

## **DEVELOPMENT AND FIELD VALIDATION OF LOW-MOLECULAR-WEIGHT AMINE-BASED COMPOSITE INHIBITORS FOR THE SIMULTANEOUS PREVENTION OF CORROSION AND SCALING IN INDUSTRIAL RECIRCULATING WATER SYSTEMS: A CASE STUDY OF THE SHORTAN OIL AND GAS PRODUCTION ENTERPRISE**

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### **ABSTRACT**

*Corrosion of carbon-steel equipment in open recirculating (cooling-tower) water systems is one of the most persistent technological and economic problems of the oil-and-gas, chemical and power industries, shortening the service life of pipelines, heat exchangers and pumps and forcing premature capital expenditure. This paper reports the development, laboratory characterization and industrial-scale validation of a family of low-molecular-weight amine-based composite inhibitors (designated AD-1, AD-2 and AD-3) intended for the simultaneous suppression of electrochemical corrosion and mineral scaling in the recirculating cooling-water system of the Shortan Oil and Gas Production Department (Kashqadarya region, Uzbekistan). The inhibitors were synthesized from locally available amine raw materials; the influence of temperature, reaction time and reagent mass ratios on the reaction yield was established. Inhibition efficiency was quantified gravimetrically on St3 steel coupons in accordance with GOST 9.905-82 across fourteen aggressive model media (cooling-tower water, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S, NaHCO<sub>3</sub>, NaClO, Na<sub>2</sub>CO<sub>3</sub>, KCl, MgSO<sub>4</sub>, CaCl<sub>2</sub>, CaCO<sub>3</sub>, CaSO<sub>4</sub> and mixed salts) at inhibitor dosages of 1-3 %. Surface films were characterized by scanning electron microscopy (SEM, Zeiss EVO MA 10) coupled with energy-dispersive X-ray spectroscopy (EDS). In aqueous medium the protection degree of AD-1 reached 98.6 %, and values of 91-98 % were recorded across the sulphate, sulphide and chloride media; the minimum corrosion rate fell to 0.004 g·cm<sup>-2</sup>·h<sup>-1</sup> and the maximum protection degree across all media reached 97.6 %. An integrated corrosion-risk coefficient ( $K_k$ ) was formulated to describe the combined action of ionic composition, dissolved gases, temperature and hydrodynamics of the Shortan water, predicting corrosivity with 15-20 % accuracy where the classical Langelier and Ryznar indices proved insufficient. Under industrial trials the optimized composite reduced the corrosion rate by 85-97 % and mineral scaling by 60-75 % at an optimal dosage of about 1 %, extending equipment*

service life by 8-12 % and yielding an economic effect of approximately 19 % through import substitution based on local raw materials.

**Keywords:** recirculating water system; carbon-steel corrosion; amine-based composite inhibitor; protection degree; gravimetric method; scanning electron microscopy; corrosion-risk coefficient; Shortan oil and gas enterprise.

## 1. INTRODUCTION

Recirculating (oborotnye) water-supply systems are closed or semi-closed hydraulic loops that perform heat exchange, cooling and process-stabilization functions in industrial enterprises. Because the water acts as an energy carrier in continuous circulation and remains in direct or indirect contact with technological equipment, its physico-chemical composition is not static but continuously changing. Temperature, pressure, dissolved gases, ionic content and flow velocity directly influence the stability of the medium, and any disturbance of their equilibrium becomes the primary cause of corrosion, scale formation and biofouling. On a global scale these processes markedly shorten the operational life of technological equipment, restrict the rational use of energy and water resources, and adversely affect the technical and economic indicators of industrial enterprises, thereby demanding the development and practical introduction of advanced, resource-saving technologies.

