

Investigation of Inhibitor Polyphosphate Properties for Rotating Steel Disk Electrode in Potassium Nitrate Solution

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Abstract

Inhibition properties of a number of glass-like polyphosphates on 65J steel were investigated using the gravimetry and methods potassium nitrate solution polarization curves in a 0,1M (pH=6,05). The possibilities of optimum experimental conditions were considered as well. Basing on the experimental data the inhibition coefficient and protective effect were found. The inhibiting action of polyphosphates, apparently, is due to the formation of inhomogeneous protecting film on the steel surface.

Introduction

Reconstruction and further development of many branches of Kazakhstan's industry - petrochemical, chemical, power, metallurgical and others - are closely connected with the improvement of their water-supply systems, the increase of the role of return water-supply, changing over to closed and waste-free industrial systems.

In this connection the problem of anticorrosive protection of such metal constructions as water cooling and domestic drinking water-supply systems becomes very urgent. As practice has showed the reduction of their service life as compared with that specified in the standards is caused by their corrosive destruction. Moreover, even the most corrosion-resistant pipe lines decrease their pipe capacity by 50 % in 10-12 years of exploitation [1] due to sedimentation on the walls, what causes considerable costs of on cleaning of the internal water pipe surfaces and extension of water supplying pipelines. Thus, the search for effective anticorrosive measures aimed at the increase of service life of different types of water supply systems and saving of the metal resources of the country is a very actual problem [2].

To solve the problem of reliable and long-term protection of different types of water supplies against internal corrosion, it is very important to choose scientifically justified protection technique.

Nowadays in technically advanced countries more

than 80 % of all new metal pipes for water-supply systems are manufactured with internal sand concrete coatings.

However, the deficiency of protective coatings and underdeveloped material and technical base do not enable to develop protective technique in Kazakhstan. Moreover, spraying of protective coatings can be carried out only under industrial conditions, hence, this technique cannot be used to protect internal surface of operating systems. The only feasible technique, which enables to protect such systems against internal corrosion, is water treatment with inhibitors. In spite of the fact that until now there have been discovered about 5,000 substances which considerably decrease the rate of steel corrosion in the wide range of natural waters, the choice of inhibitors for water-supply systems is still a very complicated problem.

At present there is no universal technique of anticorrosive water treatment. Each technique has its advantages and disadvantages. The traditional inhibitors used for internal anticorrosive protection of equipment and water-supply systems are non-organic phosphates.

During the last decade many researchers and leading world's companies have been searching for different synergetic admixtures which can improve properties of known phosphate inhibitors of steel corrosion in neutral media [3,4].

Nowadays phosphates, as a rule, are an obligatory part of combined inhibitors, which not only prevent scale formation but also considerably reduce

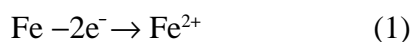
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metal corrosion.

It is already for about 50 years that many countries of the world have been using different phosphates – ortho-, pyro-, three-, polyphosphates, glass-like polyphosphates and, in particular, their calcium and manganese salts to protect internal surfaces of different water- supply systems [5,6].

The basic research of the use of glass-like phosphates as corrosion inhibitors is presented in two Hatch and Rice's papers [7,8]. The dosage of glass-like phosphates is determined by water corrosivity and specific features of water systems operation and can range from 2 to 100 mg P₂O₅ /l.

