20. Torabinejad, V. Electrodeposition of Ni-Fe alloys, composites, and nano coatings–A review [Text] / V. Torabinejad, M. Aliofkhazraei, S. Assareh, M. H. Allahyarzadeh, A. S. Rouhaghdam // Journal of Alloys and Compounds. – 2017. – Vol. 691. – P. 841–859. doi: 10.1016/j.jallcom.2016.08.329
21. Fazli, S. Effect of plating time on electrodeposition of thick nanocrystalline permalloy foils [Text] / S. Fazli, M. E. Bahrololoom // Transactions of the IMF. – 2016. – Vol. 94, Issue 2. – P. 92–98. doi: 10.1080/00202967.2015.1122918
22. Sekar, R. Effect of sulphonic acids on electrodeposition of nickel and its structural and corrosion behaviour [Text] / R. Sekar, S. Jayakrishnan // Transactions of the IMF. – 2012. – Vol. 90, Issue 6. – P. 324–329. doi: 10.1179/0020296712z.00000000032
23. Danilov, F. I. Electroplating of Ni-Fe alloys from methanesulfonate electrolytes [Text] / F. I. Danilov, I. V. Sknar, Yu. E. Sknar // Russian Journal of Electrochemistry. – 2014. – Vol. 50, Issue 3. – P. 293–296. doi: 10.1134/s1023193514030045
24. Sknar, Yu. E. Influence of Methylsulfonate Anions on the Structure of Electrolytic Cobalt Coatings [Text] / Yu. E. Sknar, N. V. Amirulloeva, I. V. Sknar, F. I. Danylov // Materials Science. – 2016. – Vol. 52, Issue 3. – P. 396–401. doi: 10.1007/s11003-016-9970-9
25. Danilov, F. I. Structure and properties of Ni–Co alloys electrodeposited from methanesulfonate electrolytes [Text] / F. I. Danilov, V. N. Samofalov, I. V. Sknar, Yu. E. Sknar, A. S. Baskevich, I. G. Tkach // Protection of Metals and Physical Chemistry of Surfaces. – 2015. – Vol. 51, Issue 5. – P. 812–816. doi: 10.1134/s2070205115050068

UDC 547.118: 547.438: 627.257
DOI: 10.15587/1729-4061.2017.106974

# STUDY OF EFFECTIVENESS OF HEAVY METALS IONS AS THE INHIBITORS OF STEEL CORROSION

**T. Shabliy**
Doctor of Technical Science, Professor*
E-mail: dsts1@ukr.net
**J. Nosachova**
PhD, Associate Professor*
E-mail: j.nosachova@gmail.com
**Y. Radovenchik**
PhD, Associate Professor*
E-mail: r.yar@ukr.net
**V. Vember**
PhD, Associate Professor *
E-mail: vvember@gmail.com
*Department of Ecology and Technology of Plant Polymers
National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

***Досліджено інгібуючі властивості відомих антискалантів – оксиетилендендифосфонової та нітрилотриметилфосфонової кислот в нейтральному водному середовищі в різних температурних режимах. Визначено здатність йонів d-металів сумісно з фосфоновими кислотами створювати захисний поляризаційний шар на поверхні металу. Встановлено ступінь захисту від корозії сталі при температурах 30 °С та 50 °С з даними композиціями***

***Ключові слова: корозія, інгібітори, важкі метали, стабілізатори накипоутворення, замкнуті водоциркуляційні системи***

***Исследованы ингибирующие свойства известных антискалантов – оксиэтилендендифосфоновой и нитрилотриметилфосфоновой кислот в нейтральной водной среде в различных температурных режимах. Определены способности ионов d-металлов совместно с фосфоновыми кислотами создавать защитный поляризационный слой на поверхности металла. Установлена степень защиты от коррозии стали при температурах 30 °С и 50 °С данным композициями***

***Ключевые слова: коррозия, ингибиторы, тяжелые металлы, стабилизаторы накипеобразования, замкнутые водоциркуляционнные системы***

## 1. Introduction

Corrosion causes significant economic losses as it leads to the failure of pipelines, parts of machines, boilers and other metal products. In addition, as a result of this process, equipment breaks down, damaged equipment can lead to an accident, or even a disaster that could affect people and environment. One of the major problems caused by corrosion is the loss of world metal reserves, which in turn leads to significant environmental damage inflicted by steel production.

A large number of industrial enterprises in Ukraine use water from natural sources. A significant amount of water is used by the enterprises of oil refining and machine building industry. Most of the water, about 80 %, in these industries is used for reversible cooling systems. The amount of wastewater discharged from these systems to water reservoirs remains significant and makes up about 8–30 % of the system's volume. This is mostly linked tp the sedimentation in water circulation systems and corrosion processes.

Based on the above, it is possible to say that the problem of protecting metal structures from corrosion processes is a relevant task. One of the directions of the protection of closed watercircular systems from corrosion is the use of ions of heavy metals and inhibitors of scale formation.

## 2. Literature review and problem statement

At present, there is a lack of quality water for the needs of inhabitants and industry needs in some regions of Ukraine [1]. Methods of ion-exchange desalination of industrial waters solve the problem of scale formation in cooling systems, but the problem of anti-corrosion protection is not considered.

At industrial enterprises, with the growth of production, volumes of water use are also increasing, and as a result, various difficultly soluble sedimentations appear on the surface of metal pipelines, which accelerate the rate of corrosional destruction of equipment. In paper [2], the composition and nature of sedimentation on the surface of metal pipelines is studied but the authors do not consider mechanisms of the influence of phosphonic acids on the mechanism of corrosion.

Closed water supply systems at the production facilities allow reusing industrial waste waters, and this significantly saves the use of fresh water and considerably reduces the discharge of sewage into the environment. The introduction of closed water systems is currently considered to be the only rational solution for the efficient use of water in industry [3, 4]. In order to achieve this goal, various kinds of water losses, which may occur as a result of corrosion of equipment and pipelines, should be avoided.