In open cooling systems the continuous evaporation of water raises the degree of mineralization, and this increase in turn strongly affects the corrosion rate, the intensity of biological growth and the composition of deposits. Under the conditions of the Shortan gas-chemical complex, evaporation in the cooling towers concentrates the salt content of the circulating water by a factor of two to eight; the sharp rise of total dissolved solids and chlorides increases the corrosion rate three- to fivefold. Field monitoring at Shortan shows electrical conductivity rising from  $2\text{-}3\text{ mS}\cdot\text{cm}^{-1}$  in the make-up water to  $5\text{-}8\text{ mS}\cdot\text{cm}^{-1}$  after three to four circulation cycles, and chloride concentration climbing from  $120\text{-}350\text{ mg}\cdot\text{L}^{-1}$  to  $400\text{-}700\text{ mg}\cdot\text{L}^{-1}$ . Chloride ions are the principal activators of localized (pitting) corrosion, while dissolved oxygen accelerates the anodic-cathodic coupling of iron and increases the corrosion rate ten- to fifteenfold, and carbon dioxide lowers pH and promotes carbonic-acid corrosion.

Chemical (reagent) treatment of the circulating water is the most effective and accessible route to prevent these undesirable phenomena, since it requires no significant capital investment and the reagent preparation and dosing units are simple and reliable in operation. Among reagents, corrosion inhibitors form a protective film on the metal surface, modify the chemical activity of the medium (for example by raising pH or reducing ionic activity) and form complexes with metal ions that slow

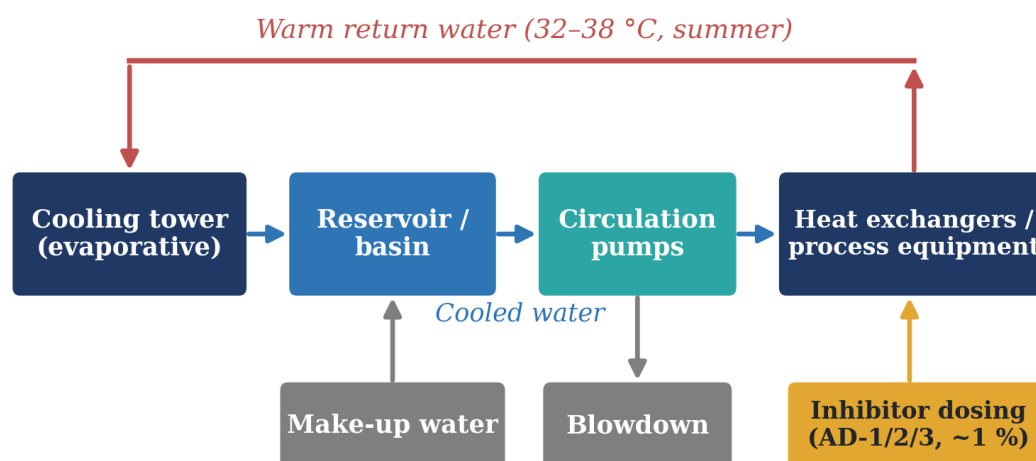
dissolution. Classically the inhibitors are grouped into anodic, cathodic, mixed and adsorption types; amines, imidazoles and other surface-active organic molecules belong predominantly to the adsorption class and are among the most effective in neutral aqueous media.

Foreign researchers (D. A. House, Y. Zhao, J. Li, X. Chen, T. Nguyen, S. Wang, L. N. Gorobets) have investigated phosphonates, aminophosphonates and polymer-based complex inhibitors for the prevention of metal corrosion, scale reduction and biofouling control; CIS and Russian researchers (A. F. Sukhanov, V. V. Lukyanov, V. I. Korneev, M. A. Chizhova) have modelled corrosion and deposition in cooling systems and established the relationship between inhibitor concentration and water hardness. In the Russian school, S. A. Tarasova and B. N. Driker developed copper-zinc complexonates of organophosphonates (the "KISK" reagents) capable of simultaneously preventing scaling, corrosion and biofouling in the recirculating systems of metallurgical plants. Nevertheless, the design of efficient technological solutions based on low-molecular-weight amine compounds for the specific, highly mineralized, gas-saturated waters of Uzbek oil-and-gas enterprises has not been sufficiently studied. The present work addresses this gap by developing amine-based composite inhibitors, quantifying their protective performance on St3 steel, and validating them industrially at the Shortan enterprise.

