; the duration of experiments is 2 hours. The studies were performed in both static and dynamic corrosive environments at the rotation speed of the magnetic stirrer w = 250, 420, 750 and 1080 rpm. Before the experiment, the samples were cleaned on an abrasive wheel (ISO 9001, grain size 60) and degreased with acetone.

The effectiveness of the inhibitors was assessed by the values of the inhibition coefficients

$$\gamma = k_0\, k_{in}^{-1}, \tag{8}$$

where k_0 and k_{in} are the corrosion rate of 08PS steel in the background solution and in the solution with the additive under study. When calculating the values of γ, a solution containing only Fe(III) cations of the appropriate concentration was taken as the background solution.

The effect of the presence of dissolved Fe(III) salt in the acid, at the same flow rate of the solution, and the nature of the flow of the corrosive medium, at a constant content of Fe(III), on the corrosion rate of steel was estimated by the increments of corrosion losses

$$\Delta k_{Fe(III)} = k_{Fe(III)} - k_0, \tag{9}$$

$$\Delta k_{dyn} = k_{dyn} - k_{st} \tag{10}$$

and the coefficient of corrosion acceleration

$$\gamma_{Fe(III)}^{-1} = k_{Fe(III)}\, k_0^{-1}, \tag{11}$$

Table 1. Values of corrosion potentials (E_{cor}) of St3 steel, Tafel slopes of polarization curves (b_c and b_a), cathode and anode current densities (i_c and i_a), deceleration coefficients of cathode and anode reactions (γ_c and γ_a) obtained at $E = -0.30$ and -0.10 V, respectively. The values of E are given in V, i in A/m^2, $n = 460$ rpm; $t = 25$ °C

$C_{Fe(III)}$, M	E_{cor}	b_c	i_c	γ_c	b_a	i_a	γ_a
2 M H_3PO_4							
0	-0.23	0.125	11.5	-	0.06	262	-
0.01	-0.20	i_{lim}*	21.5	-	0.06	236	-
0.02	-0.19	i_{lim}	31.5	-	0.06	227	-
0.05	-0.18	i_{lim}	63.1	-	0.06	226	-
0.10	-0.17	i_{lim}	119	-	0.06	215	-
2 M H_3PO_4 + 0.5 mM IFKhAN-92 + 0.5 mM KNCS							
0	-0.16	i_{lim}	0.69	16.7	i_{lim}**	0.81	323
0.01	-0.15	i_{lim}	1.2	17.9	i_{lim}**	1.2	197
0.02	-0.15	i_{lim}	3.0	10.5	i_{lim}**	1.2	189
0.05	-0.13	i_{lim}	6.0	10.5	i_{lim}**	1.2	188
0.10	-0.12	i_{lim}	12.6	9.4	i_{lim}**	1.2	179
2 M H_3PO_4 + 5 mM IFKhAN-92 + 0.5 mM KNCS							
0	-0.17	i_{lim}	0.16	71,8	i_{lim}**	0.35	749
0.01	-0.16	i_{lim}	0.20	108	i_{lim}**	0.42	562
0.02	-0.16	i_{lim}	0.22	143	i_{lim}**	0.42	540
0.05	-0.16	i_{lim}	0.23	274	i_{lim}**	0.42	538
0.10	-0.16	i_{lim}	0.24	496	i_{lim}**	0.42	512

* i_{lim} – limiting current.
** The value refers to the first linear section of the anode PC.

$$\gamma_{dyn}^{-1} = k_{dyn} k_{st}^{-1}, \quad (12)$$

where $k_{Fe(III)}$ and k_0 are the corrosion rates of 08PS steel in an acid solution in the presence and absence of Fe(III) salts, and k_{dyn} and k_{st} are the corrosion rates of steel in dynamic and static media.

The measurements were carried out on instruments of the Center for Collective Use of Physical Methods of the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (CCPM IPCE RAS).

RESULTS AND DISCUSSION

Important information about the features of the mechanism of steel corrosion in acid solutions containing Fe(III) salt can be obtained by studying the kinetics of electrode reactions of metal by voltammetry [15]. In 2 M H_3PO_4, the polarization curve shape of low carbon steel is characteristic of corrosion occurring in the range of its active dissolution potentials (Fig. 1, Table 1). In this medium, the slope of the cathode PC of steel (b_c) is close to the theoretically predictable value of 0.120 V for iron, but the slope of the anode PC of metal (b_a) is higher than the theoretical value 0.035 V [16]. The increase in the b_a steel slope was the result of the formation of a sludge layer on its surface, which was visually observed. The presence of $FePO_4$ acid in the solution shifts the potential of free corrosion of steel (E_{cor}) to more positive values, which is the result of the dissolution of this additive in the cathodic reaction. Fe(III) cations have practically no effect on the anodic process, but there is a positive order in the cathodic reaction in their concentration. The initial section of the cathode PCs is characterized by a limiting current (i_{lim}). On the contrary, the slope of the anode PC corresponds to the background dependence.