Inhibitors of corrosion of metals in aqueous media are represented by very diverse substances. The choice of inhibitor type depends on each specific type of water use and the cost of the proposed measures.

Inorganic inhibitors include phosphates, chromates, bichromates, nitrates, polyphosphates, silicates. Phosphate compounds are very effective [5] as inhibitors of corrosion. However, their influence on the processes of scale formation is rather insignificant. Organic inhibitors include amines, organic acids and salts, mercaptans et al. Most of light inhibitors are mixtures of compositions of organic substances or synthesized organic substances [6]. Phosphonic acids are well-known and quite effective stabilizers for the formation of scale [7], but their effect on anti-corrosion protection at elevated temperatures is negligible. The issues of selection of conditions and concentrations of their use as corrosion inhibitors remain unsolved.

Authors of [8] propose to use imidazoline containing substances, which show anti-corrosion and antioxidant properties, as corrosive inhibitors. However, the substances considered do not possess effective stabilizing properties.

Articles [9, 10] investigate the efficiency of aminophosphonic acids, which are almost not used in Ukrainian industry.

Some cations contribute to the reduction of the rate of corrosion, these are typically the cations of d-metals [11]. Due to d-orbitals, ions of metals are joined by oxygen, which creates an oxide film on the surface of steel, which acts as a barrier to oxygen diffusion. However, the authors do not consider the entire spectrum of d-metals, as well as protective action at elevated temperatures. Therefore, the study of the influence of heavy metal ions as corrosion inhibitors is an important task to reduce the degree of equipment corrosion in closed water supply systems.

In order to increase anti-scale and anti-corrosion effect, compositions based on organic compounds and ions of heavy metals, mainly zinc ions, have recently been used [12].

In paper [13], results of examining the inhibitory properties of EDTA and zinc ions compositions are presented, but authors applied an aggressive environment highly mineralized sea water, which is not used in water-reversible industrial cooling systems.

In articles [14, 15], research into efficiency of phosphonic acids and zinc ions was carried out in a neutral aqueous environment, but these articles do not cover issues of changes in the efficiency of these compositions if temperature is increased and if conditions of hydrodynamic regime are changed.

Thus, the issues regarding the possibility of using heavy metal ions as corrosion inhibitors remain unresolved, as well as the issues related to behavior of composites in aqueous environment depending on a number of factors (elevated temperatures, correlation between components, composition of water, etc.).

## 3. Research goal and objectives

The goal of present work was to determine a capability of heavy metal ions, individually and in compositions, to inhibit the process of steel corrosion under different temperature conditions.

To achieve this goal, the following tasks were set:

– to determine the influence of heavy metal ions on the process of steel corrosion, depending on the dose of metals, aeration conditions and temperature;

– to determine steel corrosion in water using oxyethylidenodiphosphonic and nitrilotrimethylphosphonic acids depending on the dose of inhibitor and temperature regimes;

– to evaluate the influence of phosphonic acids on the processes of steel corrosion in the presence of heavy metal ions, depending on the concentrations of inhibitory additives, aeration conditions and temperature.

## 4. Materials and methods for examining the influence of ions of heavy metals, physical conditions on the rate of steel corrosion St 20

### 4. 1. Materials and equipment used in the experiment

We used tap water (Kyiv, Ukraine) as a corrosive environment. This water is characterized by a low concentration of chlorides and sulfates, other indicators do not exceed the norms [16]. To some extent, anions can affect the process of corrosion [17], which is why this fact was taken into account when processing the results. Characteristics of tap water iare given in Table 1.

The following salts of heavy and nonferrous metals were used for the preparation of working solutions: $ZnSO_4{\cdot}7H_2O$, $PbCl_2$, $Pb(NO_3)_2$, $MnCl_2{\cdot}4H_2O$, $Cr_2(SO_4)_3{\cdot}6\ H_2O$, $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}7H_2O$, $CdSO_4{\cdot}7H_2O$, $CoNO_3{\cdot}7H_2O$, $Al(SO_4)_3{\cdot}18H_2O$. We examined the effect of the given ions on the process of corrosion at room temperature, as well as at 30–50 °C. In addition, the effect of these substances on the reduction of the rate of corrosion in compositions with known stabilizers of scale formation with oxyethylidendiphosphonic acid (OEDPhA) and nitrilotrimethylphosphonic acid (NTMPhA) was studied.

Table 1

Characteristics of Kyiv tap water

| Measure | Value |
|---|---|
| $Ca^{2+}$ ions content, mg-eq/dm$^3$ | 3.01–3.55 |
| $Mg^{2+}$ ions content, mg-ek/dm$^3$ | 0.8–1.2 |
| pH | 6.85–7.39 |
| Alkalinity, mg-eq/dm$^3$ | 3.05–5.24 |
| Hardness, mg-eq/dm$^3$ | 3.09–5.20 |
| Sulphate content, mg-eq/dm$^3$ | 15–47 |
| Chloride content, mg-eq/dm$^3$ | 12–39 |

The evaluation of corrosion by the method of polarization resistance was carried out using the indicator of polarization resistance P5126 and the two-electrode sensor from the corrosion-indicator unit UK-2 [18]. The sensor made of steel 20 was installed in a glass of 150 cm$^3$, and at a certain time intervals, the polarization resistance of $Rp$ was measured using the P5126 indicator. During the experiment, by integrating the area under the curve, which was built in the coordinates $Rp - t$ (time), and by division of the resulting total area by the total time, the average value of $Rp_{cr}$ was determined. The magnitude of polarization resistance is inversely proportional to the rate of steel corrosion.

The coefficient of reduction of corrosion rate ($j$) was determined by the ratio of the average polarization resistance ($Rp_{cp}$) of the examined solution to the average polarization resistance ($Rp_{cp}$) of the starting solution:

$$j = \frac{Rp_{cp}}{Rp_{cp}^{0}}. \quad (1)$$

The degree of corrosion protection ($Z$, %) was calculated based on the coefficient of reduction of corrosion rate, using formula:

$$Z = \left(1 - \frac{1}{j}\right) \cdot 100. \quad (2)$$

The determination of the effectiveness of corrosion inhibitors was carried out under static conditions and when the solution was agitated with a magnetic mixer at 400 rpm. Duration of the experiments was 4 hours. The concentration of inhibitors was 1–10 mg/dm$^3$. The measurement results were obtained by averaging the data from 4 parallel experiments.

