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A.B. Niyazbekova[1], T.A. Shakirov[1], L.I. Baytlesova[1],
N.M. Zhunusbekova[2], A.I. Niyazbaeva[3]*, G.M. Gubaidullina[4]

[1]West Kazakhstan Innovation Technology University, Uralsk, Kazakhstan
[2]Satbayev University, Almaty, Kazakhstan
[3]Al-Farabi Kazakh National University, Almaty, Kazakhstan
[4]Zhangir Khan West Kazakhstan Agrarian Technical University, Uralsk, Kazakhstan
*e-mail: Almagul.Niyazbaeva@kaznu.edu.kz

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Effect of phosphate nature on the inhibitory capability of phosphate compositions

Abstract. Corrosion inhibitors find ubiquitous application across diverse sectors to formulate robust coatings and chemical compounds. Serving as pivotal additives in compositions, they play a vital role in crafting coatings for circulating water systems, water supply networks, oil refining, petrochemical industries, and power plants. Incorporation extends to fuels, oils, lubricants, and construction materials. In industries oxidation inhibitors is particularly high as chemical, electrochemical, petrochemical, and gas, as well as in water supply networks and circulating water systems. The utilization of inhibitors obviates the necessity for treating metal surfaces with protective enamels and mastics. Effectively preventing oxidation involves the introduction of chemical contributions into aggressive ecology, thereby neutralizing or retarding the oxidation processes. This article explores the anti-oxidation properties of inhibitors in compositions related to St-3 steel. The study includes factors such as the pH of the medium, the nature and concentration of phosphate in compositions simulating reservoir water under stationary and aerated conditions. Investigation methods as potentiometry and photocolorimetry used in research. Experimental data, quantitative parameters of the oxidation process, oxidation rate, and degree of protection, depth index, and stability of the film formed were determined. These indicators were assessed on the oxidation resistance scale relative to steel. Analysis of the data shows that out of 63 compositions, seven systems demonstrate the most significant protective effects, with five containing sodium orthophosphate and two containing sodium hydroorthophosphate. The effective, surrounding friendly and cost-effective steel oxidation inhibitors using materials from Kazakhstan will main contribute to the development.

Key words: oxidation, inhibitor, orthophosphates, degree of protection, depth index.

Introduction

In various sectors like power engineering, mechanical engineering, and mining are used corrosion inhibitors. Through the deposition of corrosion inhibitor thin films on their surfaces is achieved metals against atmospheric corrosion. This method stands out for its technological sophistication, preserving the original dimensions of the protected product while exerting minimal impact on subsequent manufacturing processes. The approach is economically viable, as protective coatings can be readily disposed of in industrial wastewater, offering a sustainable solution that minimizes the need for re-preservation.

In based aqueous surroundings and aggressive steamy airs, metallic oxidization classically effects in contained surface damage. Traditional inhibitors similar chromates and nitrites are used no longer generally due to ecological concerns. Carbon-based acid salts have the capacity to become constant metals and compounds when showing to ecological components like chlorides and sulfates. These composites, such as carboxylic acids and alkylphosphonic acids, not only encourage inactivity but also have minimal environmental impact. Water-soluble compounds are mostly preferred due to growing ecological criteria [1].

As such composites, it is particularly worth importance the salts of carboxylic acids R-COOH, alkylphosphonic acids Alk-P(0)$(OH)_2$ and phosphoric acid esters, since in addition to protecting things, they have a low polluting effect on the surroundings. Among them, you can find composites that have good solubility in water. At the same time, there is a vital for the development of environmentally benign and effective formulations of metal corrosion inhibitors, especially those characterized by low concentrations [2].

The consequence of oxidization studies is triple. Principally, from a financial standpoint, the objective is the modification of material losses incurred due to the oxidization of pipelines, boilers, machine components, vessels, bridges, marine structures, and the like. The second is to improve the reliability of apparatus that can oxidize with catastrophic significances, such as pressure containers, vapor boilers, metal containers for toxic materials, turbine blades and rotors, bridges, aircraft parts and autonomous automated machinery. Stability is the main state in the increase of nuclear power plant equipment and radioactive waste disposal systems. The third dimension revolves around the safeguarding of the metal reserve. Assumed the limited nature of global metal resources, corrosion-induced metal losses entail supplementary expenditures in terms of energy and water resources. So imperative is the redirection of social effort spent on the design and modernization of oxidized metal apparatus toward addressing other publically useful activities [3, 4].