The presence of $FePO_4$ additives in the H_3PO_4 solution practically does not affect the nature of the anode reaction, which proceeds in accordance with equation (3) both in the absence and in the presence of Fe(III) phosphate. The nature of the cathode PC indicates the participation of Fe(III) in the cathode reaction. In concentrated acid solutions

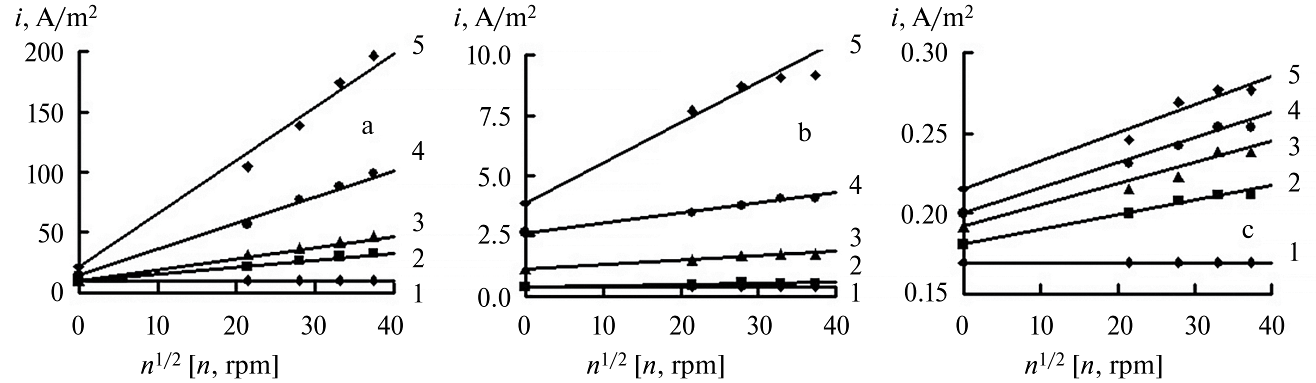

Fig. 2. Dependence of the cathode current density on the rotation frequency of a steel disc in 2 M H_3PO_4 (a) with 0.5 mM IFKhAN-92 + 0.5 mM KNCS (b) and 5 mM IFKHAN-92 + 0.5 mM KNCS (c) containing $FePO_4$, M: *1*–0; *2*–0.01; *3*–0.02; *4*–0.05; *5*–0.10. $E = -0.30$ V, $t = 25$ °C.

(pH < 2), the cathode reaction corresponding to equation (2) proceeds in the kinetic control region [18], which is confirmed by the nature of the cathode reaction. In the presence of Fe(III) phosphate, they are complicated by the limiting current, which indicates a change in the mechanism of the cathode reaction. The observed limiting current may be due to diffusion limitations associated with the delivery of oxidizing agents H^+ and Fe^{3+} present in the acid solution to the steel surface. Since the concentration of H^+ is more than an order of magnitude higher than $C_{Fe(III)}$, the limiting current is more likely to be the result of diffusion restrictions on the delivery of Fe(III) cations to the steel surface. To confirm this assumption, it is necessary to investigate the effect of the electrolyte flow on the rate of the cathode reaction of steel, which is usually carried out using a disk electrode. By changing the frequency of its rotation, the mode of liquid flow near the metal surface is regulated [19, 20].

For the cathode process of steel, determined by reaction (2) occurring in the kinetic region and reaction (4) controlled by diffusion, the equation is applicable:

$$i_c = i_k + i_d, \quad (13)$$

where i_k and i_d are the densities of kinetic and diffusion currents. In the case of laminar fluid motion near the surface of a rotating metal disk, the value of i_d is directly proportional to the square root of the rotational speed of the disk electrode (n), and therefore expression (13) is as follows:

$$i_c = i_k + fn^{1/2}. \quad (14)$$

In 2 M H_3PO_4 + $FePO_4$, the experimental dependence of i_c on $n^{1/2}$ has a linear form (Fig. 2, Table 2). However, in 2 M H_3PO_4, there is no response of the cathode current to a change in the rotation frequency of the steel disc, which indicates the kinetic nature of the reaction (2). In the presence of $FePO_4$, the kinetic component of the cathode current is the same as in its absence, which indicates the independence of reactions (2) and (4). In addition, it is clear that reaction (2) occurs in the kinetic region, and reaction (4) in the diffusion region.

