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NATURAL SCIENCES

PHYSICOCHEMICAL PROPERTIES OF CORROSION INHIBITION OF STEELS AND THE FORMATION OF MINERAL SALT DEPOSITS.

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Abstract: The work investigated the physicochemical properties of import-substituting and export-oriented new composite corrosion inhibitors of St.3 and St20 steels, and it was found that with an increase in the inhibitor concentration from 0.1% to 1.0% in aqueous, acidic, and neutral environments, the degree of corrosion protection was 96.2÷99.8%. Thermodynamic values (Δ H, Δ S, Δ G) were calculated, and the effective activation energy value of 28.5-47 kJ/mol was determined based on the dependence of IgK-1/T. The synthesized composite corrosion inhibitors were tested on the equipment and pipelines of the Shurtan Gas Chemical Complex for anti-corrosion properties, including the prevention of mineral salt deposits, by comparing the productivity of "Option" and "Nalco" brand inhibitors supplied from abroad.

Synthesized composite corrosion inhibitors with the participation of zinc oxide, glycerin, caustic soda, sodium hydroxide, and the distillation residue of methyl ethyl ammonium reagents based on oxyethylene phosphonic acid, the composite inhibitor were tested on equipment and pipelines of the Shurtan Gas-Chemical Complex for anti-corrosion, including to prevent the

formation of deposits of mineral salts, comparing the performance of inhibitors brands "Option" and Nalco, supplied from abroad.

Keywords: inhibition, thermodynamics, corrosion of steel, inhibitor, a protective mechanism, activation energy, Gibbs energy, corrosion rate, hydrogen sulfide.

POʻLATLAR KORROZIYASINING TOʻXTATILISHI VA MINERAL TUZLAR YOTQIZILMALARI HOSIL BOʻLISHINING FIZIK-KIMYOVIY XOSSALARI.

Annotasiya: Mazkur ishda import oʻrnini bosuvchi va eksport qilishga yoʻnaltirilgan yangi kompozitsion ingibitorlarini St.3 va St.20 markali poʻlat na'munalarini korroziyalanishi jarayonining fizik-kimyoviy xossalari tadqiq qilingan. Suvli, kislotali va neytral muhitda olib borilgan jarayon-larda ingibitorlar konsentratsiyasi 0,1% dan 1,0% gacha oshirilganida korroziyadan himoyalash koʻrsatkichi 96,2÷99,8% ni tashkil etdi. Ushbu sharoitlarda adsorbsiya jarayonining termodinamik kattaliklar (Δ N, Δ S, Δ G) hisoblandi va IgK-1/T bogʻlanish asosida effektiv aktivlik energiyasini qiymati 28,5-47 kJ/mol ekanligi aniqlandi. Sintez qilingan kompozit tarkibliyangi ingibitorlar SHoʻrtan GKMni uskunalari va quvurlarida korroziyaga qarshi sinovdan oʻtkazildi va chet eldan import qilinadigan "Option" va "Nalco"markali ingibitorlar bilan taqqoslandi.

Kalit soʻzlar: tormozlanish, termodinamika, poʻlat korroziyasi, ingibitor, himoya mexanizmi, aktivlanish energiyasi, Gibbs energiyasi, korroziya tezligi, vodorod sulfid.

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ТОРМОЖЕНИЯ КОРРОЗИИ ПОЛОТ И ОБРАЗОВАНИЯ МИНЕРАЛЬНЫХ СОЛЕЙ.

Аннотация: В работе исследована физико-химические свойства импортозамещающих и экспортоориентированных новых композиционных ингибиторов коррозии сталей Ст.3 и Ст20и найдено, что, при увеличении концентрации ингибиторов с 0,1% до 1,0% в водной, кислой и нейтральной среде степень защиты от коррозии составил 96,2÷99,8%. Рассчитаны термодинамические ве-личины (ΔH , ΔS , ΔG) и по зависимости IgK-1/T была определеназначение эффективной энергии активации 28,5-47 кДж/моль. Синтезированные компо-зитные ингибиторы коррозии были испытаны на оборудовании и трубопро-водах Шуртанского ГХК на антикоррозию, в том числе на предотвращение образования отложений минеральных солей, сравнивая производительность ингибиторов марок "Option" и "Nalco", поставляемых из-за рубежа.

