



Study of Properties of Manganese-Containing Waste Processing Product as a Low-Carbon Steel Corrosion Inhibitor in Neutral Aqueous Media

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Abstract

The inhibitory properties of the product obtained from manganese ore sampled from Zhairam deposit were studied on low-carbon steel (St3) in an aqueous medium. Standard gravimetric method and electrochemical measurements were used. It is shown that calcium-manganese phosphate product with composition $\text{CaO}:\text{MnO}:\text{P}_2\text{O}_5$ (1.00:0.11:1.54) and the phosphate content from phosphorus pentoxide (73.64 ± 1.33 , wt.%), reduces the corrosion rate of steel St3 in the entire studied concentration range from 1 to 100 mg/L of P_2O_5 . In contrast to the well-known sodium polyphosphate inhibitor, it has been established that anti-corrosion treatment of water with a calcium-manganese phosphate inhibitor reduces the rate of accumulation of salt rust deposited on the steel surface. This was obtained to be practically zero at a concentration of 50 mg/L of P_2O_5 . The results of electrochemical tests were confirmed by noting and calculating polarization curves of gravimetric measurements. During the study of the surface morphology of steel samples after being exposed to inhibitor solutions using scanning electron microscopy (SEM) and energy-dispersive analysis, the formation of uniform coatings consisting of compounds of calcium, manganese, iron and phosphorus was established. IR spectroscopic studies confirmed the formation of a protective coating in calcium-manganese solutions consisting of calcium, iron, and possibly manganese hydrodiphosphates.

Keywords: Carbon steel; Corrosion; Corrosion rate; Inhibitor; Inhibitory properties; Degree of protection.

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1. Introduction

Carbon steel, due to its high strength, good ductility and weldability, is the main structural material widely used to create such morally aging metal structures as steel main water pipelines. However, its main disadvantage is low corrosion resistance, including in neutral aqueous media.^[1-3] The problem of internal corrosion of pipelines and equipment made of carbon steel, which can lead to a decrease in pipe

throughput, leaks, ruptures and failure of structures, is especially relevant. In addition, corrosion can have serious consequences on the economy, the environment and human health.^[3-7] Corrosion of carbon steels in contact with aqueous media is electrochemical in nature and is caused by two coupled electrochemical reactions, including anodic ionization of metal and cathodic reduction of the oxidizing component of the corrosive medium, which for aqueous media is oxygen.^[1,2] During electrochemical corrosion of carbon steel in water, the products of cathode and anode reactions (for example, iron ions and hydroxyl ions) that communicate with each other can interact with the solution components, forming additional ions and corrosion substances.^[2,3] This phenomenon is exacerbated by various factors such as pH levels, temperature, oxygen concentration and the presence of other corrosive agents.^[2,6,7]

Effective corrosion management is essential to ensure the longevity of water infrastructure and reduce operating costs associated with repair and replacement.^[1,2] Anti-corrosion treatment of water with inhibitors is an effective method of

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mitigating the adverse effect of corrosion on the Inner surface of steel pipelines. Corrosion inhibitors are chemical compounds that, when added to a corrosive environment, form a protective layer on the surface of the metal, thereby reducing the rate of corrosion. A wide range of inhibitors, including organic compounds, polymers and green inhibitors derived from plant extracts, have been investigated for their effectiveness in various corrosive environments.^[8-10] Among these inhibitors, those that can provide long-term corrosion protection while being environmentally friendly are particularly desirable in the context of sustainable infrastructure management.^[11-13] The use of advanced materials and techniques in corrosion inhibition has gained momentum in recent years. For example, hybrid coatings that include nanoparticles along with conventional inhibitors have shown significant promise for improving corrosion resistance through synergistic effects.^[14-17] In addition, biopolymer-based inhibitors derived from natural sources have become an environmentally friendly alternative to conventional synthetic inhibitors, offering reduced toxicity and minimal environmental impact while maintaining satisfactory corrosion protection.^[18,19] Despite these advancements, challenges remain in optimizing inhibitors performance under varying conditions and ensuring compatibility with different water qualities. In Kazakhstan, this problem is also complicated by sanitary and hygienic requirements, according to which only inorganic phosphates and silicates are allowed for use in water supply systems.^[24-26]

Recent studies have confirmed the possibility of using the product of acid-thermal processing of manganese-containing ore beneficiation wastes of the Zhayrem deposit as a carbon steel corrosion inhibitor in aqueous media.^[27,28] For example, studies have shown that the molar ratio of the main components in this product is (in terms of oxides) $\text{CaO}:\text{MnO}:\text{P}_2\text{O}_5 = 1.00:0.11:1.54$ with a phosphate content of (73.64 ± 1.33) wt% P_2O_5 . The product contains dihydrodiphosphates and calcium polyphosphate as well as manganese polyphosphate. The aqueous solubility of the product is 92.4 relative%.^[27] Studies have shown that the incorporation of these inhibitors into water significantly reduces the corrosion rate of steel, while reducing the mass of corrosion products and improving overall water quality by removing heavy metal contaminants.^[27,28] In addition, the higher environmental friendliness of calcium-manganese phosphate compared to organic synthetic corrosion inhibitors highlights their potential as sustainable alternatives for corrosion protection in civil engineering and the petroleum industry.^[22-25]