The diffusion current caused by the reduction of Fe(III) on a steel cathode during laminar fluid flow is described by equation [18]:

$$i_d = 0.62zFC^*D^{2/3}\eta^{-1/6}n^{1/2}. \quad (15)$$

Here C^* is the concentration of Fe(III) in the depth of the solution, η is the kinematic viscosity of the liquid (0.011 cm^2/s [21]), and n is the angular velocity of rotation of the steel disc. Using equation (15), it is possible to calculate $D_{Fe(III)}$ in 2 M H_3PO_4 (Table 2). The obtained value of $D_{Fe(III)}$ has good convergence with the data obtained by cyclic voltammetry of a Pt electrode in 2 M H_3PO_4 containing $FePO_4$ and given in [5].

In background solutions of H_3PO_4 containing $FePO_4$, reactions (2) and (4) occur independently on steel. In further discussing the results related to the inhibition of steel corrosion in such environments, we will proceed from the assumption that both of these partial cathode processes are also implemented independently.

The introduction of 0.5 mM IFKhAN-92 + 0.5 mM KNCS and, especially, 5 mM IFKhAN-92 + 0.5 mM KNCS additives into 2 M H_3PO_4 significantly affects the parameters of the electrode reactions of St3 steel (Fig. 1, Table 1). In the presence of these CIs, both electrode reactions of St3 steel are inhibited, and the values of the E_{cor} value are shifted to the region of positive potentials in comparison with the background medium by 0.07 and 0.06 V, respectively, which indicates that these mixtures predominantly slow down the anode reaction of the metal. In media containing CIs, the slope of the cathode PC, compared with the background

2 M H_3PO_4, is increased to the limiting current. Anode PCs have two linear sections. The first section adjacent to E_{cor} is characterized by a limiting diffusion current due to the effective inhibition of the anode reaction by the protective film of the inhibitor. At higher potentials, a region of metal anodic activation is observed, characterized by a significant increase in current [22, 23]. It is primarily associated with partial desorption from the surface of the inhibitor steel. In such media, there is no response of the cathode current to the rotation frequency of the steel disc electrode (Fig. 2, Table. 2), and the cathode process, as in 2 M H_3PO_4 in the absence of $FePO_4$, should be due to reaction (2), which is realized with kinetic control. In inhibited media, especially in the presence of 5 mM IFKhAN-92 + 0.5 mM KNCS, i_k values are lower than in the background environment.

The presence of $FePO_4$ in a corrosive environment worsens the inhibition of the anode and, especially, cathode reactions of steel by mixed CIs, and this effect for the cathode reaction increases with an increase in the content of Fe(III) in the solution (Fig. 1, Table 1). There is a response of the cathode current to the rotation frequency of the disk electrode (Fig. 2, Table 2). In such a system, the cathode current will consist of kinetic current, determined by the partial reaction (2), and diffusion current, caused by the partial reaction (4). An increase in the content of $FePO_4$ in the inhibited acid leads to an increase in both i_k and i_d values. It turns out that Fe(III) salts in the inhibited acid accelerate the cathodic reaction, participating in it not only as an additional depolarizer, but also reduce the inhibition of CI cathodic hydrogen release, which generally negatively affects the protection of steel. All other things being equal, in the presence of an additive of 5 mM IFKhAN-92 + 0.5 mM KNCS, the negative effect of $FePO_4$ on the inhibition of electrode reactions in steel is significantly less pronounced than in media inhibited by 0.5 mM IFKhAN-92 + 0.5 mM KNCS. Despite this, the values of the i_k and i_d parameters in the inhibited media are significantly lower than in similar background solutions. The result obtained allows us to hope for effective protection of low carbon steel with a mixture of IFKhAN-92 and KNCS in H_3PO_4 solutions containing $FePO_4$.

It should be understood how the presence of mixed CIs in an aggressive environment will affect the value of $D_{Fe(III)}$. The values of $D_{Fe(III)}$ observed in the inhibited 2 M H_3PO_4, especially in the presence of 5 mM IFKhAN-92 + 0.5 mM KNCS, are significantly lower than those typical for the background environment with the same parameters (Table 2). It should be clarified that, unlike 2 M H_3PO_4 containing $FePO_4$, in the inhibited media equation (15) allows us to calculate not the true values of $D_{Fe(III)}$, but the effective ones. The introduction of minor CI additives (no more than 5.5 mM) into the acid solution cannot significantly change the true value of $D_{Fe(III)}$ in it. We see another reason for this phenomenon: the inhibitor molecules, being adsorbed on the steel surface, form polymolecular protective layers. The composition and structure of polymolecular protective layers formed by a mixed inhibitor of IFKHAN-92 + KNCS are discussed in [10]. To recover, the Fe(III) cation must overcome the protective layer and reach the surface of the steel. The rate of such a process will be determined by the diffusion of Fe(III) cations in the protective layer formed by the CI. It is the values of $D_{Fe(III)}$ in the near-surface protective layer of the inhibitor that largely determine the values of effective $D_{Fe(III)}$ obtained by equation (15).