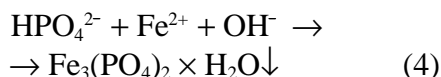
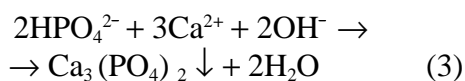
According to [7] protective action of phosphates is caused by formation of glass-like film on the cathode, which is formed in result of the process of electrodeposition and does not hamper heat transfer. Such film formation does not depend on temperature and pressure changes within conventional limits. Hatch and Rice showed [9] that polyphosphates provide protection in the temperature range from 4°C to 99°C and in wide pressure range but not less than pH = 5. Lamb and Eliassen supposed [10] that polyphosphates, being mainly cathode inhibitors, can also affect the anode reaction of iron oxidation:



The authors of [11] supposed that polyphosphates themselves only stimulated steel corrosion whereas inhibition was caused by the product of their hydrolysis - HPO₄²⁻ anion produced by the following scheme:



Interacting with calcium and iron salts anion HPO₄²⁻ produced protective layer:



It should be pointed out that the results are in contradiction with quite a number of investigations [12-14] which established amorphous structure of protective film and showed that the film contained iron oxides, FePO₄, and complex iron combination with polyphosphate anion. As it is seen from literature data, there is no common point of view on the mechanism of phosphate protection on the process of iron

and steel corrosion. And it is quite understandable as "steel – phosphate solution" system is a multicomponent system where not only the molecules of initial polyphosphates are present in the liquid phase, but there is also the whole spectrum of the products of their hydrolysis, each of them can potentially interact in different reactions.

In our country the polymer phosphates have not been widely used, though phosphate – containing compounds are considered to be perspective, and there is an experience of the usage of inhibitors on the basis of sodium polyphosphate [15]. It is well known that satisfactory protection with polyphosphates is obtained when there are calcium, manganese and zinc (mainly, ZnSO₄) in the system.

A serious disadvantage of polyphosphates, which hampers their wide application as corrosion inhibitors, is their low rate of solubility in water.

As it is known [16] the polymer phosphate solubility can be increased by introduction of alkaline metal oxide or silicon dioxide in the composition, what is easily done during the process of phosphate synthesis. Special attention is attracted to mixed phosphates, which contain P-O-Si bonds, the so-called silicopolyphosphates, as the combination of silicate and phosphate components enables to predict a higher degree of protective effect of such phosphates.

Therefore, optimal compositions of silicopolyphosphate inhibitors having both sufficient rate of solubility and high efficiency of anticorrosive action are recommended for practical usage.

In this connection the inhibiting properties of manganese-sodium, zinc-sodium polyphosphates and zinc and manganese silicopolyphosphates has been studied.

The present research is the continuation of the previous investigations in this field [2] and it studies the electrochemical characteristics of steel disk electrode in the presence of polyphosphates and the choice of optimal experimental conditions.

Experimental

Before starting electrochemical measurements, we determined protective effect of the substances under investigation against steel corrosion using the gravimetric method in static conditions.

We carried out all the experiments using 65J steel (mass composition in %: C = 0.62; Mn = 0.9; Si = 0.17; P = 0.035; S = 0.035; Cr = 0.25; Ni = 0.25) at room temperature 21±1°C. We used 0.1 M solutions of potassium nitrate (pH=6,05) with admixtures of sodium

polyphosphate as corrosion medium and their composition with solution concentrations in terms of P_2O_5 equal to 10; 25; 50; 100 mg/l. When adding polyphosphates, the pH-values of the solution being explored reduced. To obtain quantitative estimation of anticorrosive effect of compositions under investigation we carried out control tests in the working solution without admixtures (0.1 M potassium nitrate solution).

Before weighing tests the surface of steel samples was smoothed with emery cloth, treated with acetone, washed with distilled water, dried over $CaCl_2$ for several hours. Then the samples were weighed, their surface was measured and they were placed into hermetic glass flasks. 200 ml of working solution was used for a sample, they were kept in solution for 7 days. After tests, samples were washed in running distilled water, cleaned with latex and again washed by distilled water, acetone, dried up in the desiccator over $CaCl_2$ and weighed.

The rate of corrosion (V_{corr} , $mg/cm^2 \times day$) was estimated by the decrease in mass. The degree of protection (Z , %) was calculated by the conventional formula [17] (Table 1).

Analysing the data obtained, it should be noted that manganese polyphosphate reduces steel corrosion even at as low concentrations as 10 mg P_2O_5/l and the efficiency of protective effect (Z) is 35 %.