Materials and methods

Oxidization inhibitors have been essential to the oil and gas manufacturing since the 1940s, usually calculated in parts per million, ranging from 15 to 50 grams per ton of liquid. In the complicated network of field pipeline systems resembling the branches of a tree, emanating in divergent directions from a common origin point, the strategic addition of inhibitors at the pipeline inlet ensures comprehensive protection over vast distances, extending up to some hundred kilometers [5].

The NACE usual are distinguished by an appropriately significant acidity, with a hydrogen ion concentration yielding a pH of 3.6 in the absence of hydrogen sulfide and carbon dioxide additives. Summary of these acid agents does not precipitate a pH reduction. The totaling of acid substances does not lower the pH, since hydrogen sulfide and carbon dioxide in solution are current in molecular form at the specified pH values. When carbon steel corrodes in an environment saturated with carbon dioxide, the surface of the electrodes becomes covered with a gray film with rust spots, consisting of Fe_3O_4 with traces of $FeCO_3$. In the presence of hydrogen sulfide, a layer of iron sulfides forms on the metal surface, which is easily indifferent with an etching solution. The investigational results obtained confirm the essential remarkable effect of hydrogen sulfide and carbon dioxide on the oxidization rate of steel [6].

Improving device reliability, mainly for oxidation-prone modules in pressure vessels, condensation boilers, and nuclear power plants, is crucial. The presence of hydrogen sulfide and carbon dioxide can meaningfully accelerate the corrosion rate of steel, with hydrogen sulfide proving to be a stronger activating than CO_2. Inhibition of corrosion through the formation of a protective layer on the metal surface is observed over time.

Giving to the moments of daily investigations, in the occurrence of hydrogen sulfide K_0 is 0.46 g/m^2 hour, and in carbon dioxide environments, it is meaningfully lower – 0.192 g/m^2 hour, which is 2 times upper than the oxidization rate in the background solution. In a combined environment containing both hydrogen sulfide and carbon dioxide, K_0 values are slightly lower than in hydrogen sulfide. This element is probably connected with the reasonable adsorption of CO_2 and hydrosulfide ions on the active centers of the metal surface. As the time of the research increases, the oxidization rate values decrease, which is due to the adding of a deposit of oxidization produces on the surface of the steel, which builds a certain barrier to the supply of an acid average [7].

The oxidization analysis approach engaged adhered to widely accepted practices [8]. Oxidization experiments were carried out on ST-3 steel samples with the components, wt. %: C – 0.2; Mn – 0.5; Si – 0.15; P – 0.04; S – 0.05; Cr – 0.30; Ni – 0.20; Cu – 0.20; Fe – 98.36.

To carry out oxidation analysis, rectangular plates made of St-3 steel were used. The samples were cleaned, degreased and weighed. A solution volume of at least 15 cm3 per 1 cm2 of sample surface was used and tests lasted from 24 to 480 hours [9].

The oxidation rate assessed by the weight loss of the samples at certain time intervals. Quantitative oxidation indicators calculated using the Student's t coefficient with a confidence level of 0.95.

During the work, potentiometric measurements of pH, electrical conductivity and total mineralization, conductometric measurements and determination of iron (III) content using potassium thiocyanate were carried out [10].

Results and discussion

Experimental data elucidating the protective efficacy of formulations containing sodium dihydroorthophosphate are depicted on Figure 1.

Examination of pure phosphate inhibitors at concentrations of 0.01, 0.025, and 0.05 mol/dm^3, both in a composition with a simulated reservoir water under stationary conditions and with intensive aeration, unveiled a notable elevation in the corrosion process rate in pure media, correspondingly resulting in a low inhibition coefficient. In media with IPV NACE and IPV NACE during aeration, the inhibition coefficient is notably low, indicating an absence of protective effects in these systems. The highest value of the inhibition coefficient is observed at a concentration of sodium dihydrogen orthophosphate of 0.025 mol/dm^3 in the control sample – tap water.