Although the potential of calcium-manganese phosphate as an inhibitor is significant, several challenges remain to be addressed. The effectiveness of these inhibitors can vary considerably depending on the chemical composition of the water, especially the pH level and the presence of competing ions, which can affect the solubility and stability of the phosphates.^[29] In addition, long-term field studies are needed

to establish the durability of protective layers formed on the inner surfaces of pipelines under fluctuating operating conditions. The hypothesis behind this study states that calcium-manganese phosphate can provide effective corrosion protection to the inner surfaces of steel pipelines when used under optimized conditions. In particular, it is contemplated that this inhibitor may form a strong protective layer consisting of calcium, manganese and iron phosphates, which not only reduces the rate of corrosion, but also improves the performance of the pipeline system by improving water quality and reducing deposits that can lead to biofouling and other operational problems. This work is aimed at studying the anti-corrosion properties of products obtained as a result of processing waste generated during the enrichment of manganese ores in Kazakhstan, as well as their potential use as corrosion inhibitors in water supply systems for various purposes. The study will focus on evaluating their corrosion protection performance at different concentrations and characterizing the protective layers formed on steel substrates. Through this research, we aim to provide valuable insights into the practical application of these inhibitors, contributing to the development of more sustainable and efficient maintenance strategies for water distribution systems.

2. Experiment

Studies of the inhibitory properties of the synthesized product were carried out by the gravimetric method at room temperature on samples in the form of plates $20 \times 50 \times 1 \text{ mm}^3$ in size. Samples were made from low-carbon steel grade steel grade 3 (St3) composition: 0.12%C, 0.2%Cr, 0.17%Mn, 0.025%P, 0.17%Si, 0.018%S, 0.25%Ni, 0.25%Cu, and the rest is Fe.

Before testing, the surface of the samples was polished, washed with ethanol, distilled water, and dried in a desiccator with calcined calcium chloride to constant weight. For each sample, the initial mass was measured on high-precision scales (with an error of no more than $\pm 0.1 \text{ mg}$) and the surface area was measured. The tests were carried out on five parallel samples for each inhibitor and each concentration. Statistical processing of the results was carried out using the ordinary least squares (OLS) method at a confidence level of 0.90.

Purified tap water with additives of inhibitors of various compositions and concentrations was used as a protective medium. The tests were carried out in glass chemical beakers, the volume of the tested solutions was 200 cm^3 . The well-known corrosion inhibitor sodium polyphosphate (NaPO_3) served as the reference inhibitor. After the end of the tests, the samples were removed from the solutions, dried in air, and the surface was visually assessed. After visual evaluation, the corrosion products were removed with a plastic spatula, washed with ethanol and distilled water, dried in a desiccator with calcined calcium chloride, and weighed.

Potentiodynamic polarization studies were carried out using Potentiostat/Galvanostat Model “Palmsens 4” at a scan rate of 1 mV s^{-1} under static conditions. The studies were

carried out in a classical three-electrode electrochemical cell at room temperature. A chlorine-silver electrode served as a reference electrode, and a graphite electrode 5 mm in diameter was used as an auxiliary electrode. Steel plates (St3) with dimensions of $10 \times 10 \times 1 \text{ mm}^3$ served as working electrodes. Purified tap water with additives of inhibitors of different composition and concentrations was used as electrolyte. At the beginning of the test, the working electrode was immersed in a corrosive medium for 3 hours to obtain a stabilized open circuit potential. The study of the molecular structure of protective films was carried out by the infrared (IR) spectroscopic method. The infrared absorption spectra were recorded on IR-Fourier spectrometer of Nicolet 5700 in the region of $400\text{--}3600 \text{ cm}^{-1}$.

The microscopic morphology of the surface and the qualitative composition of the coatings formed on the steel surface in tap water with additives of inhibitors were recorded using a scanning electron microscopy (SEM) HITACHI TM3030 scanning microscope with a built-in Bruker Xflash MIN SVE microanalysis system. Determination of the distribution of elements in the composition of the coatings, as well as the establishment of its isotropy was carried out using the mapping method.

3. Results and discussion

The inhibitory properties of the calcium-manganese phosphate product were studied gravimetrically under static conditions at room temperature. The corrosion rate of low-carbon steel grade St3 was determined by Eq. (1):

$$V_{\text{corr}} = \frac{(m_0 - m_{\text{sac}})}{S \cdot T} \quad (1)$$

where m_0 and m_{sac} are the mass of the sample before and after the testing and removal of corrosion products from the surface of the sample, g; S is the surface area, cm^2 ; T is the time of testing, days.