## 5. Results of studies on the evaluation of effect of reagents on the processes of steel corrosion

Salts of heavy metals were used as corrosion inhibitors. Table 2 gives the dependence of polarization resistance of St 20 on the dose and type of inhibitors in stationary and mobile environment at 20 °C. Table 2 also presents results of calculations of the coefficients of reduction of corrosion rate ($j$) and the degree of protection against corrosion ($Z$, %) by ions of heavy metals.

Polarization resistance and corrosion rate depend on many factors, namely, the composition of water, aeration conditions, ambient temperature. In the absence of agitation and inhibitors, polarization resistance makes up 0.307 kΩ, while at stirring it is 0.173 kΩ. This is explained by the fact that during agitation of the medium, oxygen diffusion accelerates to the surface of the metal, which increases the rate of corrosion.

Table 2

Effect of the concentration of heavy metal ions on steel corrosion of steel St 20 in tap water during agitation (I) and under static conditions (II) at 20 °C

| Inhibitor | Dose, mg/dm$^3$ | $Rp_{cp}$, kΩ |  | $J$ |  | $Z$, % |  |
|---|---|---|---|---|---|---|---|
|  |  | I | II | I | II | I | II |
| tap water | – | 0.173 | 0.307 | – | – | – | – |
| $Zn^{2+}$ | 1 | 0.778 | 0.261 | 4.50 | 0.85 | 77 | 0 |
|  | 2 | 0.789 | 0.359 | 4.56 | 1.17 | 78 | 14 |
|  | 5 | 1.802 | 0.469 | 10.42 | 1.53 | 90 | 34 |
| $Pb^{2+}$ | 1 | 0.269 | 0.197 | 1.55 | 0.64 | 35 | 0 |
|  | 2 | 0.390 | 0.205 | 2.27 | 0.67 | 56 | 0 |
|  | 5 | 1.650 | 0.233 | 9.55 | 0.76 | 89 | 0 |
| $Cu^{2+}$ | 1 | 0.091 | 0.087 | 0.53 | 0.28 | 0 | 0 |
|  | 2 | 0.226 | 0.198 | 1.30 | 0.65 | 23 | 0 |
|  | 5 | 0.283 | 0.253 | 1.64 | 0.82 | 40 | 0 |
| $Ni^{2+}$ | 1 | 0.121 | 0.154 | 0.70 | 0.50 | 0 | 0 |
|  | 2 | 0.173 | 0.197 | 1.00 | 0.64 | 0.3 | 0 |
|  | 5 | 0.228 | 0.299 | 1.55 | 0.97 | 24 | 0 |
| $Cd^{2+}$ | 1 | 0.223 | 0.140 | 1.29 | 0.46 | 22 | 0 |
|  | 2 | 0.243 | 0.183 | 1.41 | 0.57 | 28 | 0 |
|  | 5 | 0.311 | 0.254 | 1.85 | 0.83 | 44 | 0 |
| $Co^{2+}$ | 1 | 0.162 | 0.273 | 1.22 | 0.89 | 5 | 0 |
|  | 2 | 0.169 | 0.308 | 1.28 | 1.00 | 8 | 0.3 |
|  | 5 | 0.192 | 0.327 | 1.45 | 1.07 | 20 | 6 |
| $Al^{3+}$ | 1 | 0.126 | 0.195 | 0.73 | 0.64 | 0 | 0 |
|  | 2 | 0.207 | 0.354 | 1.20 | 1.15 | 17 | 13 |
|  | 5 | 0.412 | 0.405 | 2.38 | 1.32 | 58 | 24 |
| $Mn^{2+}$ | 1 | 0.093 | 0.159 | 0.54 | 0.52 | 0 | 0 |
|  | 2 | 0.147 | 0.267 | 0.85 | 0.57 | 0 | 0 |
|  | 5 | 0.445 | 0.310 | 2.57 | 1.01 | 61 | 1 |
| $Cr^{3+}$ | 1 | 0.321 | 0.305 | 1.85 | 0.99 | 46 | 0 |
|  | 2 | 1.040 | 0.345 | 5.99 | 1.12 | 83 | 11 |
|  | 5 | 1.801 | 0.416 | 10.5 | 1.36 | 91 | 26 |

It is known that ions of d-metals are able to stabilize an oxide film on a metal surface, which hydrophobizes metal and significantly slows down the process of corrosion [8]. Ions of iron are easily oxidized to $Fe^{3+}$ and hydrolyzed under such conditions, and therefore have little effect on the stability of the oxygen film.

It should be noted that under static conditions, with insufficient aeration of the metal surface, due to the slow diffusion of oxygen, the hydrophobic oxygen film is not formed in almost all cases. Therefore, in most cases, no reduction in the rate of corrosion was observed.

A more pronounced tendency is the passivation of metal under dynamic conditions. When stirring water in the absence of ions of used metals, the hydrophobic oxygen film is unstable, which is why the rate of corrosion is significant. In the presence of metal ions with enough diffusion of oxygen to the surface of steel during agitation, a hydrophobic (passivative) oxygen film is formed, this helps to reduce the rate of corrosion, which is characterized by an increase in polarization resistance. More to the point, agitation also helps to improve the diffusion of metal ions to the surface of steel, which in turn leads to an increase in the stability of passivation film on the metal surface.