Further investigations under stationary conditions revealed that, in the mediums of IP in NACE and with IPV NACE during aeration, compositions containing NaH_2PO_4 do not manifest a significant protective effect. Experimental data on the protective effect of inhibitors in compositions containing sodium hydroorthophosphate are presented on Figure 2.

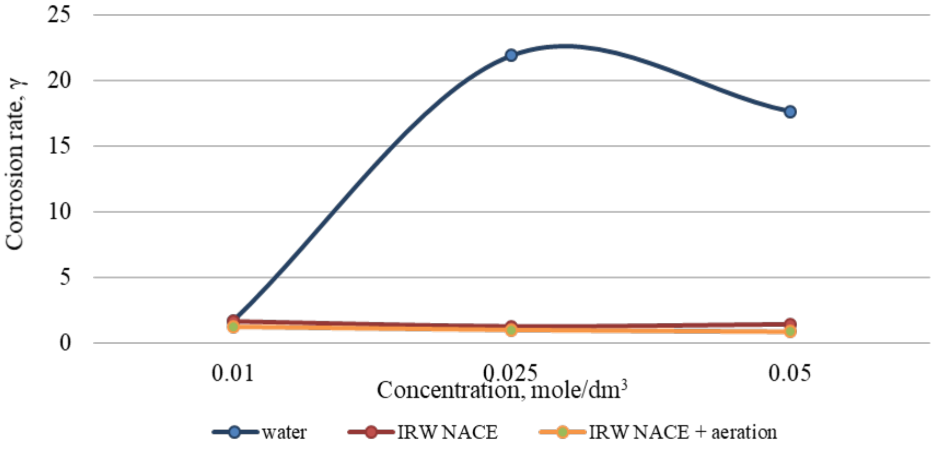

Figure 1 – Inhibition of corrosion of steel St3 by compositions with sodium dihydroorthophosphate NaH_2PO_4 in various media depending on concentration

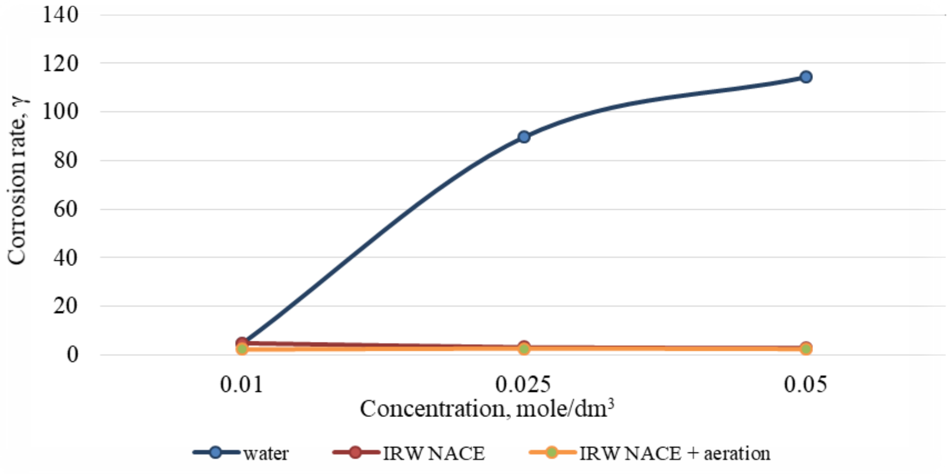

Figure 2 – Inhibition of corrosion of steel St3 by compositions with sodium hydroorthophosphate Na_2HPO_4 in various media depending on concentration

The study of the protective effect of pure Na_2HPO_4 and its compositions with IPV NACE and with IPV NACE during aeration showed that in all media at 0.01 mol/dm^3 the effect in all media of the inhibitor is insignificant. Upon escalating the concentration to 0.025 and 0.05 mol/dm^3, a substantial augmentation in the inhibitory effect of Na_2HPO_4 is observed in pure water. However, concomitantly, this enhanced effect is practically non-evident in the other two media, exhibiting a diminishing trend with the escalating concentration of the phosphate component.