The admixture of silicon dioxide to manganese silicopolyphosphate increases the efficiency of steel protection (Table 1).

The compositions of zinc – sodium polyphosphates and silicopolyphosphates of zinc also showed high protective efficiency (Table 1).

Thus, according to the data of gravimetric measurements the polyphosphates reduce the rate of steel corrosion in all the range of concentrations.

The data for the metal mass decrease obtained by gravimetric analysis give the average values of corro-

Table 1

The degree of protective action (Z , %) of phosphates and manganese and zinc silicopolyphosphates as a function of their composition and concentrations obtained as a result of gravimetric measurements (Temperature $21 \pm 1^\circ C$, static test conditions)

Phosphate composition	Phosphate concentration mg P_2O_5 / l			
	10	25	50	100
background + ZnO - P_2O_5	18	34	50.8	68.8
background + Na_2O - ZnO - P_2O_5 $Na_2O : ZnO = 2 : 1$	21.1	42.4	56.7	87.5
background + Na_2O - ZnO - P_2O_5 $Na_2O : ZnO = 6 : 1$	21.7	41	58	90.3
background + Na_2O - ZnO - P_2O_5 - SiO_2 $Na_2O : ZnO = 2 : 1$ $SiO_2 = 5 \text{ mol.}\%$	21.8	42.7	57.8	90.1
background + Na_2O - ZnO - P_2O_5 - SiO_2 $Na_2O : ZnO = 2 : 1$ $SiO_2 = 10 \text{ mol.}\%$	19.9	43	58.8	87.2
background + Na_2O - Zn - P_2O_5 - SiO_2 $Na_2O : ZnO = 6 : 1$ $SiO_2 = 5 \text{ mol.}\%$	28	45.3	71.4	90.6
background + Na_2O - ZnO - P_2O_5 - SiO_2 $Na_2O : ZnO = 6 : 1$ $SiO_2 = 10 \text{ mol.}\%$	31.3	50.9	70.1	90.8
background + Na_2O - MnO - P_2O_5 $Na_2O - MnO = 1 : 1$	35	45	63.7	83
background + MnO - P_2O_5 - SiO_2 $SiO_2 = 3 \text{ mol.}\%$	37.7	66.5	80,6	86.4
background + MnO - P_2O_5 - SiO_2 $SiO_2 = 8,5 \text{ mol.}\%$	33.7	62.43	78.21	83.5

sion. More detailed information about these quantities is obtained by electrochemical methods.

To estimate inhibitor capacity of studied polyphosphates we obtained polarization curves by electrochemical method. The electrochemical methods are more precise, they can be referred to quick methods of determination of material corrosion resistance in different media.

Polarization curves were obtained using rotating steel disk electrode. To obtain current characteristics we used CBA-1BM and measurements were made in three-electrode pressing cell with a transformer providing rotation of the main (operating) electrode with velocities: 350 cycles/min, 960 cycles/min, 1,900 cycles/min and 3,100 cycles/min. The rotation velocity of steel disk electrode was equal to 960 cycles/min in all the cases except the case when we studied the effect of electrode rotation velocity on the limiting current value.

We used a disk electrode made of 65J steel embedded into teflon shell ($S_{el} = 0.1256 \text{ cm}^2$) as the working electrode. We used silver chloride electrode as a standard electrode and the platinum wire as an auxiliary electrode. All the values of potentials are given with respect to saturated silver chloride electrode. The surface of working electrode prior to taking polarization curves was renewed mechanically, i.e. the surface was smoothened with emery cloth, degreased with acetone, washed by distilled water and dried up with filtration paper.

The experiments were carried out in the mixed solution at $21 \pm 1^\circ\text{C}$.

We used 0.1M potassium nitrate solution as a working electrolyte both without inhibitor and with its admixtures.