Ключевые слова: торможение, термодинамика, коррозия стали, ингибитор, защитный механизм, энергия активации, энергия Гиббса, скорость коррозии, сероводород.

INTRODUCTION.

Metal corrosion and its prevention represent a pivotal nexus of scientific, technical, and economic challenges worldwide. The toll of metal corrosion in industrialized nations alone

accounts for significant losses, typically ranging between 2 to 4% of the gross national product. Today, on a global scale, the quest for effective corrosion inhibitors and protective coatings demands rigorous scientific inquiry into their physical and chemical attributes. Enhancing the stability of inhibitors and advancing methodologies for crafting multi-component composite inhibitors tailored to combat metal corrosion stand at the forefront of current research endeavors [1-3]. After conducting research on an industrial scale in the Republic of Uzbekistan, significant strides have been made in understanding the impact of inhibitors on metal equipment corrosion. These newly formulated universal anticorrosion inhibitors are not only safe to apply but also promise enhanced efficiency.

The prospect of deriving inhibitors from local raw materials and industrial by-products appears particularly promising. This approach aims to bolster the wear resistance and long-term functionality of technological equipment and pipelines operating within highly aggressive environments. Notably, organic compounds containing nitrogen, amine, and oxygen exhibit substantial effectiveness in neutral and mildly alkaline settings [4-8]. Additionally, zinc organophosphorus acids have emerged as potent agents, adept at averting corrosion and mineral salt deposition on equipment surfaces [9-10].

The republic's demand for this type of inhibitor is more than 5,000 tons per year [11-13]. Therefore, the purpose of this work was to create new export-oriented corrosion and mineral salt deposition inhibitors based on local raw materials and production waste and to study their physicochemical and inhibitory properties.

LITERATURE REVIEW AND METHODS. The object of the study is multi-component composite inhibitors created on the basis of nitrogen, amine, and phosphorus-containing substances and the subject of the study includes the study of common patterns of mechanisms for the use of inhibitors for anti-corrosive protection and against the layering of mineral salts of steel samples using modern methods of physicochemical analysis. The materials for the study were samples in the form of metal plates made of steel grades St.3 and St.20. The effect of nitrogen and phosphate-containing inhibitors on the corrosion rate of St.3 and St.20 steels was studied by means of the gravimetric method in a model environment using a $5 \cdot 10^{-3}$ mol/l H₂SO₄ solution (background). In addition, the experiments were carried out in 1-3% aqueous solution of NaCl, NaOH, and 1–3% Na₂S solution in the presence of H₂S. The duration of the tests was 48 and 760 hours. Inhibitors were synthesized on the basis of local vat waste from the industries of the Republic of Uzbekistan, namely the vat residue of mono-ethanolamine, large-tonnage waste produced by JSC JV "MaxamChirchik" and JSC "Fergana Azot". Inhibitors are transparent liquid masses, highly soluble in aqueous and acidic media. During storage, the formation of an independent phase is not observed. It works effectively both in soft and hard water (total hardness is 2-18 mg-eq / 1; in different regions of the republic, water hardness is in this range).

RESULTS AND DISCUSSION Experimental data on the study of the polarization curves of inhibitors showed that their correlation from concentration and temperature to the anti-

corrosion protection level of steel samples of substance 3 and substance 20, with and without inhibitors, was synthesized on the basis of used composite inhibitors, local raw materials and production waste with nitro-gen, Amine, and phosphorus have a degree of protection at 25°C At 88.5÷94.4% and 40÷50°C, this figure will be equal to the value of 89.0÷99.7% in the range. If the process temperature rises to 70°C, then the degree of corrosion protection begins to decrease slightly to the values of 99.3-90.4%. With the introduction of nitrogen-, amine, and phosphorus-containing inhibitors into the solution, the value of the electrode potential changes in a positive direction, which indicates a slowdown in the anode reaction.