Among the investigated metals, the best results were obtained in case of using zinc ions ($Zn^{2+}$), lead ($Pb^{2+}$) and chromium ($Cr^{3+}$). Some metals ($Cu^{2+}$, $Co^{2+}$, $Al^{3+}$, $Mn^{2+}$, $Ni^{2+}$) at low concentrations and under static conditions are corrosion stimulators. In most cases this can be explained by an increase in the content of anions Cl- and $SO_4^{2-}$ when salts are dissolved in water, as well as by the acidification of water by hydrolysis of metal salts. In case when copper is used we can take into account the oxidizing capacity of $Cu^{2+}$ ions. However, all these impacts are possible only in the absence of a stable oxygen film on the surface of steel. If the concentration of metal ions is sufficient, under the conditions of effective diffusion of oxygen to the surface of metal, the formation of an oxygen hydrophobic film on the surface of steel occurs. And in almost all cases it provides a reduction in the rate of steel corrosion. At the same time, for $Zn^{2+}$, $Pb^{2+}$ and $Cr^{3+}$ the degree of corrosion protection increases to 89–90 %, for other metals the degree of protection reaches 20–60 %.

Interestingly, aluminum ions, which do not belong to d-metals and should not form complexes with oxygen, at a concentration of 5 mg/dm$^3$ provide a degree of protection of 58 %. Obviously, these ions, similar to the ions of hardness, also contribute to some extent to the formation of a passivation film on the surface of steel.

A significant amount of water in the industry is used in cooling systems. In these systems water is heated to a temperature of 30–50 °C, this has a large effect on the rate of electrochemical corrosion of metals and the degree of scale deposition. This is due to changes in the strain of electrochemical processes, the rate of diffusion and the solubility of oxygen in water, and other factors. In the vast majority of cases, the dependence of the rate of corrosion on temperature is exponential in character.

As can be seen from Fig. 1, at a temperature of 10 °C, the value of the mean polarization resistance is actually the highest and reaches 0.36 kΩ, but with an increase in temperature this indicator falls and decreases to a value of 0.07 kΩ at 50 °C. In general, this is due to the destabilization of oxygen passivation film, and to the growth of the oxidation rate of steel when temperature increases.

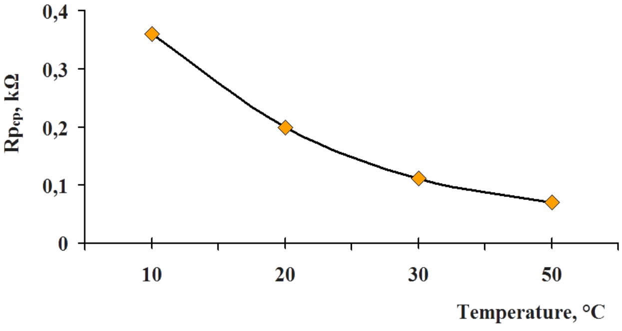

Fig. 1. Dependence of the mean polarization resistance on water temperature

In addition to corrosion in cooling systems, there is also a problem of scale formation in heat exchangers. Therefore, the metals that demonstrated the best results for corrosion protection were tested in compositions with known inhibitors of scale formation – OEDPhA and NTMPhA.

Such hydrophilic organic compounds as OEDPhA and NTMPhA belong to the inhibitors of passivation. The formation of soluble complexes and three-dimensional reticulate layers, which to some extent stabilize passivation oxygen film, which helps to protect metals from corrosion [7], occurs during the interaction of complexons with the surface of metals. Results of using OEDPhA and NTMPhA are shown in Fig. 2, 3.

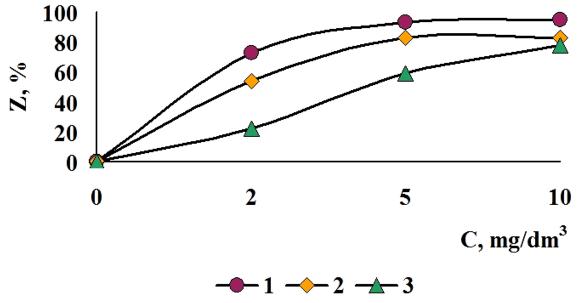

Fig. 2. Dependence of the degree of protection of steel from corrosion in aqueous medium on the concentration of OEDPhA at different temperatures:
1 – 20 °C, 2 – 30 °C, 3 – 50 °C

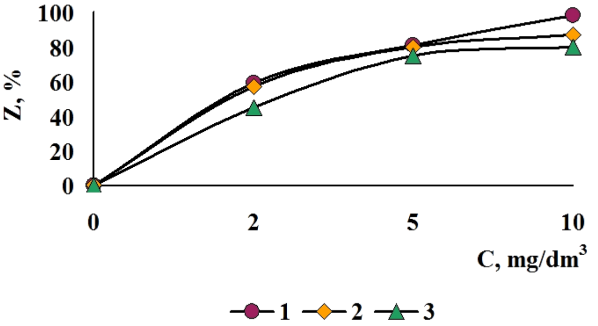

Fig. 3. Dependence of the degree of protection of steel from corrosion in aqueous environment on the concentration of NTMPhA at different temperatures:
1 – 20 °C, 2 – 30 °C, 3 – 50 °C

When temperature of the medium increases, the calcining stabilizer OEDPhA forms complexes with iron ions [7]. The products of the cathode reaction are accumulated in the near-electrode layer, which leads to the slowdown of corrosion processes.

For the best results, OEDPhA and NTMPhA were used in the composition with heavy metal ions.

It was established that the introduction of the complex OEDPhA+$Zn^{2+}$ or NTMPhA+$Zn^{2+}$ reduces the corrosive water aggressiveness to a greater extent than the introduction of $Zn^{2+}$ ion itself. The protective effect of these compounds is explained by the formation of difficultly soluble iron and zinc complexes with OEDPhA or NTMPhA on the surface of metal, as well as by the precipitation of $Zn(OH)_2$.

This tendency is observed for the rest of the examined ions. Results are given in Table 3.

Table 3 shows that all metals at a concentration of 5 mg/dm$^3$ have a high degree of protection. This allows using the composition of these substances in industry as an inhibitor of corrosion and a stabilizer of scale formation.