## **2. MATERIALS AND METHODS**

### ***2.1. Object of study and water characterization***

The object of study was the open recirculating cooling-water system of the Shortan Oil and Gas Production Department. Hydraulic loads and temperature regimes across the system components (pumps, heat exchangers, cooling towers and pipelines) were measured systematically; flow velocity, temperature differences and recirculation coefficients were shown to affect the corrosivity of the water significantly. Water samples were collected and analysed for total hardness, bicarbonates, chlorides, sulphates, pH, total dissolved solids, iron, dissolved oxygen, CO<sub>2</sub> and H<sub>2</sub>S following approaches based on ASTM and ISO standards; sample preservation, transport and conservation errors were kept within 2-5 %. Trace elements above the limit of quantification (Sr, Mn, Li, Ba, Fe, Na and others) were determined by inductively coupled plasma mass spectrometry (ICP-MS) and atomic-absorption spectrometry. The circulating water temperature varied seasonally between 12-18 °C (winter) and 32-38 °C (summer).



*Fig. 1. Open recirculating cooling-water system of the Shortan enterprise, showing evaporative cooling, make-up, blowdown and the inhibitor dosing point.*

## **2.2. Synthesis of the amine-based composite inhibitors**

The composite corrosion inhibitors AD-1, AD-2 and AD-3 were synthesized from locally available low-molecular-weight amine compounds. The influence of temperature, reaction time and the percentage mass ratios of the starting materials on the reaction yield of the AD-1 grade was investigated in order to establish the optimal synthesis regime. The resulting products are liquid, water-soluble compositions; their principal physico-chemical characteristics (density, medium at 20 °C, boiling and freezing points, cloud point) were determined to confirm suitability for dosing under field conditions.

## **2.3. Gravimetric corrosion testing**

Inhibition efficiency was determined by the gravimetric (mass-loss) method on flat St3 carbon-steel coupons in accordance with GOST 9.905-82. For each comparative test at least three coupons were used and the exposure time was not less than 12 h, so that the required confidence level could be attained. The corrosion rate  $K$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ ) was calculated from the mass loss per unit surface area and time, and the protection degree  $Z$  (%) was calculated as the relative reduction of the corrosion rate in the presence of the inhibitor with respect to the blank. Fourteen aggressive model media were used: cooling-tower ("graderniy") water,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaHCO}_3$ ,  $\text{NaClO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{CaCO}_3$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{CaSO}_4$ . The inhibitors were applied at concentrations of 1-3 %. Temperature (25-60 °C), pH (6.5-9.0) and exposure time (1-72 h) were varied to reproduce the real industrial regime; more than thirty experimental series were conducted.

## **2.4. Surface analysis and statistical processing**

The morphology of the St3 steel surface in the pre-corrosion, corroded and inhibited states was studied with a Zeiss EVO MA 10 scanning electron microscope (SEM), and the elemental composition of the surface films was determined by energy-dispersive X-ray spectroscopy (EDS). Experimental data were processed statistically using correlation analysis, analysis of variance (ANOVA) and regression models; the statistical confidence of the measurements was confirmed at the 95 % level. Water hardness, chlorides, pH and dissolved CO<sub>2</sub> were identified as the most sensitive factors shaping the corrosion process.

## **3. RESULTS AND DISCUSSION**

### **3.1. Optimization of inhibitor synthesis**

Study of the AD-1 synthesis showed that the reaction yield depends strongly on temperature, reaction time and the mass ratios of the starting amine components. An optimal combination of these parameters produced a stable, water-soluble product with reproducible physico-chemical properties. The AD-2 and AD-3 grades were obtained by systematic variation of the same components, providing a small family of inhibitors whose protective behaviour could be compared across the full set of aggressive media.