The readings for polarization curves on the rotating steel disk electrode were taken when the stationary corrosion potential (E_{corr}) was achieved. At first, the readings for the cathode curve versus E_{corr} ($V=2\text{mV/s}$) were taken, then in 10 minutes the readings for the anode curve were taken ($V=2\text{mV/s}$).

While obtaining the data for polarization curves for steel disk electrode at different speeds of potential sweep (1mV/s, 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, 500 mV/s), it was found that the optimal sweep speed for electrochemical parameter calculation was equal to $V=2 \text{ mV/s}$. We also obtained polarization curves at different rotation velocities of working steel electrode. The velocity of electrode rotation varied from 0 up to 3,100 cycles/min. The increase in the frequency of electrode rota-

tion increases the density of anode and cathode currents and the dependence $E - \lg J$ turns into a linear function. While recording polarization curves, the optimal speed of electrode rotation was equal to 960 cycles/min.

Results and discussion

Fig. 1 gives current density for rotating disk electrode as a function of $W^{1/2}$, where W is the angular velocity of electrode rotation. Analysis of obtained functions enables to establish the nature of the limiting reaction stage [18].

Indeed, if the diffusion is the slowest stage of the process, then the dependence of the current measured on the rotating disk electrode on $W^{1/2}$ must be rectilinear and cross the origin of coordinates. If the rate of process is limited by the stage of discharge - ionization, then the current does not depend on the velocity of rotation. In our case non-linear current dependence on $W^{1/2}$ was obtained, what is indicative of the mixed kinetics of the process.

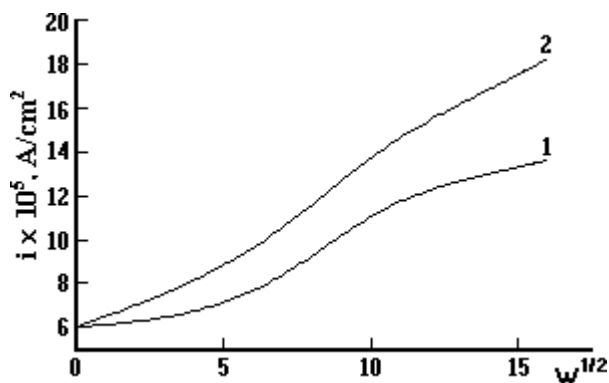


Fig.1. Densities of anodic (1) at $E=0.40$ (sce) V and cathodic (2) at $E=0.44$ (sce) V currents for different rotation velocities of operating electrode.

To determine the effect of inhibitor concentration on the rate of corrosion we obtained potentiodynamical polarization curves in the 0.1M potassium nitrate solution with admixtures of studied substances. Using these polarization curves we determined degree of corrosion ($Z, \%$) and the degree of corrosion deceleration by inhibitor (g_{corr}). Coefficients of corrosion deceleration were determined both by traditional extrapolation technique [19] and by the graphical method suggested in [20]. Discrepancies between the coefficients of corrosion obtained

by extrapolation and graphical methods (Table 2) are rather small.

Table 2

Inhibitor action on 65Jsteel corrosion in 0.1 M KNO₃ potassium nitrate solution determined by electrochemical measurements. (Temp.21±1°C, V_{rot}=960 cycles/min, V=2mV/s)