Table 2. Values of constants i_k and f in equation (14) at $E = -0.30$ V for the cathode reaction of a steel rotating disk electrode in 2 M H_3PO_4 containing $FePO_4$. Values of i_k in A/m^2, f in A rpm$^{-1/2}$ m^{-2}, $t = 25$ °C

$C_{Fe(III)}$, M	i_k	f	D, μm^2/s,
2 M H_3PO_4			
0	10.2	0	-
0.01	10.2	0.50	130±10
0.02	10.2	0.97	
0.05	10.2	2.34	
0.10	10.2	4.84	
2 M H_3PO_4 + 0.5 mM IFKhAN-92 + 0.5 mM KNCS			
0	0.38	0	-
0.01	0.38	0.0046	0.1
0.02	1.12	0.020	0.3
0.05	2.61	0.042	0.3
0.10	3.85	0.17	0.8
2 M H_3PO_4 + 5 mM IFKhAN-92 + 0.5 mM KNCS			
0	0.17	0	-
0.01	0.18	0.0010	Less than 0.01
0.02	0.19	0.0013	
0.05	0.20	0.0015	
0.10	0.22	0.0017	

Our identification of the kinetic parameters of the system under study allows us to predict the nature of corrosion of low carbon steel in it. Corrosion of steel in 2 M H_3PO_4 containing $FePO_4$ proceeds through stages characterized by both kinetic control and diffusion restrictions. Therefore, the nature of steel corrosion in such systems should

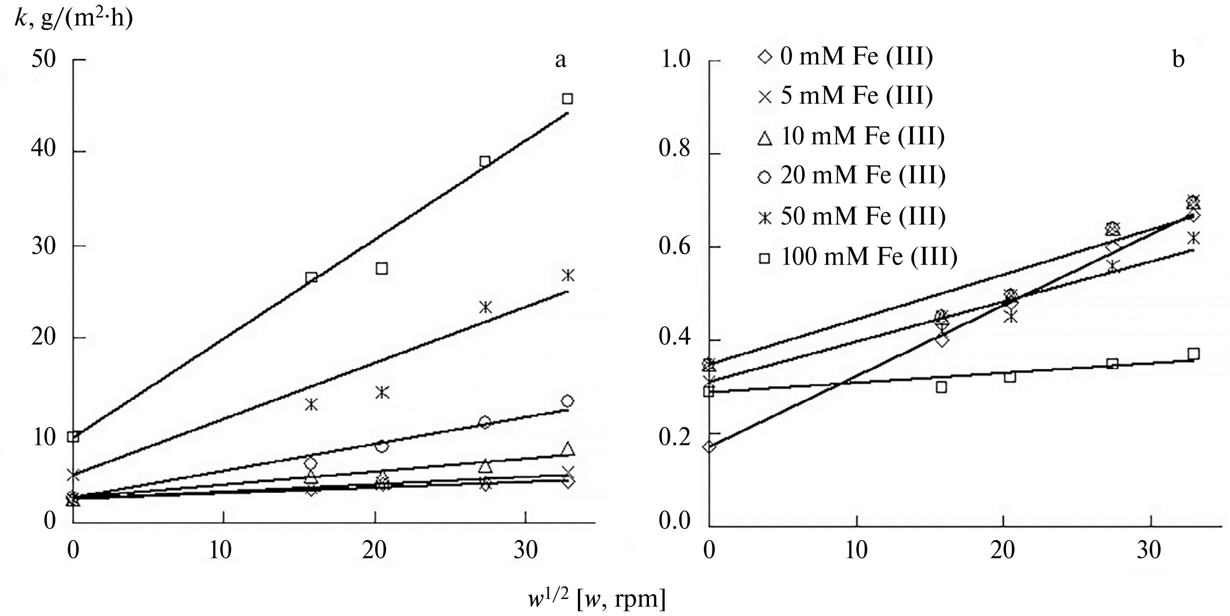

Fig. 3. Dependence of the corrosion rate of 08PS steel on the rotation speed of a propeller agitator in a corrosive environment at 20±2 °C in 2 M H_3PO_4 (a) with the addition of 5 mM IFKhAN-92 + 0.5 mM KNCS (b) containing $FePO_4$. The duration of the experiments is 2 hours.