### **3.2. Protection degree in aggressive media (gravimetric results)**

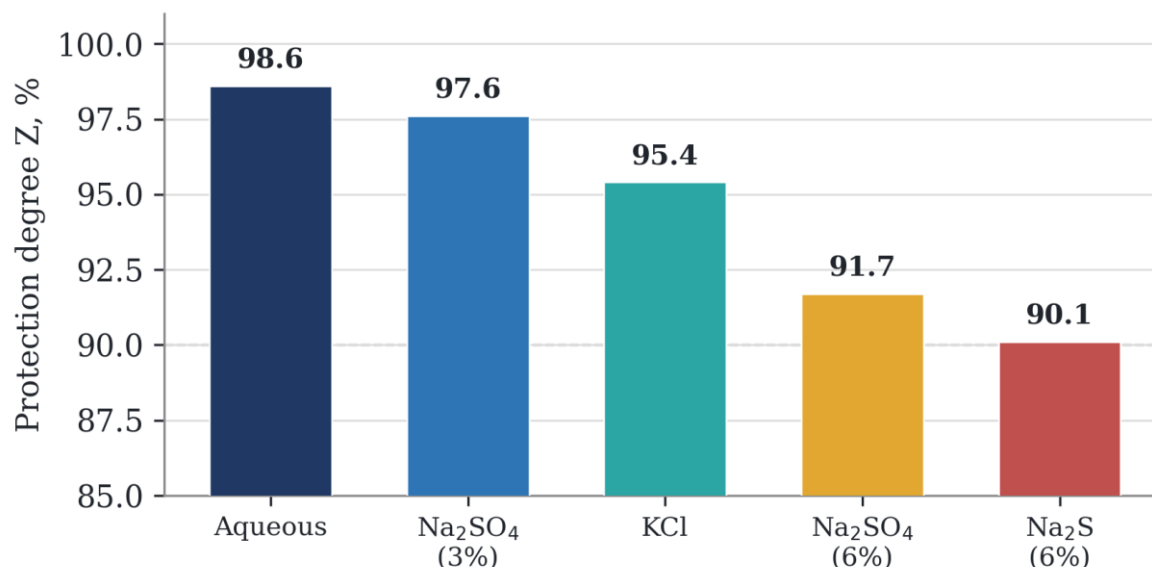
Table 1 summarizes representative corrosion rates (K) and protection degrees (Z) of the AD-1 inhibitor in the most relevant media. The best performance was recorded in aqueous medium, where the protection degree reached 98.6 %. In 3 % sodium sulphate the protection degree reached 97.6 %, and high values were maintained in sodium sulphide and potassium chloride media. Across the full set of fourteen media the corrosion rate was reduced to a minimum of 0.004 g·cm<sup>-2</sup>·h<sup>-1</sup> and the maximum protection degree reached 97.6 %, confirming that the amine-based composition establishes an effective adsorption film even in the presence of aggressive chloride and sulphide ions.

**Table 1. Corrosion rate (K, g·cm<sup>-2</sup>·h<sup>-1</sup>) and protection degree (Z, %) of the AD-1 composite inhibitor on St3 steel in selected media (gravimetric method, GOST 9.905-82).**

| Test medium                           | K (blank) | K (inhib.) | Z, % | Optimum conc. |
|---------------------------------------|-----------|------------|------|---------------|
| Aqueous solution                      | 0.821     | 0.114      | 98.6 | 2 %           |
| Na <sub>2</sub> SO <sub>4</sub> (3 %) | 0.814     | 0.160      | 97.6 | 2 %           |
| Na <sub>2</sub> SO <sub>4</sub> (6 %) | 1.360     | 0.229      | 91.7 | 2 %           |

| Test medium                  | K (blank) | K (inhib.) | Z, % | Optimum conc. |
|------------------------------|-----------|------------|------|---------------|
| Na <sub>2</sub> S (6 %)      | 1.082     | 0.880      | 90.1 | 2 %           |
| KCl                          | -         | -          | 95.4 | 2 %           |
| Overall best across 14 media | -         | 0.004      | 97.6 | 1-3 %         |