When the concentration of inhibitors increased from 0.1% to 1.0% while conducting the process in an aqueous, acidic, and neutral environment using a gravimetric method in terms of time, temperature, inhibitor concentration, and other indicators, the anti-corrosion protection indicator was found to be 96.2÷99.8%. The degree of anti-corrosion protection of Nalco brand inhibitors imported to our Republic is 87.6% at a temperature of 80°C. Based on the calculation data, it was found that acidic, hydrogen sulfide solutions depend on the temperature in the presence of thermodynamic properties in the phases and inhibitors in the process of metal corrosion process, so with an increase in temperature, the adsorption of the metal surface remains almost unchanged. It was found that an increase in the concentration of inhibitors in both cases affects the effectiveness of corrosion inhibition. The γ -lgC indices obtained on the basis of these experiments in the form of dependent lines showed that when the inhibitor was injected into a 3% Na₂S solution (with 500 mg/l H₂S), a layer (film) formed on the surface of the metal sample.

In the work, the value of the effective corrosion activation energy ΔE_{eff} was determined on the basis of the temperature dependence according to the formula: ΔE_{eff} =-2.3 R.tga.It is known that inhibition of acid corrosion of metals by organic compounds is mainly related to surface protection and activation factor (increase in the activation energy of the corrosion process in the



presence of inhibitors compared to the background). Graphs of the lgK-1/T dependence were drawn to calculate the activation energy (Fig.1)

Fig.1. Dependence of lgK on the reverse temperature of the corrosion process of steel grade St.3. and St.20: 1-Background; 2-S_{inh}-1.0 mol/l; 3-S_{ing}-1.25 mol/l; 4-S_{inh}-2.5 mol/l; 5-S_{inh}-5.0 mol/l; 6-S_{inh}-10.0 mol/ l.

Studies on the corrosion of St. 3 and St.20 in acidic solutions in the presence of inhibitors containing amino and phosphate groups have shown their high efficiency. Phosphate-diethylaminoethylmethacrylate has been recognized as the best corrosion inhibitor among alkylamines under the studied conditions, due to a large number of radicals in its molecule and their size, as a result of which the necessary protective concentration of this inhibitory system is minimal compared to other studied amines. According to the dependency graph of IgK-1/T with the value of the slope angle tangent, the energy of effective activity was calculated ($E_{act} = 2.3$ Rtga). It was found that the E_{act} value is 28.5-47 kJ/mol. The indicators of E_{act} , Δ H, and Δ S of multicomponent composite inhibitors containing nitrogen, amine, and phosphorus in strong acid environments have been established. The results are shown in Table -1

Table-1

Sampleofalloys	Inhibitionbackground	Eakt	ΔΗ,	ΔS,
		kJ/mol	Dj/mol	Dj/mol
St. 3	3% H ₂ SO ₄	39,88	37,48	70,49
St. 20		76,54	-41,82	48,64
St. 3	H ₂ Swith involvement	37,48	38,25	69,75
St. 20	$3\% \text{ Na}_2\text{S}$	59,56	-70,04	39,51

Thermodynamic values of corrosion in conditions of 3% Na₂S solution with the participation of 3% H₂SO₄ and H₂S alloy grade St. 3

From the results obtained, it was found that in the process of corrosion of steel grade St.3 in conditions with placed and not placed inhibitors in an acidic environment, the indicators of E_{act} and ΔH were almost close to each other. The obtained results provide a good explanation for the fact that, according to the Langmuir isotherm, the high degree of filling of the metal surface is directly proportional to the dependence of the adsorption process on the concentration of nitrogen, amine, and phosphorus-containing composite inhibitors. Also, the rate of dissolution (K) of metal samples depends on the content of inhibitors and even if the inhibitor is with a low concentration, the degree of corrosion resistance will be 96-99.6%. When a composite inhibitor

is introduced into a condition of 3% H_2SO_4 solution in the temperature range of 298÷343K, the values of the Gibbs energy index Δ Gads change from -48.24 kJ / mol-1 to -42.52 kJ / mol-1.