Table 3. Values of constants k_{st} (g/(m^2 h)) and λ (g rpm$^{-1/2}$ m^{-2} h^{-1}) in equation (16) for corrosion of low carbon steel 08PS at $t = 20\pm2$ °C in a solution of 2 M H_3PO_4 containing $FePO_4$

$C_{Fe(III)}$, M	2 M H_3PO_4		2 M H_3PO_4 + 5 mM IFKhAN-92 + 0.5 mM KNCS	
	k_{st}	λ	k_{st}	λ
0	2.5	0.065	0,17	0,015
0.005	2.6	0.079	0,35	0,010
0.01	2.7	0.14	0,35	0,010
0.02	2.8	0.29	0,35	0,010
0.05	5.2	0.60	0,31	0,009
0.10	9.2	1.1	0,29	0,002

significantly depend on the nature of the convection of an aggressive medium. Effective protection of low carbon steel in 2 M H_3PO_4 containing $FePO_4$ with mixed CIs is to be expected, since they effectively slow down the partial electrode reactions of steel, including the reduction of Fe(III) cations. The higher the content of IFKhAN-92 in the mixed CI, the more significant its effect on the partial reactions of steel.

These assumptions were confirmed when studying the corrosion of low carbon steel 08PS in a stream of 2 M H_3PO_4 containing $FePO_4$ by the mass loss of metal samples (Fig. 3, Table 3). Both in the absence of mixed CI and in its presence, the corrosion of low carbon steel in 2 M H_3PO_4 containing $FePO_4$ increases with increasing $C_{Fe(III)}$. In almost all the media studied, the response of the corrosion process to the mixing rate of the corrosive medium is observed. The experimental dependence of the corrosion rate of low carbon steel on the rotational speed of a propeller agitator used to create forced convection of an aggressive medium can be described by the equation

$$k = k_{st} + \lambda w^{1/2}, \tag{16}$$

where k_{st} is the corrosion of low carbon steel in a static environment, w is the speed of rotation of the propeller agitator, λ is an empirical coefficient characterizing the intensity of the corrosion rate increment. Equation (16) formally corresponds to equation (14), which characterizes electrode reactions occurring with diffusion control. It should be noted that in 2 M H_3PO_4, both in the absence of CI and in their presence, there is a slight response of the corrosion process to an increase in the flow rate of the corrosive medium, which is explained by the presence of dissolved aerial oxygen in the media under consideration. Since the observed effect of oxygen is insignificant, we will not take it into account in our further discussions.

In media inhibited by 5 mM IFKhAN-92 + 0.5 mM KNCS, the values of k_{st} and λ are significantly lower than those observed in solutions without CI at all concentrations of $FePO_4$ (Table 3). Effective protection of low carbon steel in a flow of a corrosive medium containing $FePO_4$ occurs. A decrease in the content of substituted triazole in the IFKhAN-92 + 0.5 mM

KNCS mixture leads to a decrease in its protective effect (Fig. 4, Table 4). The residual protective effect is manifested even at $C_{\text{IFKhAN-92}} = 0.01$ mM.

Analysis of experimental data shows that an increase in the content of $FePO_4$ in a corrosive medium accelerates the corrosion of low carbon steel (Table 5). The most significant increase in $C_{\text{Fe(III)}}$ affects the rate of corrosion of steel in an environment that does not contain inhibitors. Also, in the presence of $FePO_4$ in an H_3PO_4 solution, corrosion of steel accelerates during the transition from a static to a dynamic medium. On the contrary, in inhibited media, the response of the corrosion rate to an increase in $C_{\text{Fe(III)}}$ and an acceleration of the flow of aggressive media is insignificant. The considered mixed CIs provide metal protection in the studied solutions in both static and dynamic environments (Table 6).

The result has important theoretical and practical significance. It has been shown that by using mixtures of substances capable of forming polymolecular protective layers on the metal surface as corrosion retardants, it is possible to provide effective protection of steels in the flow of an acid solution containing Fe(III) salts. For the first time, a mixed individual inhibitor, IFKhAN-92 + KNCS, capable of protecting steel in the flow of an H_3PO_4 solution containing Fe(III), has been proposed. In harsh conditions of aggressive medium flow (750 rpm) containing 0.1 M Fe(III), the addition of 5 mM IFKhAN-92 + 0.5 mM KNCS slows down the corrosion of low carbon steel by almost 110 times, providing $k = 0.35$ g/(m^2 h).