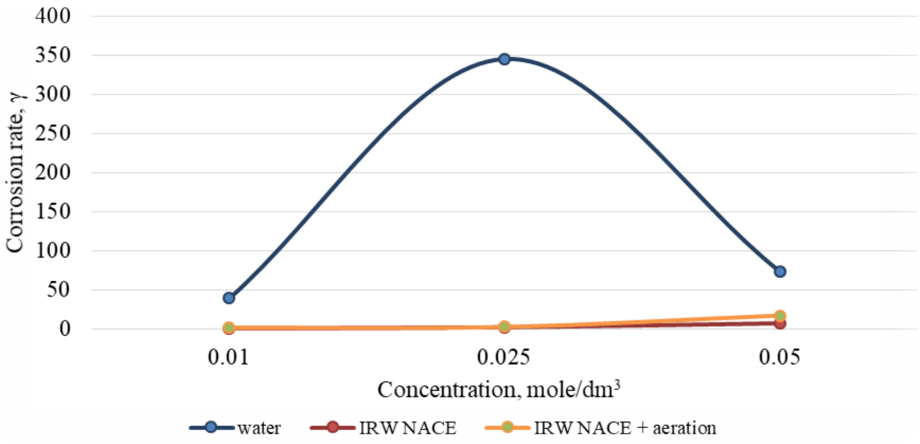

Figure 3 – Inhibition of corrosion of steel St3 by compositions with sodium orthophosphate Na_3PO_4 in various media depending on concentration

Figure 3 presents experimental data elucidating the protective efficacy of compositions incorporating sodium orthophosphate. For compositions of Na_3PO_4 with IPV NACE and IPV NACE with intense aeration at concentrations of 0.01, 0.025, 0.05 mol/dm^3, it was found that the best inhibitory effect is demonstrated by Na_3PO_4 in pure water at a concentration of 0.025 mol/dm^3 ($\gamma = 345.22$), which is the best result. All data show that a concentration of 0.025 mol/dm^3 for sodium orthophosphate is optimal.

Experimental data on the protective effect of compositions containing sodium dihydrodiphosphate is presented on Figure 4.

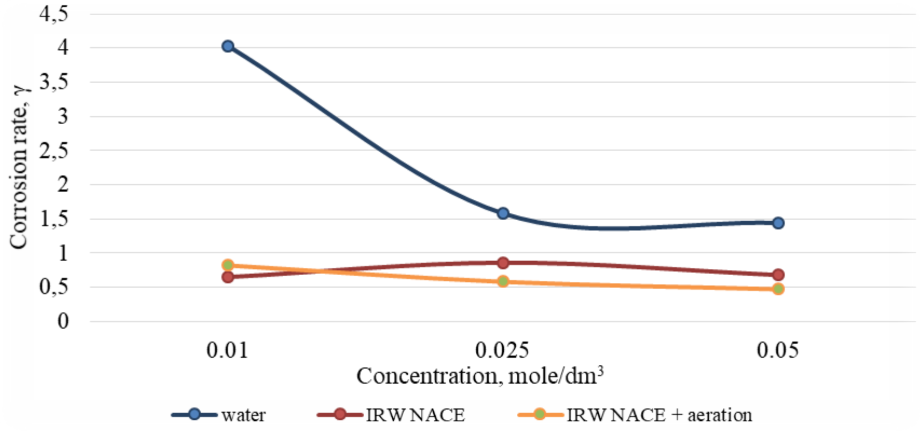

Figure 4 – Inhibition of corrosion of steel St3 by compositions with sodium dihydrogen phosphate $Na_2H_2P_2O_7$ in various media depending on concentration

The investigation into the inhibitory effect of compositions incorporating $Na_2H_2P_2O_7$ reveals that the composition with water attains the highest inhibition coefficient at a concentration of 0.01 mol/dm^3. Notably, an augmentation in the concentration of sodium dihydrodiphosphate systematically diminishes the protective effect. In compositions involving $Na_2H_2P_2O_7$ with IPV NACE and compositions under IPV NACE with intensive aeration, the inhibition coefficient falls below unity. Consequently, under these conditions, $Na_2H_2P_2O_7$ serves as a corrosion stimulator.