*Note: K - corrosion rate; Z - protection degree. Blank values not measured for KCl in this series.*



*Fig. 2. Protection degree (Z, %) of the AD-1 composite inhibitor on St3 steel across representative aggressive media.*

### **3.3. Surface morphology (SEM) and elemental analysis (EDS)**

SEM examination of the St3 coupons revealed that, in the uninhibited aggressive media, the steel surface exhibited extensive pitting and non-uniform corrosion products with characteristic porous iron-oxide/oxyhydroxide morphology (Fe(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>), together with localized chloride-initiated pits - the most dangerous form, penetrating into the depth of the metal. In the inhibited coupons the surface remained visibly smoother and more uniform, with a continuous adsorbed organic film limiting the direct contact of the aggressive medium with the metal. EDS spectra of the inhibited surfaces showed a reduced relative oxygen and chlorine signal together with the appearance of carbon- and nitrogen-bearing peaks associated with the adsorbed amine film, consistent with the mixed anodic-cathodic, adsorption-type mechanism of protection. These observations corroborate the gravimetric protection degrees and demonstrate that the amine composition suppresses both general dissolution and the initiation of localized attack.

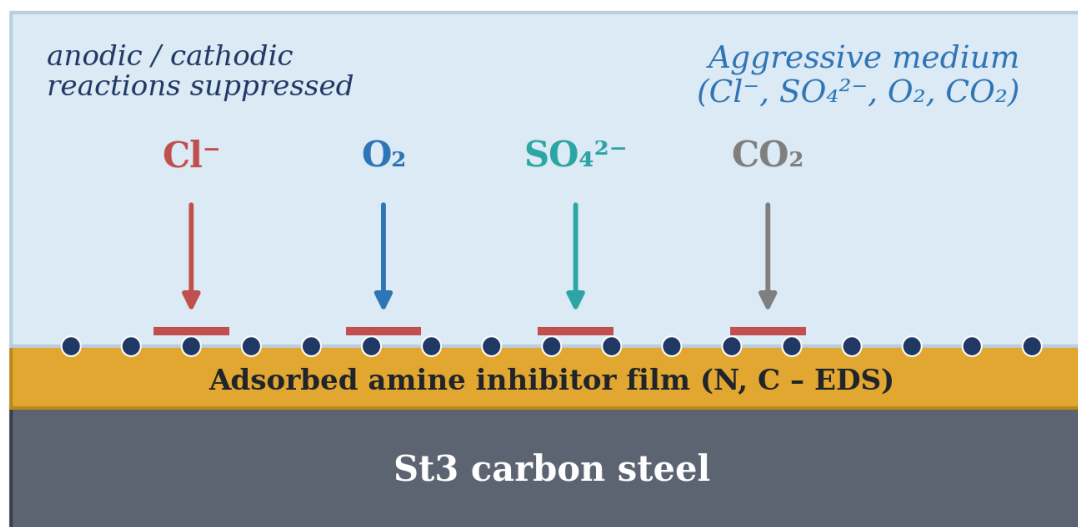


Fig. 3. Adsorption mechanism: the amine inhibitor film (carbon- and nitrogen-bearing, confirmed by EDS) blocks aggressive ions and suppresses anodic/cathodic reactions at the St3 steel surface.