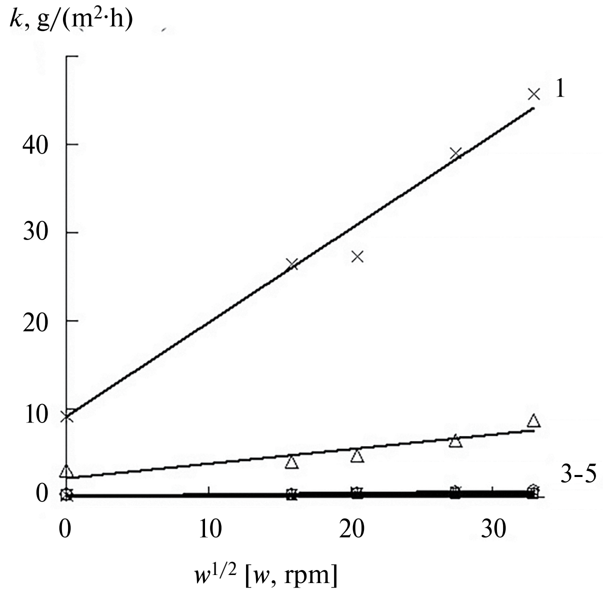

Fig. 4. Dependence of the corrosion rate of 08PS steel on the rotation speed of a propeller agitator in a corrosive environment at 20±2 °C in 2 M H_3PO_4 + 0.1 M $FePO_4$ (1) with additives 0.01 mM IFKhAN-92 + 0.5 mM KNCS (2), 0.1 mM IFKhAN-92 + 0.5 mM KNCS (3), 0.5 mM IFKhAN-92 + 0.5 mM KNCS (4), 5 mM IFKhAN-92 + 0.5 mM KNCS (5). The duration of the experiments was 2 hours.

Table 4. Values of constants k_{st} (g/(m^2 h)) and λ (g rpm$^{-1/2}$ m^{-2} h^{-1}) in equation (16) for corrosion of low carbon steel 08PS at t = 20±2 °C in a solution of 2 M H_3PO_4 containing 0.1 M $FePO_4$ + 0.5 mM KNCS

$C_{\text{IFKhAN-92}}$, mM	k_{st}	λ
0.01	3.0	0.13
0.1	0.34	0.010
0.5	0.30	0.008
5	0.29	0.002

CONCLUSION

1. The corrosion of low carbon steel in a dynamic H_3PO_4 solution containing $FePO_4$ accelerates with an increase in the flow rate of the medium and an increase in the concentration of Fe(III) salt in it. The empirical dependence of the corrosion rate of steel on the intensity of the flow of the media under study, mixed by a propeller agitator, can be represented as a linear relationship:

$$k = k_{\text{st}} + \lambda w^{1/2},$$

where k_{st} is the rate of corrosion of steel in a static medium, w is the speed of rotation of the propeller agitator, and λ is the empirical coefficient.

2. Corrosion of low carbon steel in the flow of an H_3PO_4 solution containing $FePO_4$ is realized as a result of three partial reactions on the metal: anodic ionization of iron and cathodic reduction of protons and Fe(III) cations.

3. For the first time, the possibility of inhibitory protection of low carbon steel in the flow of an H_3PO_4 solution containing $FePO_4$ by additives of a mixture of IFKhAN-92 and KNCS has been shown. Mixed CIs provide a significant slowdown in steel corrosion in these environments. The reason for the high inhibitory effects of IFKhAN-92 and KNCS mixtures when protecting steel in the flow of an H_3PO_4 solution containing $FePO_4$ is their effective deceleration of partial electrode reactions of the metal: anodic ionization of iron and cathodic reduction of protons and Fe(III) cations.

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Table 5. Corrosion rate (k), corrosion loss increment (Δk) and corrosion acceleration coefficient (γ^{-1}) of 08PS steel in 2 M H_3PO_4 solutions containing Fe(III). k and Δk in g/(m^2 h). The duration of the experiments was 2 hours, $t = 20\pm2$ °C