Mixture composition	Phosphate concentration mg P ₂ O ₅ / l	γ_{gr}	γ_{extr}	Z%
background + ZnO - P ₂ O ₅	10	1.28	1.26	21
	25	1.54	1.56	36
	50	2.36	2.38	58
	100	4.66	4.80	79.2
background + Na ₂ O - ZnO - P ₂ O ₅ Na ₂ O : ZnO = 2 : 1	10	1.28	1.28	22
	25	1.77	1.81	45
	50	2.45	2.50	60
	100	10.5	10.8	90.8
background + Na ₂ O - ZnO - P ₂ O ₅ Na ₂ O : ZnO = 6 : 1	10	1.20	1.29	23
	25	1.79	1.81	44.8
	50	2.70	2.70	63
	100	16.10	13.88	92.8
background + Na ₂ O - ZnO - P ₂ O ₅ - SiO ₂ Na ₂ O : ZnO = 2 : 1 SiO ₂ = 5 mol.%	10	1.28	1.28	22.3
	25	1.78	1.75	43
	50	2.62	2.59	61.5
	100	14.50	14.28	93
background + Na ₂ O - ZnO - P ₂ O ₅ - SiO ₂ Na ₂ O : ZnO = 2 : 1 SiO ₂ = 10 mol.%	10	1.24	1.26	20.8
	25	1.78	1.77	43.7
	50	2.55	2.53	60.5
	100	14.7	14.7	93.2
background + Na ₂ O - ZnO - P ₂ O ₅ - SiO ₂ Na ₂ O : ZnO = 6 : 1 SiO ₂ = 5 mol.%	10	1.30	1.38	28
	25	2.30	2.32	53
	50	3.50	3.58	72.1
	100	19.91	16.66	94
background + Na ₂ O - ZnO - P ₂ O ₅ - SiO ₂ Na ₂ O : ZnO = 6 : 1 SiO ₂ = 10 mol.%	10	1.45	1.47	32
	25	2.15	2.19	54.4
	50	3.40	3.42	70.8
	100	22.5	18.51	94.6
background + Na ₂ O - MnO - P ₂ O ₅ Na ₂ O - MnO = 1 : 1	10	1.50	1.53	35
	25	1.84	1.86	46.4
	50	2.95	2.98	66.5
	100	5.55	5.78	82.7
background + MnO - P ₂ O ₅ - SiO ₂ SiO ₂ = 3 mol.%	10	2.50	2.70	60
	25	5.90	5.95	83.2
	50	9.00	9.09	89
	100	12.20	12.2	91.8
background + MnO - P ₂ O ₅ - SiO ₂ SiO ₂ = 8,5 mol.%	10	1.58	1.4	37
	25	3.5	3.0	66.7
	50	8.8	8.7	88.51
	100	12.3	12.4	91.94

Comparison of steel polarization curves in pure standard electrolyte and electrolyte with inhibitor admixtures (Fig. 2) is indicative of the decrease in the rate of corrosion. Electrochemical measurements showed that as the inhibitor concentration increased, E_{corr} shifted in the range of positive potentials (Table 3). This fact points to the increase in anode reaction deceleration.

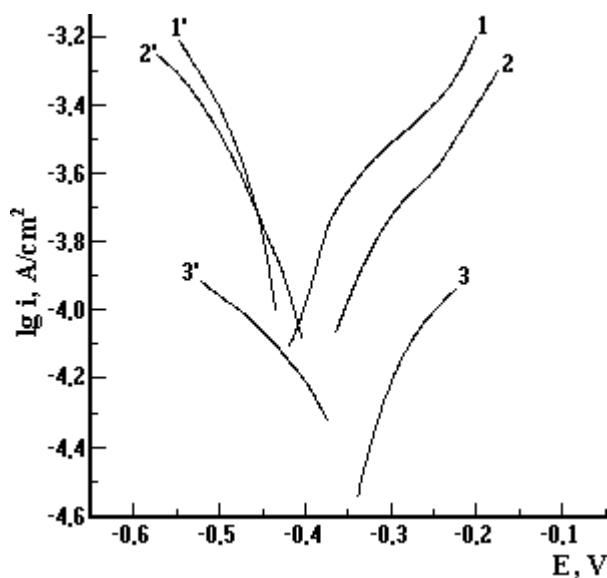


Fig. 2. Anodic (1', 2', 3') and cathodic (1,2,3) polarization curves obtained for 65J steel in 0.1 M KNO_3 without admixtures (1', 1) and in the presence of manganese silicopolyphosphate ($\text{MnO}-\text{P}_2\text{O}_5-\text{SiO}_2$, $\text{SiO}_2=8.5\text{mol.}\%$) with phosphate concentration in $\text{mg P}_2\text{O}_5/\text{l}$: 10 (2',2); 25 (3',3)

Deceleration of the anode process, E_{corr} displacement to the anode region and change in the slopes of cathode polarization curves in the presence of polyphosphate admixtures point to the possibility of formation of a protective film on steel surface.