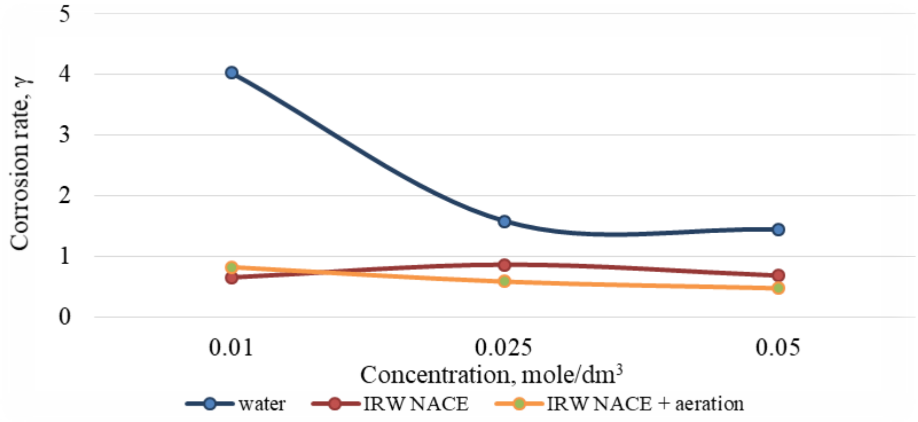

Figure 5 – Inhibition of oxidation of steel St3 by compositions with sodium diphosphate $Na_4P_2O_7$ in various media depending on concentration

Experimental data on the protective effect of compositions containing sodium diphosphate is presented in Figure 5.

Analysis of the obtained data on the main indicators characterizing the corrosion process of the composition of sodium diphosphate with 0.01 mol/dm^3 shows the manifestation of similar values of the protective effect.

Upon escalating the inhibitor concentration in compositions with reservoir water during aeration, a slight increase in protective efficacy was observed. Conversely, in other conditions, an elevation in concentration resulted in corrosion stimulation. Generally, these compositions lack discernible effectiveness in the studied media.

Information on the protective effect of compositions containing sodium cyclotriphosphate was obtained from experiments and is presented on Figure 6.

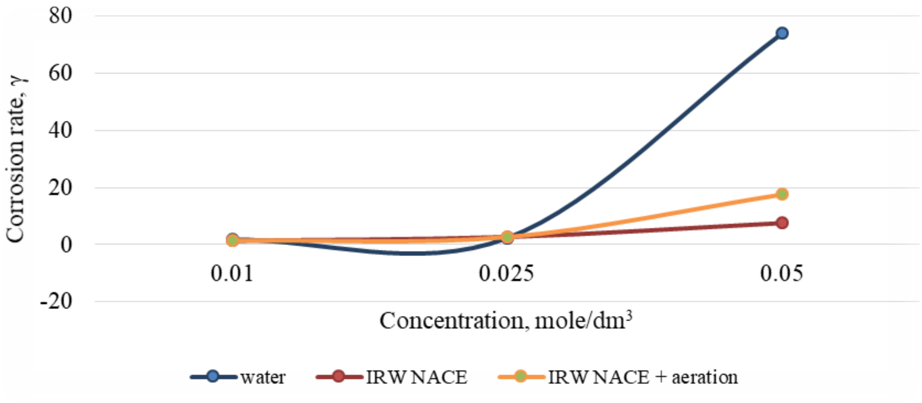

Figure 6 – Inhibition of corrosion of steel St3 by compositions with sodium cyclotriphosphate $Na_3P_3O_9$ in various media depending on concentration

The inhibitory capabilities of trimetaphosphate compositions were systematically explored, both in their pure form and as compositions with IPV NACE and compositions with IPV NACE under intensive aeration.

The findings indicate that the $Na_3P_3O_9$ inhibitor, within the composition involving IPV NACE under intensive aeration, exhibits superior protective efficacy compared to other systems, albeit not surpassing 3 in terms of the protective effect. Increasing in the content of inorganic components in the compositions leads to a slight increase in the protective effect. Experimental data shows that the best combination of anti-corrosion components for maximum protection in clean water is a composition with Na_3PO_4 at 0.025 mol/dm^3.