Inhibitor efficiency, IE (%) was calculated by Eq. (2):

$$\text{IE} = \frac{100(V_{\text{corr}}^0 - V_{\text{corr}}^{\text{inh}})}{V_{\text{corr}}^0} \quad (2)$$

where V_{corr}^0 and $V_{\text{corr}}^{\text{inh}}$ are the corrosion rate in absence and in presence of inhibitor.

The protection coefficient γ was determined according to Eq. (3):

$$\gamma = \frac{(V_{\text{corr}}^0)}{V_{\text{corr}}^{\text{inh}}} \quad (3)$$

The rate of accumulation of corrosion-salt deposits on the surface of a steel sample was calculated by Eq. (4):

$$V_{\text{dep}} = \frac{(m_f - m_0)}{S \cdot T} \quad (4)$$

where m_0 and m_f are the mass of the sample before and after the testing, g.

The results obtained are presented in Tables 1 and 2. It can be seen that the $(\text{Ca,Mn})(\text{PO}_3)_2$ obtained on the basis of enrichment waste reduces the corrosion rate of St3 in the entire studied concentration range from 1.0 to 100.0 mg/L of P_2O_5 . At the same time, the inhibitor efficiency even at a concentration of 1.0 mg/L of P_2O_5 , is 20.2% (Table 2). For comparison, the inhibitor efficiency of sodium polyphosphate at the same concentration is twice as low as 11.5% (Table 1).

At a $(\text{Ca,Mn})(\text{PO}_3)_2$ concentration of 50.0 mg/L of P_2O_5 , steel corrosion is practically absent, and the inhibitor efficiency is 98.2% (Table 2). Whereas NaPO_3 at this concentration reduces the corrosion rate of St3 by 1.7 times with an inhibitor efficiency of 41.1% (Table 1).

Comparative analysis of corrosion inhibition efficacy between commercially available sodium polyphosphate (NaPO_3) and synthesized calcium-manganese phosphate $(\text{Ca,Mn})(\text{PO}_3)_2$ shows significant differences in inhibition efficacy. As shown in Tables 1 and 2, both inhibitors decrease the corrosion rate V_{corr} of metal surfaces as concentrations increase. However, $(\text{Ca,Mn})(\text{PO}_3)_2$ shows significantly higher inhibition efficiency, reaching 99.6% at 100 mg P_2O_5 /L, with almost complete corrosion suppression ($V_{\text{corr}} = 0.001 \text{ mg/cm}^2 \cdot \text{day}$) and no accumulation of deposits ($V_{\text{dep}} = 0.000 \text{ mg/cm}^2 \cdot \text{day}$). In contrast, NaPO_3 at the same concentration achieves only a 38.3% inhibition efficiency with a residual corrosion rate of $0.171 \text{ mg/cm}^2 \cdot \text{day}$. The rate of accumulation

Table 1: Dependence of corrosion parameters on the concentration of Na polyphosphate inhibitor.

Index	NaPO ₃ concentration (mg/L as P ₂ O ₅)						
	0.0	1.0	5.0	10.0	20.0	50.0	100.0
Corrosion rate V_{corr} , mg/cm ² day	0.277 ±0.032	0.245 ±0.003	0.235 ±0.033	0.227 ±0.021	0.202 ±0.012	0.163 ±0.013	0.171 ±0.005
The protection coefficient γ	0	1.13	1.18	1.22	1.37	1.70	1.62
Inhibitor efficiency IE, %	0	11.5	15.2	18.0	24.5	41.1	38.3
The rate of accumulation of deposits on the surface of the metal, V_{dep} , mg/cm ² day	0.289	0.332	0.293	0.340	0.315	0.307	0.332

Table 2: Dependence of corrosion parameters on the concentration of the synthesized $\text{CaMn}(\text{PO}_3)_2$.

Index	CaMn(PO ₃) ₂ concentration (mg/L as P ₂ O ₅)						
	0.0	1.0	5.0	10.0	20.0	50.0	100.0
Corrosion rate, V_{corr} , mg/cm ² day	0.277 ±0.032	0.221 ±0.005	0.211 ±0.043	0.167 ±0.008	0.058 ±0.013	0.005 ±0.0006	0.001
The protection coefficient, γ	0	1.25	1.31	1.66	4.77	55.4	277.0
Inhibitor efficiency, IE %	0	20.2	23.8	39.7	79.0	98.2	99.6
The rate of accumulation of deposits on the surface of the metal, V_{dep} , mg/cm ² day	0.289	0.140	0.173	0.152	0.128	0.001	0.000

of deposits on the surface of the metal in this case exceeds the reference indicator by 1.15 times.