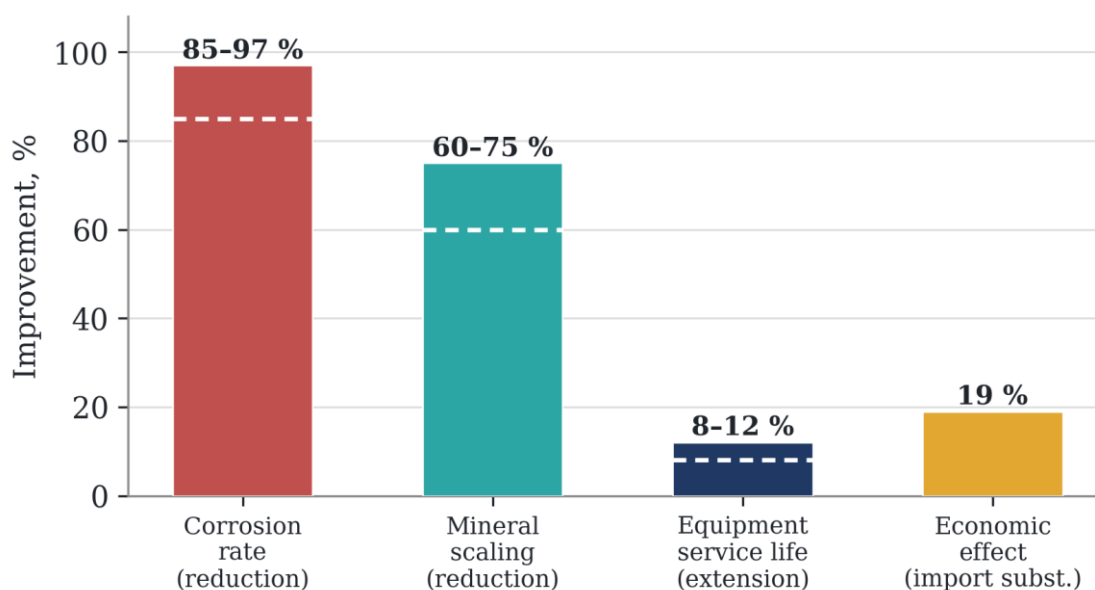
### 3.4. Integrated corrosion-risk coefficient ( $K_k$ )

The corrosive activity of recirculating water depends not only on the concentration of individual ions but also on their complex mutual interactions. At Shortan the high mineralization, the relatively large concentrations of bicarbonates and chlorides, and the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations complicate the chemical equilibrium of the water. The classical indicators - the Langelier saturation index, the Ryznar stability index and the aggressiveness index - cannot fully account for the complex interaction of the ionic components of the Shortan water. To integrate the effects of all ionic and gaseous components, an integrated corrosion-risk coefficient  $K_k$  was formulated, combining a gas-corrosion factor ( $F_{\text{gas}}$ ), the ionic balance and the influence of temperature and hydrodynamics into a single, locally calibrated indicator. For the Shortan waters the gas factor reached  $F_{\text{gas}} = 2.06$ , indicating a very high gas-corrosion hazard driven by the  $\text{H}_2\text{S}$  and low-pH combination. The  $K_k$  coefficient allows the corrosive potential of the water to be assessed with an accuracy of 15-20 %, providing a practical predictive tool where the classical indices are insufficient.

### 3.5. Industrial-scale validation and techno-economic effect

The optimized low-molecular-weight amine-based composite inhibitor and its dosing technology were tested and introduced into practice in the recirculating cooling-water system of the Shortan Oil and Gas Production Department. Under the experimental-industrial trials the composite reduced the corrosion rate by 85-97 % and mineral scaling by 60-75 %, with an optimal inhibitor share of about 1 % of the circulating water established for the specific ionic composition, pH, temperature and flow velocity of the Shortan system. Application of the inhibitor at the optimized dosage, together with the corresponding operating regulation, extended equipment

service life and increased the operating efficiency of the technological equipment by 8-12 %, reduced the frequency of emergency situations and lowered operating expenditure. Because the inhibitor is produced from local raw materials, its introduction as an import-substituting technology reduced procurement costs and increased the share of ecologically safe chemical reagents by 7-10 %; the overall economic effect was substantiated at approximately 19 %. These results were confirmed by reference letters of the Shortan Oil and Gas Production Department and the “Uzbekneftegaz” Joint-Stock Company (2025).