Conclusion

According to the concepts of steel protection being developed, the mechanism of inhibition is connected with the formation of films of non-uniform composition on the metal surface.

The formation of the protective film on the steel surface is likely to be caused by the formation of several compounds. It can be ferrosilicate, zinc, iron and manganese phosphates. The inhibiting action of polyphosphates is obviously caused by their capacity to prevent oxygen reduction on the electrode surface what facilitates adsorption of dissolved oxygen and

Table 3

Inhibitor action on corrosion potential of 65J steel in 0.1 M potassium nitrate solution.

Mixture composition	Phosphate concentration $\text{mg P}_2\text{O}_5/\text{l}$	$\tilde{A}_{\text{cor.}}$, V
0.1M KNO_3 (background)		-0,42
background + ZnO - P_2O_5	10	-0,375
	25	-0,355
	50	-0,350
	100	-0,340
Na_2O - ZnO - P_2O_5 $\text{Na}_2\text{O} : \text{ZnO} = 2 : 1$	10	-0,375
	25	-0,370
	50	-0,365
	100	-0,360
Na_2O - ZnO - P_2O_5 $\text{Na}_2\text{O} : \text{ZnO} = 6 : 1$	10	-0,361
	25	-0,358
	50	-0,354
	100	-0,350
Na_2O - ZnO - P_2O_5 - SiO_2 $\text{Na}_2\text{O} : \text{ZnO} = 2 : 1$ $\text{SiO}_2 = 5 \text{ mol.}\%$	10	-0,385
	25	-0,380
	50	-0,375
	100	-0,370
Na_2O - ZnO - P_2O_5 - SiO_2 $\text{Na}_2\text{O} : \text{ZnO} = 2 : 1$ $\text{SiO}_2 = 10 \text{ mol.}\%$	10	-0,382
	25	-0,372
	50	-0,368
	100	-0,360
Na_2O - ZnO - P_2O_5 - SiO_2 $\text{Na}_2\text{O} : \text{ZnO} = 6 : 1$ $\text{SiO}_2 = 5 \text{ mol.}\%$	10	-0,373
	25	-0,360
	50	-0,348
	100	-0,346
Na_2O - ZnO - P_2O_5 - SiO_2 $\text{Na}_2\text{O} : \text{ZnO} = 6 : 1$ $\text{SiO}_2 = 10 \text{ mol.}\%$	10	-0,375
	25	-0,375
	50	-0,370
	100	-0,365
Na_2O - MnO - P_2O_5 $\text{Na}_2\text{O} - \text{MnO} = 1 : 1$	10	-0,380
	25	-0,375
	50	-0,373
	100	-0,370
MnO - P_2O_5 - SiO_2 $\text{SiO}_2 = 3 \text{ mol.}\%$	10	-0,370
	25	-0,368
	50	-0,358
	100	-0,340
MnO - P_2O_5 - SiO_2 $\text{SiO}_2 = 8,5 \text{ mol.}\%$	10	-0,390
	25	-0,355
	50	-0,350
	100	-0,345

results in metal passivation. The layers of protective film hamper depolarizer and metal ions diffusion.

Thus, in 0.1 M potassium nitrate solution studied the substances show inhibitor properties. Under dynamic and static conditions the degree of polyphosphate glass protection achieves $\geq 80\%$.

Silicopolyphosphate corrosion inhibitors studied in this research have been subjected to industrial tests in the system of the oil stratum pressure up keeping at the Kumkol oil field [21]. Tests showed high efficiency of metal protection. The same inhibitors were tested in the system of electrode head holders cooling in the electric furnace for yellow phosphorus production at "TARAZ-phosphorus" joint stock Company.