Table 3

Effect of heavy metal ions in the composition of OEDPhA and NTMPhA on the reduction of corrosion rate in Kyiv tap water at agitation (*t*=20 °C)

| Inhibitor | Dose, mg/dm$^3$ | $Rp_{cp}$, kΩ | *J* | *Z*, % |
|---|---|---|---|---|
| tap water | – | 0,173 | – | – |
| $Cd^{2+}$ OEDPhA | 1;5 | 1.04 | 8.60 | 88 |
| | 2;5 | 1.087 | 9.00 | 89 |
| | 5;5 | 1.080 | 9.00 | 89 |
| $Zn^{2+}$; OEDPhA | 1;5 | 0.744 | 4.30 | 77 |
| | 2;5 | 1.080 | 6.22 | 84 |
| | 5;5 | 2.041 | 11.81 | 92 |
| $Pb^{2+}$ OEDPhA | 1;5 | 0.240 | 1.39 | 28 |
| | 2;5 | 0.271 | 1.57 | 36 |
| | 5;5 | 0.841 | 4.88 | 80 |
| $Cr^{3+}$ OEDPhA | 1;5 | 1.600 | 9.30 | 89 |
| | 2;5 | 2.671 | 15.40 | 94 |
| | 5;5 | 2.901 | 16.91 | 94 |
| $Al^{3+}$ OEDPhA | 1;5 | 0.159 | 0.93 | 0 |
| | 2;5 | 0.326 | 1.904 | 48 |
| | 5;5 | 1.045 | 6.11 | 84 |
| $Mn^{2+}$ OEDPhA | 1;5 | 0.450 | 2.60 | 61 |
| | 2;5 | 0.901 | 5.21 | 81 |
| | 5;5 | 1.571 | 9.08 | 89 |
| $Cd^{2+}$ NTMPhA | 1;5 | 0.260 | 1.50 | 33 |
| | 2;5 | 1.260 | 7.28 | 86 |
| | 5;5 | 1.991 | 11.5 | 91 |
| $Zn^{2+}$ NTMPhA | 1;5 | 0.242 | 1.40 | 29 |
| | 2;5 | 0.931 | 5.37 | 81 |
| | 5;5 | 1.860 | 10.75 | 91 |
| $Pb^{2+}$ NTMPhA | 1;5 | 0.267 | 1.54 | 35 |
| | 2;5 | 0.602 | 3.47 | 71 |
| | 5;5 | 1.400 | 8.09 | 87 |
| $Cr^{3+}$ NTMPhA | 1;5 | 0.420 | 2.43 | 59 |
| | 2;5 | 0.741 | 4.28 | 77 |
| | 5;5 | 1.101 | 6.35 | 84 |
| $Al^{3+}$ NTMPhA | 1;5 | 0.160 | 0.92 | 0 |
| | 2;5 | 0.266 | 1.53 | 34 |
| | 5;5 | 0.272 | 1.57 | 36 |
| $Mn^{2+}$ NTMPhA | 1;5 | 0.361 | 2.08 | 52 |
| | 2;5 | 0.451 | 2.60 | 62 |
| | 5;5 | 1.430 | 8.26 | 88 |

Studies were also carried out on the influence of temperature on the process of corrosion in the case of using inhibitors. The best results were shown at temperatures of 20 °C by the ions of $Zn^{2+}$, $Pb^{2+}$, $Cr^{3+}$, which is why it was decided to investigate the efficiency of these ions at elevated temperatures, namely 30 °C and 50 °C.

The studies have shown that the process of deceleration of corrosion by means of heavy metal ions at a temperature of 30 °C and 50 °C degrades considerably due to a decrease in the solubility of oxygen in water when the temperature rises, which prevents the formation of a stable passivation film on the surface of steel (Table 4, 5).

The situation changes considerably during complex application of metal ions and phosphonic acids. First of all, phosphonates bind well to corroded metal and to metal ions in solution [19–21]. The resulting three-dimensional structures retain oxygen well, which contributes to the passivation of metal surface.

Table 4

Effect of inhibitors on the reduction of rate of the St 20 steel corrosion in tap water at agitation (*t*=30 °C)

| Inhibitor | Dose, mg/dm$^3$ | $Rp_{cp}$, kΩ | *J* | *Z*, % |
|---|---|---|---|---|
| tap water | – | 0.108 | – | – |
| $Cr^{3+}$ | 1 | 0.070 | 0.69 | 0 |
| | 2 | 0.124 | 1.15 | 13 |
| | 5 | 0.151 | 1.40 | 29 |
| $Zn^{2+}$ | 1 | 0.066 | 0.61 | 0 |
| | 2 | 0.090 | 0.86 | 0 |
| | 5 | 0.139 | 1.29 | 22 |
| $Pb^{2+}$ | 1 | 0.066 | 0.60 | 0 |
| | 2 | 0.116 | 1.07 | 7 |
| | 5 | 0.143 | 1.32 | 25 |
| $Pb^{2+}$ OEDPhA | 1;5 | 0.101 | 0.93 | 0 |
| | 2;5 | 0.135 | 1.25 | 20 |
| | 5;5 | 0.325 | 3.00 | 67 |
| $Pb^{2+}$ NTMPhA | 1;5 | 0.180 | 1.71 | 40 |
| | 2;5 | 0.207 | 1.90 | 48 |
| | 5;5 | 1.070 | 9.91 | 90 |
| $Zn^{2+}$ OEDPhA | 1;5 | 0.259 | 2.40 | 58 |
| | 2;5 | 1.301 | 12.03 | 91 |
| | 5;5 | 1.502 | 13.90 | 93 |
| $Zn^{2+}$ NTMPhA | 1;5 | 0.183 | 1.69 | 40 |
| | 2;5 | 0.245 | 2.27 | 55 |
| | 5;5 | 0.335 | 3.10 | 68 |
| $Cr^{3+}$ OEDPhA | 1;5 | 0.440 | 4.07 | 75 |
| | 2;5 | 1.030 | 9.54 | 89 |
| | 5;5 | 1.071 | 8.86 | 90 |
| $Cr^{3+}$ NTMPhA | 1;5 | 0.602 | 5.55 | 82 |
| | 2;5 | 1.120 | 10.46 | 90 |
| | 5;5 | 2.253 | 20,80 | 95 |