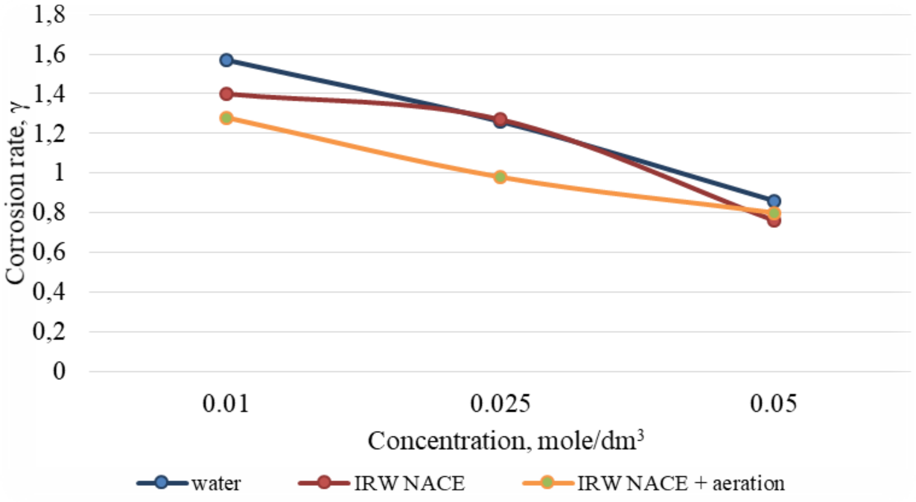

Figure 7 – Inhibition of corrosion of steel St3 by compositions with sodium cyclohexane phosphate $Na_6P_6O_{18}$ in various media depending on concentration

Experimental data on the protective effect of compositions containing sodium cyclohexaphosphate is presented on Figure 7.

The outcomes from the investigation into the protective efficacy of compositions containing sodium cyclohexaphosphate $Na_6P_6O_{18}$ across diverse media lead to the conclusion that an elevation in concentration does not contribute to the enhancement of the inhibitor's protective properties. The inhibition coefficient values remain small across all systems. In the composition with IPV NACE, sodium cyclohexaphosphate acts as a corrosion stimulant, but under conditions of intensive aeration, the protective effect experiences a marginal increase, albeit insignificant.

1. The anticorrosive efficacy of phosphorus-containing inorganic compositions in diverse media has been systematically evaluated. Quantitative parameters delineating the corrosion process were ascertained employing both chemical and physicochemical methodologies.

2. Based on the results of experimental work, it established that the more effective combination of anti-corrosion components to ensure the maximum possible protection for the environment is:

- tap water – composition with Na_3PO_4 at 0.025 mol/dm^3;
- for IPV NACE – composition with Na_3PO_4 at 0.025 mol/dm^3;
- for IPV NACE during aeration – composition Na_3PO_4 at 0.05 mol/dm^3.

It was found that, compared to tap water, the protective effect of phosphate compositions in IPV is reduced, and becomes even less with intense aeration.

In pure water medium the anticorrosive activity increases in the following range:

$Na_4P_2O_7 < Na_6P_6O_{18} < Na_3P_3O_9 < Na_2H_2P_2O_7 < NaH_2PO_4 < Na_2HPO_4 < Na_3PO_4$.

In the IPV NACE medium, the anticorrosive activity increases in a number of:

$Na_2H_2P_2O_7 < Na_6P_6O_{18} < NaH_2PO_4 < Na_4P_2O_7 < Na_3P_3O_9 < Na_2HPO_4 < Na_3PO_4$.

In the IPV NACE media with intensive aeration, the anticorrosive activity increases in the row:

$Na_2H_2P_2O_7 < Na_6P_6O_{18} < NaH_2PO_4 < Na_4P_2O_7 < Na_3P_3O_9 < Na_2HPO_4 < Na_3PO_4$.

Conclusions

The undeniable importance and significance of metal corrosion inhibitors are highlighted, as evidenced by the extension of the service life of metal structures from the conventional 2 years to an impressive 5-6 years, exceeding the baseline by 2.5-3 times, contingent upon the steel grade.

In the largest countries globally, the production landscape of metal corrosion inhibitors is characterized by a diverse array of chemical products, yielding substantial financial returns for producers [11]. Annually, manufacturers from both non-CIS and CIS countries introduce new, ostensibly more effective metal corrosion inhibitors to the market. However, industrial viability depends on the economic costs of a particular product and its compliance with chemical reagent specifications.

The experimental exploration involved the study of 63 compositions, analyzing their anticorrosive effectiveness in relation to the concentration and nature of the phosphate component. Additionally, three systems without inhibitors were investigated.

The use of all systems depends on the pH of the solution and the overall mineralization. An increase in pH and mineralization corresponds to an increase in the protective effect.