The tested polyphosphates can be used for steel equipment protection in the systems of return water-supply and cooling systems.

The polyphosphate systems need further investigation, it seems reasonable to study the dependence of the protective action of polyphosphate upon different factors and features of the influence over kinetics of electrode processes.

References

1. S. Konstantinov. Inventor and Rationalizer, 4:20, 1986.
2. V.I. Kapralova, et al. Application of silicopolyphosphate inhibitors for protection of water-supply systems, // Petroleum and gas, 1999, № 2, P. 114-120.
3. Lo Zhu, Hu Rong // Proc. Conf. 28: Corros. - Tax Forever, Perts. 21-25 Nov., 1998. Vol.1. - Leederville, 1988. - P. 4/3. 1-4/3. 8.
4. Yashiro H., Kami H., Kosaks T., Tanno K. // Werkst. Und Korros. - 1994 - 45, #1. P. R10.
5. B.L. Geizin, I.V. Strizhevsky, F.A. Shevelev. Corrosion and protection of municipal water-pipes. M., 1979. P.398.
6. D.S. Robinson. Corrosion inhibitors. - M., 1983. P.271.
7. G.B. Hatch, O. Rice. Threshold treatment of water systems prevention of corrosion and scale formation by means of glass-like phosphate, Ind. Eng. Chem; 37, #8, 710-715 (1945).
8. G.B. Hatch, O. Rice. Prevention of corrosion by means threshold water treatment—factors effecting formation of protective films on a surface of steel in water treated with glass-like phosphates, Ind. Eng. Chem, 32, 1572-1579 (1940).
9. I.E. Apeltsin, E.F. Zolotova. Application of low soluble metaphosphates for water treatment // Water-supply and satinary facilities, №4, 34-36 (1959).
10. I.C. Lamb, R. Eliassen . Mechanism of Corrosion Inhibition by the metaphosphate sodium // I. Am. Water Works Ass. - 1954 - 46. 445-460.
11. I.B. Sumcden, Z.Szklarska - Smialonska . The properties of the Films Formed on Iron exposed to Suhibition Solution // Corrosion. 1978. - 345.169 - 176.
12. S. Horner, E. Plifke. Corrosion inhibitor // Werkst und Rorrosion. - 1985. - 36, 12.545 - 553.
13. R. B. Meaus . The Electrochemical Action of Inhibitors // Corrosion. - 1985. - 11, 8.50 - 52.
14. G. B. Hatch, Formation of protective film by glass-like phosphates, Ind. Eng. Chem., 44, 1775 - 1780 (1952).
15. D.A. Yakovleva, R.M. Bikchektaev et.al. . Corrosion protection and increase in service life of heat-exchange equipment in cooling systems of petroleum refineries and petroleum-chemical plants. - 1985. - p. 38.
16. A.B. Bekturov, D.Z. Serazetdinov, V.A. Urikh. Physicochemical basis for polyphosphate manure/ fertilizers production. Alma-Ata, 1979. - p. 248.
17. L.I. Antropov . Theoretical electrochemistry. M.: Higher School, 1984. p. 519.
18. B.B. Damaskin, O.A. Petriy , B.I. Poglovchenco . Electrochemistry Practicum . M.: Higher School, 1991., p. 247.
19. L.I. Antropov. Theoretical electrochemistry. M.: Higher School, 1969, p. 474.
20. O.M. Agres . Alternative technique of graphical determination of corrosion inhibitor efficiency basing on polarization measurements. – Journ. Appl. Chem., 1992, v.65, № 3, p. 567-570.
21. O. Yu. Fishbbein, V.I. Kapralova . et al . Inhibiting compositions on the basis of manganese polyphosphates. // Petroleum and gas. 1999 №1.P. 55-57.

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