Table 5

Effect of inhibitors on the reduction of rate of the St 20 steel corrosion in tap water at agitation ($t$=50 °C)

| Inhibitor | Dose, mg/dm$^3$ | $Rp_{cp}$, kΩ | $J$ | $Z$, % |
|---|---|---|---|---|
| tap water | – | 0.070 | – | – |
| $Cr^{3+}$ | 1 | 0.053 | 0.76 | 0 |
| | 2 | 0.069 | 0.99 | 0 |
| | 5 | 0.078 | 1.12 | 11 |
| $Zn^{2+}$ | 1 | 0.065 | 0.92 | 0 |
| | 2 | 0.066 | 0.94 | 0 |
| | 5 | 0.113 | 1.61 | 38 |
| $Pb^{2+}$ | 1 | 0.066 | 0.94 | 0 |
| | 2 | 0.077 | 1.10 | 10 |
| | 5 | 0.080 | 1.14 | 13 |
| $Pb^{2+}$ OEDPhA | 1;5 | 0.426 | 6.08 | 84 |
| | 2;5 | 0.480 | 6.86 | 85 |
| | 5;5 | 0.862 | 12.31 | 92 |
| $Pb^{2+}$ NTMPhA | 1;5 | 0.257 | 3.67 | 73 |
| | 2;5 | 0.807 | 11.52 | 91 |
| | 5;5 | 0.922 | 13.17 | 92 |
| $Zn^{2+}$ OEDPhA | 1;5 | 0.117 | 1.67 | 40 |
| | 2;5 | 0.287 | 4.10 | 76 |
| | 5;5 | 0.348 | 4.97 | 80 |
| $Zn^{2+}$ NTMPhA | 1;5 | 0.153 | 2.19 | 54 |
| | 2;5 | 0.964 | 13.77 | 92 |
| | 5;5 | 0.997 | 14.24 | 93 |
| $Cr^{3+}$ OEDPhA | 1;5 | 0.294 | 4.20 | 76 |
| | 2;5 | 0.447 | 6.39 | 84 |
| | 5;5 | 0.633 | 9.04 | 89 |
| $Cr^{3+}$ NTMPhA | 1;5 | 0.139 | 1.98 | 49 |
| | 2;5 | 0.171 | 2.44 | 59 |
| | 5;5 | 1.120 | 16.01 | 94 |

In the study of corrosion processes at 50 °C it was found that the metal ions themselves protect steel from corrosion worse than at 30 °C and 20 °C. However, when adding OEDPhA and NTMPhA to them, the degree of protection against corrosion increases as a result of the formation of strong complex three-dimensional structures, which, even at insignificant concentrations of oxygen, reliably passivate the surface of steel.

## 6. Discussion of results of examining the effect of the dose and inhibitor type, physical conditions on the course of corrosion processes

As a result of the studies conducted, the capability of all ions of d-metals to slow down the processes of corrosion in neutral aqueous environment was explored. It is shown that metal ions at sufficient aeration of water are able to stabilize the passivation oxygen film on the surface of steel, which helps to protect it from corrosion. High efficiency in protecting steel from corrosion under conditions of effective aeration is provided by ions of d-metals – zinc, chromium and lead. However, at sufficient concentrations of ions of metals, at appropriate concentrations of oxygen, passivation of corrosive metal is possible even when using aluminum salts as an inhibitor.

Stability of the passivation film decreases with an increase in temperature, which is due to a decrease in the concentration of oxygen in water. In the case of using heavy metal ions only, a sharp decrease in the degree of protection against corrosion by increasing the temperature due to destabilization of the passivation film is observed.

Protective effect increases significantly with the use of metal ions in compositions with phosphonic acids, which are passivation-type corrosion inhibitors.

Phosphonic acids form complex compounds with ions on the surface of steel, which helps to concentrate these substances on the scaling surface. In addition, phosphonic acids are capable of forming complex compounds with d-metal ions, which, in turn, effectively bind with oxygen ions. This contributes to the formation of a solid passivation film on the surface of steel and effective protection against corrosion. As the temperature increases, only a slight decrease in the degree of protection against corrosion is observed.

The paper considers tdependence of corrosion inhibiting processes on the dose of reagents, temperature and aeration regimes. However, there is a fairly wide range of substances of different nature that can be used as passivation inhibitors. In addition, depending on the purpose of industrial water, enterprises use higher temperatures, and other saline water compositions. It is planned in the future to carry out research taking into account such parameters and characteristics of production requirements to the quality of industrial water.

Results of the research performed could be used as recommendations for measures to prevent the destruction of equipment as a result of corrosion. The obtained data will be of interest in the transition of industrial water supply from reversible system to the closed systems.

## 7. Conclusions

1. The influence of ions of d-metals on the processes of corrosion in a neutral aqueous environment has been determined. It is shown that zinc, chromium and lead ions in concentrations of 2–5 mg/dm$^3$ are the most effective due to the creation of a passivation oxygen film at room temperature and under conditions of high aeration. There is a significant decrease in the inhibitory properties of ions of d-metals under conditions of lowering the concentration of oxygen and accelerating the course of electrochemical reactions. For example, for zinc ions, the degree of protection decreases from 89–91 % at 20 °C to 11–38 % at 50 °C.
2. It was determined that oxyethylidenidiphosphonic and nitrilotrimethylphosphonic acids stabilize the passivation oxygen film, providing a degree of corrosion protection at 95–98 % at acid doses of 10 mg/dm$^3$. However, with an increase in the temperature of aqueous medium from 20 °C to 50 °C, the protective effect is reduced from 93 % to 59 % and from 81 % to 75 % for OEDPhA and NTMPhA, respectively, at a dose of 5 mg/dm$^3$.

3. In order to increase efficiency of protection against corrosion of closed water-circulation systems, it is proposed to use as inhibitors of corrosion of steel in water a composition of heavy metal ions together with phosphonic acids. Due to the formation of three-dimensional complexes of phosphonic acids with metal ions and corroded iron, one observes a better retention of oxygen and creation a stable oxygen film on the corroded surface. Due to the joint application of OEDPhA/NTMPhA and Zn/Pb/Cr ions, the degree of protection of steel St20 increases to 90–94 % when zinc ions are used with phosphonic acids at 50 °C.