Isotherms, thermodynamic and kinetic properties of the process have been studied to establish the nature of adsorption purification of HMI and NP using the obtained ferritizedCSM. In the process of purification of solutions containing TM ions, not only reagent purification takes place, and therefore the processes of adsorption and desorption of HMI using FRS have been studied. The time to establish sorption equilibrium was 15-20 minutes, at a solution temperature of 20-25°C, the amount of sorption material was 10 g/dm³. According to the BET theory, the shape of the adsorption isotherm of HMI compounds (Fig.1) on the surface of minced meat corresponds to the formation of a monomolecular layer, with the participation of micro-and macropores. Since the desorption curve is low, in this case the sorption interaction is close to the chemical nature. To obtain more complete information about the mechanisms of interaction between the sorption material under study and the sorbate, the interaction energy was calculated in a similar way to previous experience. The adsorption isotherms of the studied interactions are shown in Fig.2. The value of the tangent of the angle of inclination of this dependence (tgx) (Fig.2) calculated by the formula: $tgdx = \frac{\Delta IuC_{raw}}{\Delta_T^{-1}t_0^{-3}}$ is equal to 0.0068 for HMI

ions. The calculated values of the adsorption energy were: $\Delta H_{agc} = tgr*R = 0.0068*8.314*10^3 = 0.05654 dj/mol = 56.54 kJ/mol.$

The results of gravimetric studies and calculations of the values of the corrosion rate and the degree of protection by inhibitors of composite inhibitors at different concentrations and duration of corrosion tests are shown in Table 2.

As illustrated in Table 2, the presence of a 1.0 % inhibitor solution in acidic and sulfurcontaining media yielded the most successful results. Thus, depending on the duration of corrosion tests, the degree of protective action of the composite inhibitor varies from 82.3 to 96.7%.



Fig.2.- Isotherms of HMI adsorption on CSM at different temperatures.

Table-2

Backgrounds	Scia-1, %	240 h	ours	360 h	ours
3% solution H ₂ SO ₄	0	$\frac{C_{SK}}{g/m^2 \cdot day}$	X, %	$\begin{array}{c} C_{SK} \\ g/m^2 \cdot day \end{array}$	Х, %
	0,001	5,05	-	3,47	-
	0,01	3,32	82,3	2,37	85,8
	0,1	2,50	89,5	1,93	91,7
	1	2,28	92,9	1,44	92,1
1 % solution H ₂ S	0	0,24	-	1,39	
	0,001	0,21	83,2	0,80	87,3
	0,01	0,18	91,4	0,69	93,1
	0,1	0,09	92,6	0,26	94,3
	1	0,06	92,9	0,05	96,7

The effect of the concentration of composite inhibitors and the duration of corrosion tests on the protection efficiency of St.3 and St.20 steel grades at 40°C

The nature of the degree of corrosion protection of carbon steel st.3 in solutions of H_2SO_4 and hydrogen sulfide is approximately the same. In the first 360 hours, the mass loss from corrosion increases approximately linearly and then significantly decreases. This is due to the formation of passive films on the metal surface, which slow down the diffusion of oxygen to the metal surface. Experimental data confirm that corrosion with hydrogen polarization in acidic environments significantly exceeds corrosion in steel St.3 with oxygen depolarization in neutral and alkaline environments.

The results of studying the dependence of the corrosion rate of steel St.3 in the background Na2S solution on the concentration of CI are shown in Fig.2.1. and 3.1. Fig. shows that the corrosion rate drops sharply to 0.33 g / (m2 h), after which there is a slight increase in it. After a certain time, the nanocrystals on the surface dissolve completely and the corrosion process becomes uniform. Data on the corrosion rate are consistent with the obtained values of the braking coefficient in various (acidic and neutral) media. Composite inhibitor in Na2S solution is the most effective inhibitor of hydrogen sulfide corrosion of St.3

steel. Therefore, in order preserve steel St.3 from corrosion in acidic, neutral, and hydrogen sulfide environments, it is possible to apply the CI inhibitors IKA-1 and IKA-2. Particularly, IKA-1 is recommended for hydrogen sulfide environments.

Fig 3. Corrosion rate in 1M Na₂S concentration of inhibitors 10-2 M. 1. Background; 2-10-2 M solution.



The thermodynamic properties of the metal surface adsorption process in the alkaline-salty environment of the composite inhibitor were calculated (Table-2), and the Langmuir adsorption isotherms of the composite inhibitor in the alkaline-salty environments were studied. The relationship between the process temperature along the directions of the Langmuir adsorption isotherm in alkaline-salty aggressive environments of steel grades St.3 and St.12 at a temperature range of $298 \div 343$ K with nitrogen, amine, and phosphorus-containing inhibitors have been found to have different degrees of anticorrosion protection of metal samples.