The difference in characteristics can be explained by the difference in the composition and morphology of the protective layers formed on the steel surface in the solution of the studied inhibitors. Known sodium polyphosphate is an inorganic polymer of linear structure having a complexing ability with respect to heavy metal cations.^[29] The effect of inhibiting sodium polyphosphate consists in the interaction of its hydrolysis product H_2PO_4^- ion with iron cations with the formation of poorly soluble hydrophosphates on the metal surface.

However, the rate of hydrolysis of polyphosphate decreases with an increase in its concentration, and polyphosphate anions can reduce the inhibition efficiency due to the formation of soluble complexes.^[29-31] Calcium-manganese phosphate, obtained on the basis of ore beneficiation wastes, consists mainly of calcium dihydro- and dihydrodiphosphates, which, under the conditions of the corrosion process, form insoluble hydrophosphates of calcium, iron and, possibly, manganese, enhancing the protective properties of the film. At the same time, polyphosphate anions forming soluble compounds are absent, which provides higher inhibition efficiency. Although sodium polyphosphates are still widely used in industrial systems due to their low cost and availability, there is now a growing demand for alternative inhibitors that provide high efficiency at lower phosphate loads.^[32-34] In this context, the use of $(\text{Ca}, \text{Mn})(\text{PO}_3)_2$ is a promising direction. Even at low concentrations (eg, 20 mg/L P_2O_5), it achieves an inhibition efficiency of 79%, significantly exceeding NaPO_3 at the same level (24.5%). In addition, the accumulation of surface deposits is noticeably lower at $(\text{Ca}, \text{Mn})(\text{PO}_3)_2$ in all tested concentrations, which minimizes the overgrowth of the inner surface of pipes with corrosion products, which is a key operational problem in water systems. These results confirm the development of multifunctional phosphate corrosion inhibitors based on manganese ore beneficiation wastes adapted to modern corrosion control strategies in the petrochemical, energy and water treatment sectors.^[5,7,25]

The morphological features of the surface deposits formed in water without additives, as well as in solutions containing the synthesized $(\text{Ca}, \text{Mn})(\text{PO}_3)_2$ inhibitor and sodium polyphosphate at concentrations of 50 mg/L and 100 mg/L (expressed as P_2O_5), were investigated using a HITACHI TM3030 scanning electron microscope (SEM) at 1500× magnification and an accelerating voltage of 15.0 kV. The corresponding results are presented in Fig. 1. Qualitative elemental analysis of the deposits was performed using the integrated Bruker XFlash MIN SVE microanalysis system, employing energy-dispersive X-ray spectroscopy (EDS). The weight percentages of the detected elements are summarized in Table 3.

According to the results, the deposits formed on the surface of the steel sample in distilled water without any inhibitors consist of grains of irregular shapes and sizes. Relatively large voids are observed between the grains, suggesting the formation of loose, uneven coatings with low protective capacity (Fig. 1a). Elemental mapping revealed that these deposits are composed predominantly of iron oxide compounds, with an Fe:O ratio of approximately 3.7:1. Calcium and phosphorus were not detected, while the presence of manganese, silicon, and chromium is attributed to the base composition of St3 steel (Table 3). Furthermore, the dendrite-like morphology of the inclusions indicates a rapid oxidation process on the metal surface, promoting accelerated surface growth and degradation.

The coating formed on the steel surface in a solution of calcium-manganese phosphate inhibitor $(\text{Ca}, \text{Mn})(\text{PO}_3)_2$ at a concentration of 50 mg $\text{P}_2\text{O}_5/\text{L}$ is formed by smaller grains of almost the same size and shape, which makes it possible to present the overall morphology more ordered and homogeneous (Fig. 1b), and explains the high protective properties of this inhibitor. In addition to iron compounds, the coating also contains calcium, phosphorus and manganese from mapping (Table 3), which confirms the participation of inhibitor components in the process of forming protective films on the metal surface, which help to reduce both the rate of corrosion and the formation of surface deposits.

Increasing the $(\text{Ca}, \text{Mn})(\text{PO}_3)_2$ inhibitor concentration to