## References

1. Trus, I. N. Razdelenie hloridov i sul'fatov pri ionoobmennom obessolivanii vody [Text] / I. N. Trus, N. D. Gomelya, T. A. Shabliy // Metallurgicheskaya i gornorudnaya promyshlennost'. – 2014. – Issue 5. – P. 119–122.
2. Chichenin, V. V. Study of corrosion rate and accumulation of deposits under circulating water concentration in bench experiments [Text] / V. V. Chichenin, V. A. Kishnevskiy, A. S. Gricaenko, V. G. Ahrameev, I. D. Shulyak // Eastern-European Journal of Enterprise Technologies. – 2015. – Vol. 5, Issue 8 (77). – P. 14–20. doi: 10.15587/1729-4061.2015.51205
3. Pilipenko, A. The study of inhibiting structural material corrosion in water recycling systems by sodium hydroxide [Text] / A. Pilipenko, H. Pancheva, A. Reznichenko, O. Myrgorod, N. Miroshnichenko, Alexander Sincheskul // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 2, Issue 1 (86). – P. 21–28. doi: 10.15587/1729-4061.2017.95989
4. Cervova, J. Corrosive protection of metal materials in cooling water [Text] / J. Cervova, M. Hagarova, P. Lackova // American Journal of Materials Science and Application. – 2014. – Vol. 2, Issue 1. – P. 6–10.
5. Tamazashvili, A. T. Comparison of the efficiency of phosphate inhibitors of steel corrosion in tap water [Text] / A. T. Tamazashvili, Yu. I. Mazna, L. V. Sirenko // Eastern-European Journal of Enterprise Technologies. – 2012. – Vol. 2, Issue 13 (56). – P. 28–31. – Available at: http://journals.uran.ua/eejet/article/view/3943/3611
6. Gomelya, N. D. Novye ingibitory korrozii i otlozheniya osadkov dlya sistem vodocirkulyacii [Text] / N. D. Gomelya, T. A. Shabliy, A. G. Trohimenko, M. M. Shuriberko // Himiya i tekhnologiya vody. – 2017. – Vol. 39, Issue 2. – P. 169–177.
7. Stepin, S. N. Primenenie fosforsoderzhashchih kompleksonov i kompleksonatov v kachestve ingibitrov korrrozii metallov [Text] / S. N. Stepin, O. P. Kuznecova, A. V. Vahin, B. I. Habibrahmanov // Vestnik Kazanskogo tekhnologicheckogo universiteta. – 2012. – Vol. 15, Issue 13. – P. 88–98.
8. Liu, S. H. Corrosion inhibition of a composite inhibitor containing imidazoline on carbon steel in simulated reverse osmosis product water of seawater [Text] / S. H. Liu, Y. N. Wang, B. X. Yuan, W. T. Dong et. al. // International Journal of Corrosion and Scale Inhibition. – 2016. – Vol. 5, Issue 4. – P. 325–332. doi: 10.17675/2305-6894-2016-5-4-3
9. Muthumani, N. Corrosion Inhibition by Amino Trimethylene Phosphonic Acid (ATMP) – Zn2+ System for Carbon Steel in Ground Water [Text] / N. Muthumani, S. Rajendran, M. Pandiarajan, J. L. Christy, R. Nagalakshmi // Portugaliae Electrochimica Acta. – 2012. – Vol. 30, Issue 5. – P. 307–315. doi: 10.4152/pea.201205307
10. Barthelemy, B. Phynox Improved Corrosion Resistance with MPC Initiated from Mixed Monolayers of Phosphonic Acids [Text] / B. Barthelemy, F. Kanoufi, C. Combellas, J. Delhalle, Z. Mekhalif // Journal of the Electrochemical Society. – 2014. – Vol. 161, Issue 12. – P. C544–C549. doi: 10.1149/2.0531412jes
11. Mobin, M. The effect of heavy metal ions on the localized corrosion behavior of steels [Text] / M. Mobin, A. U. Malik, I. N. Andijani // Desalination. – 2007. – Vol. 217, Issue 1-3. – P. 233–241. doi: 10.1016/j.desal.2007.03.005
12. Prabakaran, M. Corrosion inhibition behavior of propyl phosphonic acid–Zn2+ system for carbon steel in aqueous solution [Text] / M. Prabakaran, M. Venkatesh, S. Ramesh, V. Periasamy // Applied Surface Science. – 2013. – Vol. 276. – P. 592–603. doi: 10.1016/j.apsusc.2013.03.138
13. Manivannan, M. Ethylenediaminetetraacetic acsd–Zn2+ system as corrosion inhibition for carbon steel in seawater [Text] / M. Manivannan, S. Rajendra // Asian journal of chemistry. – 2012. – Vol. 10. – P. 4713–4716.
14. Prabakaran, M. The corrosion inhibition performance of pectin with propyl phosphonic acid and Zn2+ for corrosion control of carbon steel in aqueous solution [Text] / M. Prabakaran, S. Ramesh, V. Periasamy, B. Sreedhar // Research on Chemical Intermediates. – 2014. – Vol. 41, Issue 7. – P. 4649–4671. doi: 10.1007/s11164-014-1558-0
15. Prabakaran, M. Enhanced corrosion inhibition behavior of carbon steel in aqueous solution by Phosphoserine-$Zn^{2}$+system [Text] / M. Prabakaran, P. Durainatarajan, S. Ramesh, V. Periasamy // Journal of Adhesion Science and Technology. – 2016. – Vol. 30, Issue 14. – P. 1487–1509. doi: 10.1080/01694243.2016.1150661
16. DSanPiN 2.2.4-171-10 Hihienichni vymohy do vody pytnoi, pryznachenoi dlia spozhyvannia liudynoiu [Text]. – Ministerstvo okhorony zdorovia, 2010. – No. 452/17747.
17. Saida, T. Effects of Temperature and Anion-species on the Susceptibility to Chloride Stress Corrosion Cracking of Stainless Steels in Hot Water [Text] / T. Saida, K. Sato, K. Kuroda, M. Okido // Zairyo-to-Kankyo. – 2013. – Vol. 62, Issue 6. – P. 224–230. doi: 10.3323/jcorr.62.224
18. Gomelya, N. D. Vliyanie osnovnyh reagentov na korroziyu stali v vode pri povyshennyh temperaturah [Text] / N. D. Gomelya, Yu. A. Omel'chuk, T. A. Nezviskaya // Ehkotekhnologii i resursosberezhenie. – 2007. – Issue 6. – P. 57–60.
19. Thangakani, J. A. Corrosion Inhibition of Carbon Steel in Well Water by L-Cysteine-Zn2+ System [Text] / J. A. Thangakani, S. Rajendran, J. Sathiabama, R. J. Rathish, S. Santhanaprabha // Portugaliae Electrochimica Acta. – 2017. – Vol. 35, Issue 6. – P. 13–25. doi: 10.4152/pea.201701013
20. Chausov, F. F. Synthesis and structure of tetrasodium nitrilotrismethylenephosphonato zincate tridecahydrate $Na_4[ZnN(CH_2PO_3)_3]\cdot 13H_2O$, a corrosion inhibitor [Text] / F. F. Chausov, E. A. Naimushina, I. N. Shabanova, N. V. Somov // Journal of Structural Chemistry. – 2015. – Vol. 56, Issue 3. – P. 582–588. doi: 10.1134/s0022476615030270