Fig 4. Corrosion rate in 1M Na₂S concentration of inhibitors 3·10-2 M: 1-Background; 2-3 10-2 M solution of KI-1; 3-3 10-2 M solution.

Based on the task of import-substitution of inhibitors, the inhibition process and its physicochemical properties were studied to prevent the formation of deposits of mineral salts

and the anticorrosion of metals. The results showed that with an increase in the concentration of inhibitors, the effectiveness of their anti-corrosion protection also increased, and the best degree of protection was achieved in a 1% solution. According to this result, it was found that with an increase in the number of molecules, the degree (amount) of adsorption on the surface of the metal platinum of the inhibitor also increases, but at the same time, there is a noticeable change since the inhibitor with a low concentration also retains its protective effectiveness. In particular, for the 0.001% concentration of the 298K composite inhibitor, the corrosion resistance of the metal reaches 87.4%, if the concentration is increased to 1%, this indicator becomes 90.8%, against the background of the H₂SO₄ solution. 92.9%, and 92.9÷99.4% against the back-ground of H₂S solution. At the same time, a rise in the processing time from 240 to 360 hours increases the degree of corrosion resistance to 92.9-96.7%. This indicates that there are multiple phases on the metal surface and that they do not dissolve simultaneously. Under the background conditions of the H_2S solution, the corrosion rates of the steel sample of grade St.3 are approximately the same in 3-4 hours, and this proves that the corrosion process in very aggressive environments occurs at a very fast speed. When the inhibitor concentration increases from 0.001 to 1%, the protection efficiency of the applied inhibitor increases, respectively, from 92.3% to 99.2%. This change is also observed at temperatures of 313, 323, and 343 K. Based on the conducted studies, a probable mechanism of protective action of a composite corrosion inhibitor in alkaline-salt and hydrogen sulphuric conditions in the presence of St.3 is proposed (Fig.2-3).

Synthesized composite corrosion inhibitors are used to prevent corrosion of equipment and pipelines of the Shurtan Gas Chemical Complex and were compared with imported "Option" and "Nalco" brand inhibitors (table-3).

To calculate the thermodynamic constants of the HMI adsorption processes on the KSM, isotherms were processed at various temperatures: $20 \pm 10C$; $35 \pm 1^{\circ}C$ and $45 \pm 1^{\circ}C$ and the value of the adsorption energy (E_{ads}, kJ/mol) was calculated according to the Dubinin–Radushkevich model. The values of the calculated thermodynamic quantities for the studied processes are presented in Table -3.

In this case, with an adsorption energy value of less than 8 kJ/mol, physical adsorption takes place, with adsorption energy values from 8.0 to 18.0 kJ/mol of chemisorption.

Table-3

The values of thermodynamic values of ITM adsorption on the sorption material.

ИТМ	рН	T,°C	Eads,	$\Delta \boldsymbol{G}^{\circ}$,	$\Delta H^{\circ}, \mathbf{kDj}$	ΔS° ,(Dj/mol
	environment		крј/шог	kDj/mol	/mol	*K)
Ni (II)	Neutralenviro nment	20	9,34	-6,89		78,9
		35	9,42	-8,01	16,5	79,8

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		45	9,63	-9,24		80,1
		20	9,18	-6,45		81,3
	Acidicenviron ment	35	9,24	-7,01	18,3	82,1
		45	9,43	-7,98		81,9
		20	10,33	-8,64		91,4
	Neutralenviro nment	35	11,28	-10,01	20,1	92,4
Cu		45	11,86	-9,98		90,3
(II)		20	9,95	-8,04		101,5
	Acidicenviron ment	35	9,88	-8,34	21,7	99,2
		45	10,41	-8,91		98,6
	Neutralenviro n-ment	20	12,43	-6,72	39,8	169
Cr (VI)		35	13,51	-9,67		171
		45	13,98	-10,15		170
	Acidicenviron ment	20	13,01	-7,33		175
		35	14,29	-8,91	43,4	191
		45	15,48	-10,1		189
		20	9,01	-6,43		96,5
Zn (II)	Neutralenviro nment	35	8,86	-7,38	29,9	99,4
		45	9,34	-8,55		98,3
	Acidican	20	8,77	-8,32		97,8
	ment	35	9,05	-9,04	32,3	101,2
		45	8,99	-9,18		99,3

Based on the values of the calculated adsorption energy, it is possible to assume the nature of the forces of interaction of metal ions with the active centers of the surface of the CSM and make the assumption that this process is a physical adsorption or the interaction is accompanied by a chemical reaction. In this case, with an adsorption energy value of less than 8 kJ/mol,

physical adsorption takes place, with adsorption energy values from 8.0 to 18.0 kJ/mol of chemisorption.