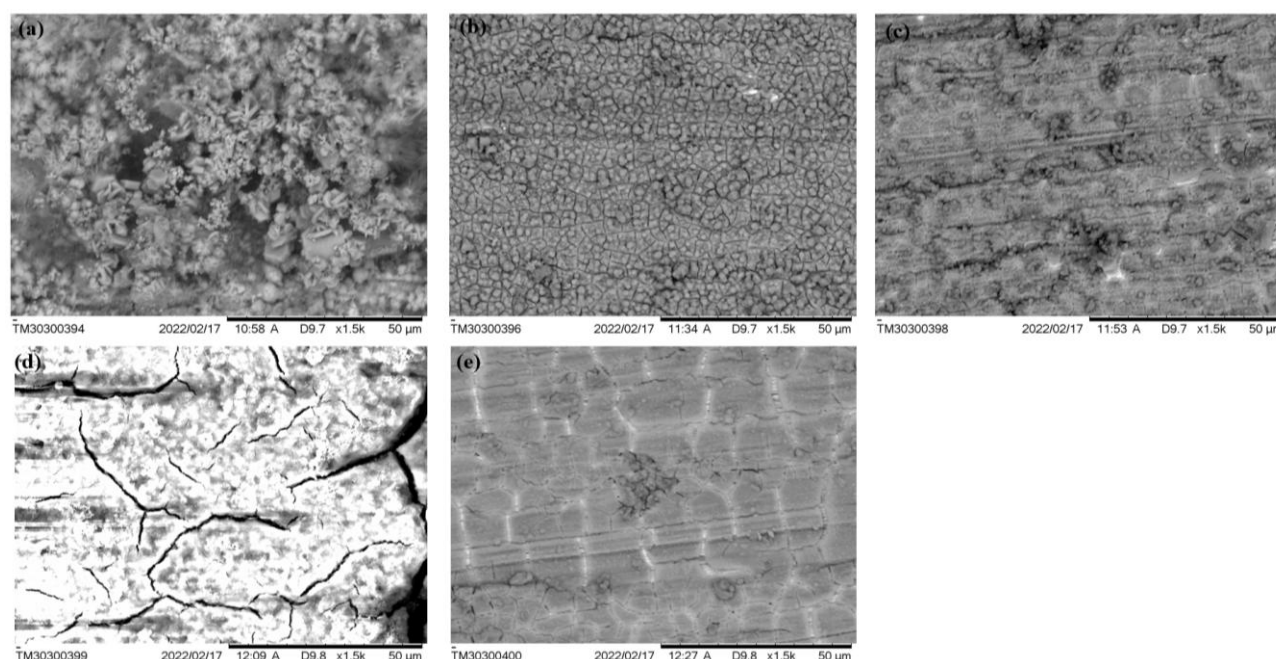


Fig. 1: SEM images of the surface of the studied coatings after corrosion tests: (a) water without inhibitor; (b) 50 mg/L of P_2O_5 $CaMn(PO_3)_2$; (c) 50 mg/L of P_2O_5 $CaMn(PO_3)_2$; (d) 50 mg/L of P_2O_5 $NaPO_3$; (e) 100 mg/L of P_2O_5 $NaPO_3$.

100 mg/L P_2O_5 leads, according to SEM analysis (Fig. 1e), to the appearance of isolated grains at certain points on the steel surface, and not to the formation of a continuous protective coating. The presence of these discrete inclusions indicates that the interaction of the inhibitor components with iron cations occurs at the most active places on the metal surface from the point of view of the corrosion process. Despite this microstructural change, no noticeable differences in surface morphology were observed on visual inspection. In addition, elemental analysis shows a significant decrease in the concentrations of the key components of the inhibitor in the coating: the content of calcium decreases by 2.7 times, phosphorus - by 1.9 times, manganese - by 1.25 times compared to the coating formed in 50 mg/L P_2O_5 of the solution of the same inhibitor (Table 3).

The EDS elemental mapping results from various corrosion tests conducted in water without inhibitor, and with 50 mg/L (as P_2O_5) of $(Ca, Mn)(PO_3)_2$, 100 mg/L (as P_2O_5) of

$(Ca, Mn)(PO_3)_2$, and 50 and 100 mg/L (as P_2O_5) of $NaPO_3$ are provided in the supplementary document (see Supporting information, Figs. S1a-e).

The coating formed on the steel surface in a solution of the commercial sodium polyphosphate inhibitor $NaPO_3$ at a concentration of 50 mg P_2O_5 /L, has a vitreous character (Fig. 1d), a rather high content of phosphorus (12.03 wt%) and calcium (4.05 wt%) in the absence of manganese (Table 3). The presence of calcium in the coating is probably due to deposits of calcium carbonate from natural water. The formation of such inclusions with the formation of a large number of microcracks on the surface of the resulting coatings indicates a decrease in the strength of the coating, as well as its brittleness as a result of corrosion processes. When the $NaPO_3$ concentration increases to 100 mg P_2O_5 /L, separate accumulations of small grains on the surface are also noted (Fig. 1e). The phosphorus content in the coating is reduced by half (Table 3), and calcium by 1.17 times.

Table 3: Elemental composition of deposits formed on the surface of steel specimens after soaking in water and solutions of phosphate inhibitors.