21. Chausov, F. F. Linear organic–inorganic heterometallic copolymers [(Fe, Zn)$(H_2O)_3${NH$(CH_2PO_3H)_3$}] n and [(Fe, Cd) $(H_2O)_3${NH$(CH_2PO_3H)_3$}] n : The missing link in the mechanism of inhibiting local steel corrosion with phosphonates [Text] / F. F. Chausov, N. V. Somov, R. M. Zakirova, A. A. Alalykin, S. M. Reshetnikov, V. G. Petrov et. al. // Bulletin of the Russian Academy of Sciences: Physics. – 2017. – Vol. 81, Issue 3. – P. 365–367 doi: 10.3103/s106287381703008x

UDC 546.02
DOI: 10.15587/1729-4061.2017.108946

# INVESTIGATION INTO ACID-BASIC EQUILIBRIUM ON THE SURFACE OF OXIDES WITH VARIOUS CHEMICAL NATURE

**Yu. Danchenko**
PhD, Associate Professor
Department of General Chemistry
Kharkiv National University of
Civil Engineering and Architecture
Sumska str., 40, Kharkiv, Ukraine, 61002
E-mail: u_danchenko@ukr.net
**V. Andronov**
Doctor of Technical Sciences, Professor*
E-mail: andronov@nuczu.edu.ua
**E. Rybka**
PhD*
E-mail: rybka@nuczu.edu.ua
**S. Skliarov**
PhD*
E-mail: bezpeka@nuczu.edu.ua
*Research Center
National University of Civil Protection of Ukraine
Chernyshevska str., 94, Kharkiv, Ukraine, 61023

***Досліджено кислотно-основну рівновагу на поверхні оксидів CaO, MgO, FeO, $Al_2O_3$, $Fe_2O_3$, $SiO_2$, $TiO_2$. З використанням квантово-хімічного моделювання запропоновані моделі безводних та гідратованих активних центрів на поверхні оксидів. Встановлені закономірності зміни кислотно-основних та енергетичних параметрів модельних поверхневих активних центрів в залежності від природи центрального елемента кристалічної решітки, кількості ОН-груп та числа гідратації***

***Ключові слова: оксидний наповнювач, композиційний матеріал, поверхневий активний центр, кислотно-основна рівновага***

***Исследовано кислотно-основное равновесие на поверхности оксидов CaO, MgO, FeO, $Al_2O_3$, $Fe_2O_3$, $SiO_2$, $TiO_2$. С использованием квантово-химического моделирования предложены модели безводных и гидратированных активных центров на поверхности оксидов. Установлены закономерности изменения кислотно-основных и энергетических параметров модельных поверхностных активных центров в зависимости от природы центрального элемента кристаллической решетки, количества ОН-групп и числа гидратации***

***Ключевые слова: оксидный наполнитель, композиционный материал, поверхностный активный центр, кислотно-основное равновесие***

## 1. Introduction

Ukraine has virtually inexhaustible deposits of various mineral oxides, which can replace foreign ones in a manufacture of building polymer-based composites. The use of Ukrainian materials as fillers for building purposes is conditioned by affordability, low cost, and a capability of obtaining materials with a variety of necessary operational and technological properties. Interest in this area is primarily due to the study of the physicochemical properties of surface phenomena in composite materials [1–6]. The relevance of this trend arises in the process of creating new polymeric building composites which constitute heterogeneous systems with highly developed interphase boundaries. Properties of the dispersed phase surface determine the initial stage of adhesion interaction between the components: adsorption, wetting, spreading of the dispersion media over the filler surface, forming the interphase boundary, impregnation of filled and reinforced systems [3–5]. Of all existing theories of interphase interaction in polymeric composite materials, the acid-base one is the least studied. Its existence is confirmed by studies over recent years [2, 7]. When choosing components for a composite material, it is important to predict interactions on the interphase surface which are simultaneously determined by the acid-base properties of the polymer and the acidic strength of the adsorption centers on the filler surface [2]. Therefore, investigation of the acid-base equilibrium on the surface of oxide fillers of various chemical natures is relevant both from theoretical and practical points of view.

## 2. Literature review and problem statement

In connection with the natural origin of mineral oxide fillers, chemical and mineralogical composition and, consequently, surface properties, are extremely unstable. Besides, mineral particles have a redundant surface energy which includes acid-base (polar) energy of surface centers [8, 9] and easily adsorb molecules of water from air [10–12]. The effect of chemically and physically adsorbed water on the acid-base