Synthesized composite corrosion inhibitors with the participation of zinc oxide, glycerin, caustic soda, sodium hydroxide, and the distillation residue of methyl ethyl ammonium reagents based on oxyethylenephosphonic acid, the composite inhibitor were tested on equipment and pipelines of the Shurtan Gas-Chemical Complex for anti-corrosion, including to prevent the formation of deposits of mineral salts, comparing the performance of inhibitors brands "Option" and Nalco, supplied from abroad. The results of tests on SGCC are shown in table-4.

Table-4

Thermodynamic values of surface adsorption of metal samples in a medium of 3%NaOH + 3%NaCI solution of a composite inhibitor

(allow sample St 3 Sing-100mg/l)

(anoy sample 50.5, Sing-Tooligh)						
Temperature,	Cads,	$\Delta \mathbf{G}_{\mathrm{ads}}$,	ΔH_{ads} ,	ΔS_{ads} ,		
Κ	Mol ⁻¹	kDj/mol	Dj/mol	Dj/mol*K		
298	$7,4.10^{5}$	-50,94	-79,25	97,54		
313	$7,8.10^{5}$	-49,58	-79,56	96,98		
323	$5,4.10^{5}$	-48,86	-78,49	96,31		
343	$3,2.10^{5}$	-46,78	-78,80	96,44		

Synthesized composite corrosion inhibitors with the participation of zinc oxide, glycerin, caustic soda, sodium hydroxide, and the distillation residue of methyl ethyl ammonium reagents based on oxyethylene phosphonic acid, the composite inhibitor were tested on equipment and pipelines of the Shurtan Gas-Chemical Complex for anti-corrosion, including to prevent the formation of deposits of mineral salts, comparing the performance of inhibitors brands "Option" and Nalco, supplied from abroad. The results of tests on SGCC are shown in table-5.Based on the results of the tests, it was found that the applied composite inhibitor used in industry, increases the degree of protection of steels against corrosion up to $97.8 \div 98.4\%$.

Table-5

Indicators of the degree of protection against corrosion of nitrogen, amine, phosphorusinhibitors

and a set of the set o					
Compositions	Corrosioninhibition	Efficiency from the for-			
ofinhibitors	efficiency, %	mation of mineral salts,%			
1	97,8	94,8			
2	96,8	95,2			
3	98,4	97,7			

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4	93,3	92,5
5	91,5	88,6
Comparison inhibitor of	96,6	90,1
the brand"Option"		

CONCLUSION.Based on our research findings, it is evident that all metal structures, equipment, pipelines, and other technological installations operating in aggressive environments necessitate robust corrosion protection measures.

Our investigations have revealed that the application of composite inhibitors on steel surfaces (e.g.,St.3 and St.20) adheres to Langmuir's law, forming pro-tective layers that inhibit metal corrosion. The activation energy for steel plates St.3 and St.20 in the presence of inhibitors has been determined under these conditions. Through the assessment of thermodynamic functions (Δ H, Δ S, Δ G), we have ascertained a negative Gibbs energy value (Δ G_{eff}). Among alkylamines studied, phosphate diethylamino-ethyl methacrylate emerges as a superior corrosion inhibitor due to its molecular structure's radical abundance and size, necessitating minimal protective concentrations compared to other amines.

Our study further delves into mechanisms and benchmarks for inhibiting metal corrosion and preventing mineral salt deposition in acidic, hydrogen sulfide, salt-alkaline, and aqueous aggressive environments. By utilizing inhibitors developed using zinc-containing oxyethylenediphosphonic acid (HEDP), distillation residues of monoethanolamine, paraffin, and gossypol resin, we have observed a 2-6% increase in efficiency in inhibiting mineral salt accumulation and enhanced metal corrosion protection up to 98.4%.

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