The effectiveness of all systems depends on the pH of the solution and the total mineralization. An increase in pH and mineralization corresponds to an increase in the protective effect.

Based on the acquired investigational data, it was assumed that among the 63 compositions, 7 systems exhibit the most basically significant protective result. This subset comprises 5 systems with sodium orthophosphate and 2 with sodium hydroorthophosphate.

The patterns established during the study not only develop, but also addition current ideas about the protective effect of compounds based on inorganic phosphate compounds. The results obtained promise a significant support to the increasing of effective, ecologically responsive and cost-effective steel oxidation inhibitors based on Kazakhstani raw materials. The collected data represents a significant step in advancing the scientific frontiers of effective inhibitory protection of metals.

References

1. McCafferty E. (2010) Introduction to Corrosion Science. Springer, New York, NY.
2. Tosun A., Ergun M. (2006) Protection of corrosion of carbon steel by inhibitors in chloride containing solutions. Gazi Univ. J. Sci., 19(3), 149-154.
3. Fouda A.S., Elewady G.Y., El-Haddad M.N. (2011) Corrosion inhibition of carbon steel in acidic solution using some azodyes. Can. J. Sci. Ind. Res., 2(1), 1-19.
4. Niyazbekova A.B., Akatyev N.V., Sulekeshova G.K., Shakirov T.A. (2013) Chromatographic study of systems cyclotri-, cyclotetra- and cyclohexaphosphate with two and trivalent cations of p- and d-elements. Materials of the VI international research and practice conference, Munich, Germany.
5. Kuanysheva G.S., Makasheva G.R., Kamalova G., Niyazbekova A.B. (1999) Complexa formation of salts of some d-elements with a diphosphate anion. Bull. of KazGU, 1(13), 71-73.
6. Brown B., Saleh A., Moloney J. (2016) A comparison of mono- to di- phosphate ester ratio in inhibitor formulations in the mitigation of under deposit corrosion. CORROSION, Vancouver, Canada.
7. Narayana N., María Rao, Gómez-García R., Kornberg A. (2009) Inorganic polyphosphate: essential for growth and survival. Annu. Rev. Biochem., 78, 605-647.
8. Durif A. (2005) The development of cyclophosphate crystal chemistry. Solid State Sci., 7(6), 760-766.
9. Bhajiwala H.M., Vashi R.T. (2001) Ethanolamine, diethanolamine and triethanolamine as corrosion inhibitors for zinc in binary acid mixture [HNO_3 + H_3 PO_4]. Bull. Electrochem., 17(10), 441-448.
10. Kura G. (1987) Hydrolysis reaction of inorganic cyclophosphates at various acid strengths. Polyhedron, 6(3), 531-533.
11. Niazbekova A., Akatyev N., Mukasheva M., Rakhova A. (2012) Quantum- chemical calculations of electronic structure of polyphosphate complexes of manganese, cobalt, copper and zinc. Materials of the international research and practice conference “European Science and Technology”, Wiesbaden: Germany, 82-85.

Information about authors:

Niyazbekova Aktoty – candidate of chemical Science, Associate Professor, West-Kazakhstan Innovation Technology University (Uralsk, Kazakhstan, e-mail: abnyazbekova@mail.ru)

Shakirov Timur – magister of engineering and technology, West-Kazakhstan Innovation Technology University (Uralsk, Kazakhstan, e-mail: Shakirov.timur.0585@gmail.com)

Baytlesova Laura – candidate of chemical Science, Associate Professor, West-Kazakhstan Innovation Technology University (Uralsk, Kazakhstan, e-mail: beu@mail.ru)

Zhunusbekova Nazym – candidate of chemical Science, Associate Professor, Satbayev University (Almaty, Kazakhstan, e-mail: znazym@mail.ru)

Niyazbayeva Almagul (corresponding author) – candidate of chemical science, associate professor, Al-Farabi Kazakh National University (Almaty. Kazakhstan, e-mail: Almagul.Niyazbaeva@kaznu.edu.kz)

Gubaidullina Gulkhan – candidate of technical Sciences, Associate Professor, West-Kazakhstan agrarian-technical University named after Zhangir Khan (Uralsk, Kazakhstan, e-mail: ggulkhan@mail.ru)