Corrosive environment	Elemental composition, wt. %								
	O	Fe	Ca	C	P	Mn	Si	Cr	Cl
Water without additives	20.66	76.60	0.0	1.85	0.0	0.52	0.13	0.24	0.0
$CaMn(PO_3)_2$, 50mg/L P_2O_5	37.10	43.08	4.48	3.06	11.80	0.99	0.10	0.0	0.0
$CaMn(PO_3)_2$, 100 mg/L P_2O_5	25.99	63.15	1.68	2.0	6.20	0.79	0.04	0.09	0.07
$NaPO_3$, 50 mg/L P_2O_5	49.07	30.90	4.05	3.60	12.03	0.0	0.25	0.08	0.02
$NaPO_3$, 100 mg/L P_2O_5	29.76	57.11	3.44	2.67	6.05	0.45	0.03	0.03	0.01

These findings from SEM/EDS analyses are consistent with the results of gravimetric and electrochemical tests (Figs. 2-3, Table 4). Electrochemical studies reveal that increasing the concentration of the synthesized $(\text{Ca,Mn})(\text{PO}_3)_2$ inhibitor leads to a positive shift in the corrosion potential by 122 mV, while the corrosion current density decreases by a factor of 2.2 at 1 mg/L P_2O_5 and by 11.7 times at 100 mg/L P_2O_5 (Fig. 2, Table 4). These results confirm the high protective efficiency of the $\text{CaMn}(\text{PO}_3)_2$ inhibitor, which can be attributed to the formation of stable, passivating films on the steel surface.

Previous studies also support the idea that manganese-containing phosphates improve steel passivation by forming stable surface films.^[26,27,35]

The dependence of the Inhibitor efficiency of sodium polyphosphate on its concentration is extreme. The current density decreases as the NaPO_3 concentration increases from 1 mg/L of P_2O_5 to 10 mg/L of P_2O_5 from $28.9 \mu\text{A}/\text{cm}^2$ to $10.7 \mu\text{A}/\text{cm}^2$. A further increment in concentration to 100 mg/L of P_2O_5 increases the current density to $26.96 \mu\text{A}/\text{cm}^2$, while the IE decreases to 32.68%.

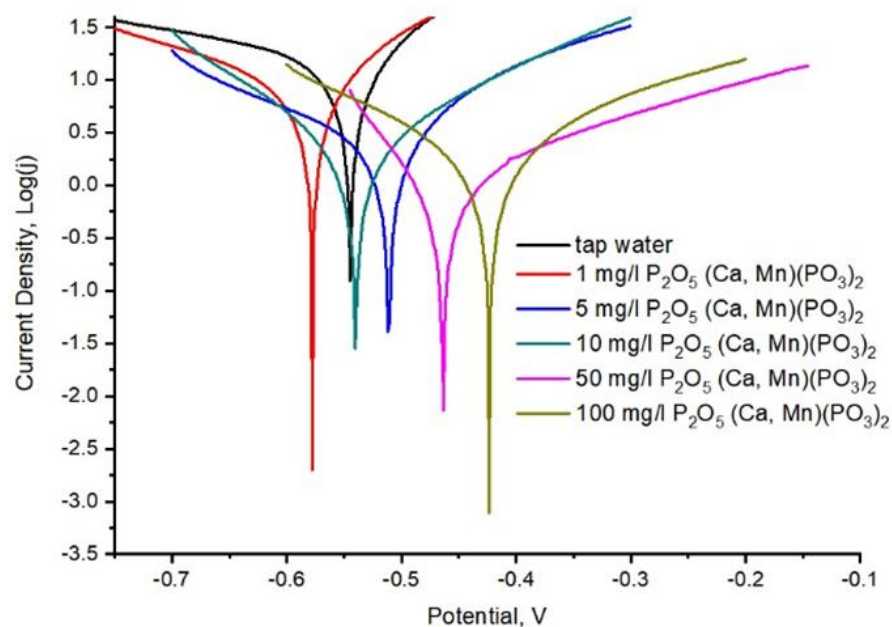


Fig. 2: Polarization curves taken for steel (St3) in water and in solutions of the synthesized $\text{CaMn}(\text{PO}_3)_2$ inhibitor.