$C_{\text{Fe(III)}}$, M	Static medium			Dynamic medium (750 rpm)			Δk_{dyn}**	γ_{dyn}^{-1}**
	k	$\Delta k_{\text{Fe(III)}}$*	$\gamma_{\text{Fe(III)}}^{-1}$*	k	$\Delta k_{\text{Fe(III)}}$*	$\gamma_{\text{Fe(III)}}^{-1}$*		
2 M H_3PO_4								
0	2.5	-	-	4.2	-	-	1.7	1.7
0.005	2.6	0.1	1.0	4.4	0.2	1.0	1.8	1.7
0.01	2.6	0.1	1.0	6.2	2.0	1.5	3.6	2.4
0.02	2.8	0.3	1.1	11	6.6	2.6	8.0	3.9
0.05	5.2	2.7	2.1	23	19	5.5	18	4.4
0.10	9.2	6.7	3.7	39	30	9.3	30	4.2
2 M H_3PO_4 + 0.01 mM IFKhAN-92 + 0.5 mM KNCS								
0.10	3.0	-	-	6.5	-	-	3.5	2.2
2 M H_3PO_4 + 0.1 mM IFKhAN-92 + 0.5 mM KNCS								
0.10	0.34	-	-	0.62	-	-	0.28	1.8
2 M H_3PO_4 + 0.5 mM IFKhAN-92 + 0.5 mM KNCS								
0.10	0.30	-	-	0.56	-	-	0.26	1.9
2 M H_3PO_4 + 5 mM IFKhAN-92 + 0.5 mM KNCS								
0	0.17	-	-	0.60	-	-	0.43	3.5
0.005	0.35	0.18	2.1	0.64	0.04	1.1	0.29	1.8
0.01	0.35	0.18	2.1	0.64	0.04	1.1	0.29	1.8
0.02	0.35	0.18	2.1	0.64	0.04	1.1	0.29	1.8
0.05	0.31	0.14	1,8	0.56	-0.04	0.93	0.25	1.8
0.10	0.29	0.12	1,7	0.35	-0.29	0.58	0.06	1.2

* – Change in value as a result of the presence of Fe(III) in the solution at the same flow rate of the solution.

** – Change in value as a result of acceleration of the solution flow at a constant content of Fe(III) in it.

Table 6. Corrosion inhibition coefficients (γ) of 08PS steel in 2 M H_3PO_4 solutions containing Fe(III) with IFKhAN-92 + KNCS additives. The duration of the experiments was 2 hours, $t = 20\pm2$ °C

$C_{\text{Fe(III)}}$, M	Static medium	Dynamic medium (750 rpm)
5 mM IFKhAN-92 + 0.5 mM KNCS		
0	15	7.0
0.005	7.4	6.9
0.01	7.4	9.7
0.02	8.0	17
0.05	17	41
0.10	32	110
0.5 mM IFKhAN-92 + 0.5 mM KNCS		
0.10	30	70
0.1 mM IFKhAN-92 + 0.5 mM KNCS		
0.10	27	63
0.01 mM IFKhAN-92 + 0.5 mM KNCS		
0.10	3.1	6.0