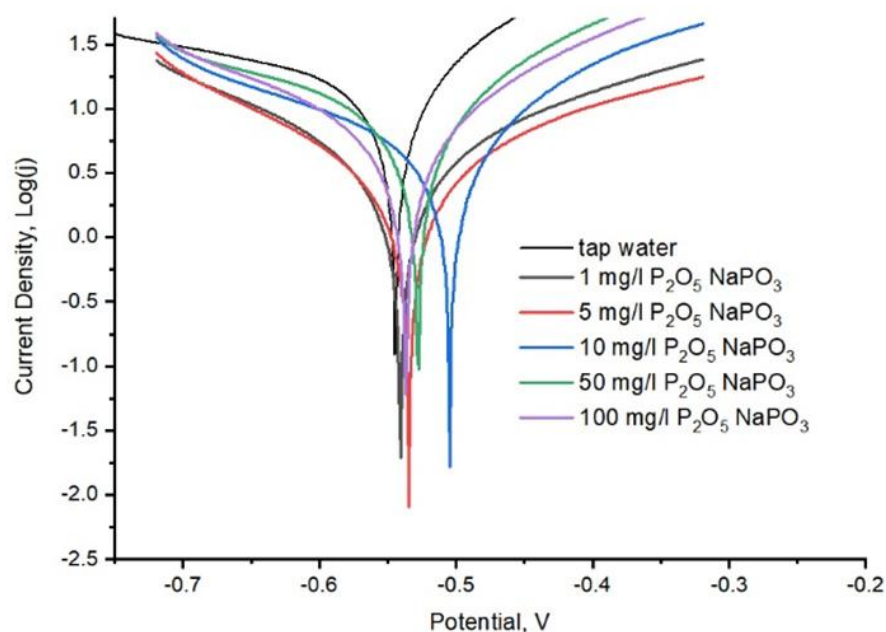


Fig. 3: Polarization curves taken for steel (St3) in water and in solutions of the known NaPO_3 inhibitor

Table 4: Indicators of corrosion resistance of steel during exposure to water and solutions of various inhibitors according to the results of electrochemical tests.

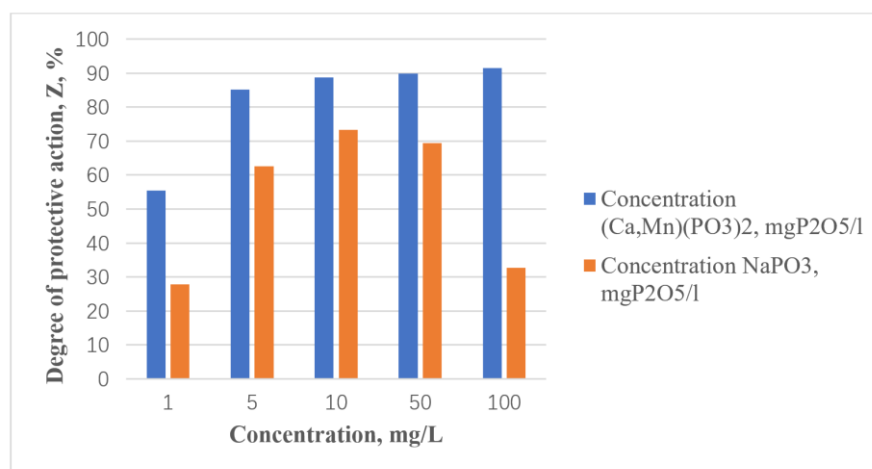
Corrosive environment	Inhibitor concentration, mg/L P_2O_5	Potential, V	Current density, $\mu A/cm^2$	Corrosion rate, mm/year	Inhibitor efficiency, IE %
Water without additives (control)	0.0	-0.545	40.047	0.469	0.00
	1.0	-0.578	17.860	0.207	55.40
	5.0	-0.512	5.946	0.069	85.15
$CaMn(PO_3)_2$	10.0	-0.540	4.487	0.052	88.80
	50.0	-0.464	4.090	0.047	89.79
	100.0	-0.423	3.425	0.040	91.45
	1.0	-0.603	28.9	0.335	27.8
$NaPO_3$	5.0	-0.566	14.996	0.158	62.6
	10.0	-0.561	10.700	0.124	73.28
	50.0	-0.537	12.250	0.142	69.41
	100.0	-0.594	26.960	0.313	32.68

For a more visual presentation of the results of the influence of the studied inhibitors on the corrosion resistance of steel samples, a histogram shown in Fig. 4 was constructed based on the data of electrochemical studies. The composition of the coatings formed on steel samples during exposure to sodium polyphosphate solutions, tap water, and $(Ca,Mn)(PO_3)_2$ inhibitor solutions was also studied by IR spectroscopy (see supporting information Fig. S2).

From the results of IR spectroscopic analysis, it follows that in water without inhibitors, a coating of hydrated iron oxide compounds is formed on the steel surface. On the IR spectrum (see supporting information Fig. S2B), a wide band is observed in the region of $3200-3400\text{ cm}^{-1}$, corresponding to the valence fluctuations of OH groups for iron compounds of the FeOOH goethite type which corresponds to literature results.^[36] The absorption band in the region $2340-2360\text{ cm}^{-1}$ indicates the presence of water in the microemulsion state. Bands in region $1430, 875, \text{ and } 712\text{ cm}^{-1}$ indicate the presence of calcite carbonate compounds. The IR data confirm the SEM/EDS analysis.