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Kuzin, A.V., Gorichev, I.G., Shelontsev, V.A., Kuzmenko, A.N., Plakhotnaia, O.N., and Ovsyannikova, L.V., The Role of a Complex Formation in the Dissolution of Iron Oxides in Orthophosphoric Acid, *Moscow Univ. Chem. Bull.,* 2021, vol. 76, no. 6, p. 398. DOI: 10.3103/S0027131421060055
2. Kuzin A. V., Gorichev I. G., Shelontsev, V.A., Eliseeva, E.A., and Mamankov, A.V., Dissolution of magnetite in orthophosphoric acid: study and modeling, *Russ. Metall.*, 2021, vol. 2021, p. 260. DOI: 10.1134/S0036029521030083
3. Kuzin, A.V., Gorichev, I.G., and Lainer, Y.A., Stimulating effect of phosphate ions on the dissolution kinetics of iron oxides in an acidic medium, *Russ. Metall.*, 2013, vol. 2013, p. 652. DOI: 10.1134/S0036029513090073
4. Prodan, I.E., Yeshchenko, L.S., and Pechkovsky, V.V., Study of the crystallization of iron phosphates in the system iron (III) – phosphoric acid – water, *Russ. J. Inorg. Chem.*, (in Russian), 1989, vol. 34, no. 7, p. 1860.
5. Avdeev, Ya.G., Panova, A.V., and Andreeva, T.E., Corrosion of Low-Carbon Steel in a Flow of Phosphoric Acid Solution Containing Iron (III) Phosphate, *Russ. J. Electrochem.*, 2023, vol. 59, p. 512. DOI: 10.1134/S1023193523070030
6. Avdeev, Ya.G., Panova, A.V., and Anfilov, K.L., Effect of Fe(III) salts on the protection of low carbon steel in sulfuric acid solutions by some corrosion inhibitors, *Int. J. Corros. Scale Inhib.*, 2024, vol. 13, no. 2, p. 1135. DOI: 10.17675/2305–6894–2024–13–2–26
7. Avdeev, Ya.G., and Andreeva, T.E., Mechanism of Steel Corrosion in Inhibited Acid Solutions Containing Iron (III) Salts, *Russ. J. Phys. Chem. A.,* 2022, vol. 96, no. 2, p. 423. DOI: 10.1134/S0036024422020030
8. Kuznetsov, Yu.I., Andreev, N.N., and Marshakov, A.I., Physicochemical Aspects of Metal Corrosion Inhibition, *Russ. J. Phys. Chem., A,* 2020, vol. 94, no. 3. p. 505. DOI: 10.1134/S0036024420030152
9. Avdeev, Ya.G., Tyurina, M.V., and Kuznetsov, Yu.I., Protection of low-carbon steel in phosphoric acid solutions by mixtures of a substituted triazole with sulfur-containing compounds, *Int. J. Corros. Scale Inhib.,* 2014, vol. 3, no. 4, p. 246. DOI: 10.17675/2305–6894–2014–3–4–246–253
10. Avdeev, Ya.G., Tyurina, M.V., Kuznetsov, Yu.I., Pronin, Yu.E., and Kazanskiy, L.P., Protection of low-carbon steel in phosphoric acid solutions with IFKhAN-92 inhibitor. Part 2, *Corros.: mater., prot.* (in Russian), 2013, no. 6, p. 17.
11. Kaesche, H., *Die Korrosion der Metalle. Physikalischchemische Prinzipien und Aktuelle Probleme* (in German), Springer, Berlin, 1979.
12. Pletnev, M.A. and Reshetnikov, S.M., Cooperative Effects in the Problem of Acid Corrosion of Metals, *Prot. Met.*, 2004, vol. 40, p. 460. DOI: 10.1023/B:PROM.0000043064.20548.e0
13. Antropov, L. I. *Theoretical Electrochemistry* (in Russian), Vysshaya Shkola, Moscow, 1965, p. 348–380.
14. Bockris, J.O'M., Drazic, D., and Despic, A.R., The electrode kinetics of the deposition and dissolution of iron, *Electrochim. Acta,* 1961, vol. 4, no. 2–4, p. 325. DOI: 10.1016/0013–4686(61)80026–1
15. Katrevich, A.N., Florianovich, G.M., and Kolotyrkin, Ya.M., Elucidation of the kinetic parameters of the reaction of active dissolution of iron in phosphate solutions, *Prot. Met.,* (in Russian), 1974, vol. 10, no. 4, p. 369.
16. Reshetnikov, S.M., and Makarova, L.L., Kinetics and mechanism of cathodic and anodic processes that determine acid corrosion of metals in the area of active dissolution, *Redox and adsorption processes on the surface of solid metals* (in Russian), Udmurt State University, Izhevsk, 1979, p. 25–49.
17. Reshetnikov, S.M., *Inhibitors of acid corrosion of metals*, (in Russian), Leningrad: Khimiya, 1986.
18. Pleskov, Yu.V., and Filinovskii, V. Yu., *The Rotating Disk Electrode,* Consultants Bureau, New York, 1976.
19. Du, C., Tan, Q., Yin, G., and Zhang, J., Rotating Disk Electrode Method, *In Rotating Electrode Methods and Oxygen Reduction Electrocatalysts,* Eds. W. Xing, G. Yin, J. Zhang, Elsevier B. V. 2014, p. 171–198. DOI: 10.1016/B978–0–444–63278–4.00005–7
20. Jia, Z., Yin, G., and Zhang, J., Rotating Ring-Disk Electrode Method, *In Rotating Electrode Methods and Oxygen Reduction Electrocatalysts,* Eds. W. Xing, G. Yin, J. Zhang, Elsevier B. V. 2014, p. 199–229. DOI: 10.1016/B978–0–444–63278–4.00006–9
21. Xing, W., Yin, M., Lv, Q., Hu, Y., Liu, C., and Zhang J., Oxygen solubility, diffusion coefficient, and solution viscosity, *In Rotating Electrode Methods and Oxygen Reduction Electrocatalysts,* Eds. W. Xing, G. Yin, J. Zhang, Elsevier B. V. 2014, p. 1–31. DOI: 10.1016/B978–0–444–63278–4.00001-X
22. Avdeev, Ya.G., About the nature of iron anodic activation in solutions of mineral acids, *Int. J. Corros. Scale Inhib.*, 2020, vol. 9, no. 4, p. 1375. DOI: 10.17675/2305–6894–2020–9–4–10
23. Pletnev, M.A., Effect of inhibitors on the desorption potentials in the anodic dissolution of iron in acid solutions – A review, *Int. J. Corros. Scale Inhib.*, 2020, vol. 9, no. 3, p. 842. DOI: 10.17675/2305–6894–2020–9–3–4