On the IR spectrum of the coating formed on steel in $(Ca,Mn)(PO_3)_2$ at a concentration of 50 mg/L of P_2O_5 , there are no absorption bands of calcite (see supporting information Fig. S2A). Although the presence of calcium in the coating is confirmed by energy dispersion analysis (Table 3). The main absorption bands at $2387, 1650, 1098, 903, 538, \text{ and } 467\text{ cm}^{-1}$ (see supporting information Fig. S2A) corresponds to hydrodiphosphates. This indicates the formation of protective coatings on the surface of the steel from calcium phosphates, and probably iron and manganese. Bands in region $3330, \text{ and } 3400\text{ cm}^{-1}$ correspond to the valence fluctuations of OH-groups, which are part of constitutional water in the hydrodiphosphate structure.^[36]

On the IR spectrum of coating formed on steel in a solution of sodium polyphosphate with a concentration of 50 mg P_2O_5/L , (see supporting information Fig. S2C) there are absorption bands corresponding to the valence fluctuations of hydrodiphosphates ($2387; 1650; 1098; 538 \text{ and } 467\text{ cm}^{-1}$).^[36] Absorption bands corresponding to polyphosphate anion fluctuations ($1120; 903; 796\text{ cm}^{-1}$) and carbonate ions due to

**Fig. 4:** Histogram of the Inhibitor efficiency of $NaPO_3$ and the proposed $CaMn(PO_3)_2$ inhibitor depending on the concentration.

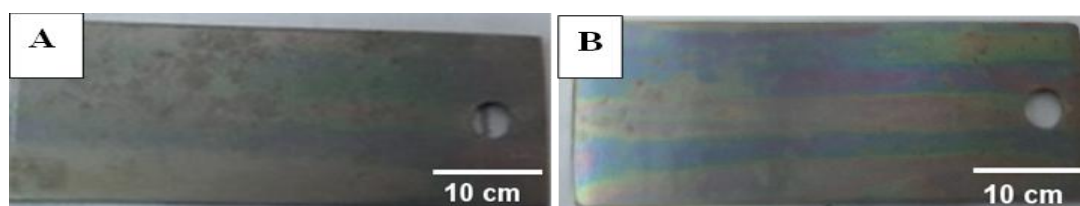


Fig. 5: Steel surface samples after soaking in solutions of $\text{CaMn}(\text{PO}_3)_2$ inhibitor at a concentration of 100 mg/L of P_2O_5 .

calcite (1430 ; 710 cm^{-1}) are also present. The presence of calcite CaCO_3 explains the presence of calcium in the SEM/EDS analysis (Table 3), but does not contribute to the protective properties of the resulting coating. An increase in the concentration of NaPO_3 to 100 mg/L of P_2O_5 forms a layer on the surface of the steel containing, in addition to hydrodiphosphates, polyphosphates. On the IR spectrum absorption bands are present in the region 1294 ; 1123 ; 1102 ; 901 ; 796 ; 672 cm^{-1} (see supporting information Fig. S2D).^[6] Polyphosphates with the ability to form soluble complexes with metal cations can probably explain the decrease in the degree of protective effect of NaPO_3 with an increase in its concentration.

An IR spectroscopic study of the composition of films formed in solutions of $(\text{Ca,Mn})(\text{PO}_3)_2$ inhibitor at a concentration of 100 mg/L of P_2O_5 was not possible due to the impossibility of removing the film mechanically. Visually, on the surface of the samples after exposure to these solutions, an interference pattern was observed, indicating the formation of a very thin protective film (Fig. 5). Although the results of energy dispersive analysis (Table 3) indicates the presence of calcium, iron and phosphorus compounds in the film.

Thus, tests have shown that the $(\text{Ca,Mn})(\text{PO}_3)_2$ product synthesized on the basis of manganese ore enrichment wastes of the Zhairem deposit has high inhibitory efficiency even in the region of low concentrations (1 mg/L of P_2O_5). This makes it possible to recommend this product for corrosion protection of the inner surface of steel pipelines of various domestic and potable water supply systems.

4. Conclusion

- The study demonstrates the significant anticorrosive properties of calcium-manganese phosphate $\text{CaMn}(\text{PO}_3)_2$ obtained from manganese ore enrichment wastes of the Zhairem deposit in protecting low-carbon steel in neutral aqueous environments. The findings reveal that calcium-manganese phosphate effectively reduces the corrosion rate of mild steel across the tested concentration range from 1.0 to 100.0 mg/L of P_2O_5 .
- At a concentration of calcium-manganese phosphate 50.0 mg/L of P_2O_5 , steel corrosion is almost entirely prevented, achieving an impressive inhibitor efficiency of 98.2%, in stark contrast to the 41.1% efficiency of sodium polyphosphate at the same concentration. Additionally, the compound significantly minimizes the accumulation of corrosion-salt deposits, which becomes negligible at 50 mg/L of P_2O_5 .

- Electrochemical analysis further confirms the inhibitor's effectiveness, as an increase in concentration leads to a positive shift in the corrosion potential and an 11.7-fold reduction in corrosion current density at 100 mg/L of P_2O_5 . These results underscore the strong inhibitory effect of $\text{CaMn}(\text{PO}_3)_2$.

- Morphological studies and elemental mapping reveal enhanced steel surface resistance against degradation, with the formation of passivating coatings or inclusions that slow down corrosion and deposit accumulation.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

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