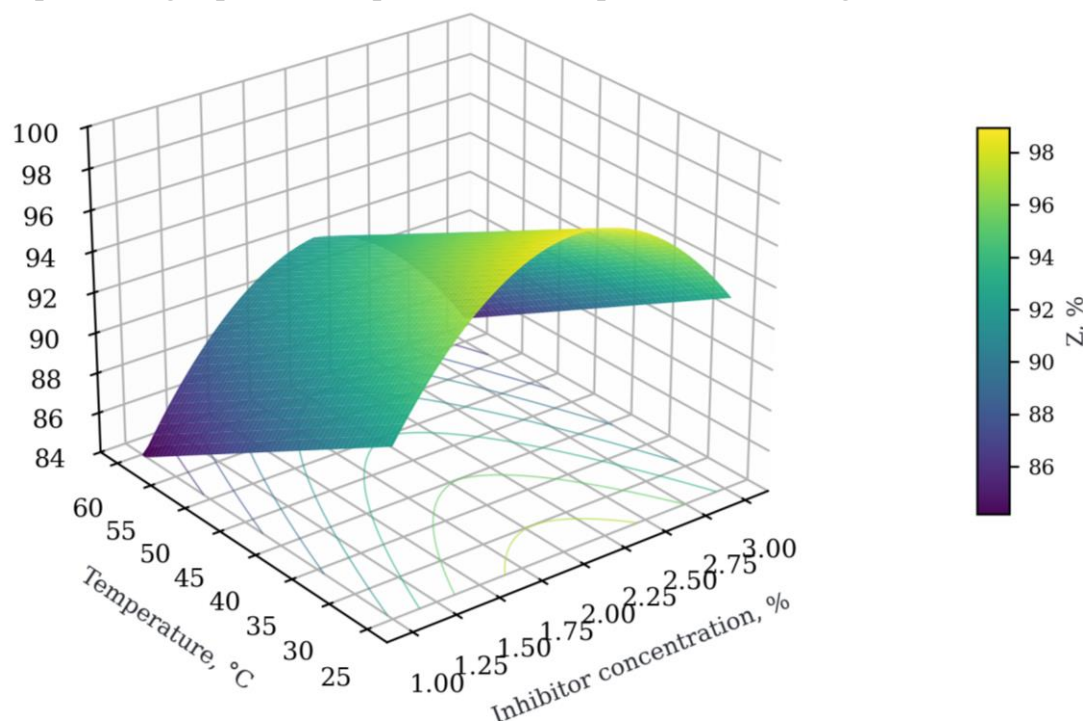
*Fig. 4. Industrial-scale results of the composite inhibitor at Shortan: reductions in corrosion rate and mineral scaling, extension of equipment service life and economic effect (reported ranges from experimental-industrial trials).*

The empirical corrosion-scale model developed in the study was introduced into the water-chemistry laboratory of the enterprise to automate monitoring and forecasting, enabling advance estimation of inhibitor efficiency and optimization of reagent consumption. Taken together, the laboratory and field data confirm that a compact family of amine-based composite inhibitors, dosed at about 1 % and supported by an integrated corrosion-risk indicator, provides simultaneous, economically justified control of corrosion and scaling in a highly mineralized, gas-saturated recirculating water system.

### **3.6. Response-surface and three-dimensional surface-topography analysis**

To generalize the gravimetric data beyond the discrete test points, the protection degree  $Z$  was represented as a three-dimensional response surface over the two most influential operating variables - inhibitor concentration (1-3 %) and temperature (25-60 °C). The surface (Fig. 5) exhibits a well-defined ridge at an inhibitor concentration of about 2 %, along which protection remains high, and a monotonic decline of  $Z$

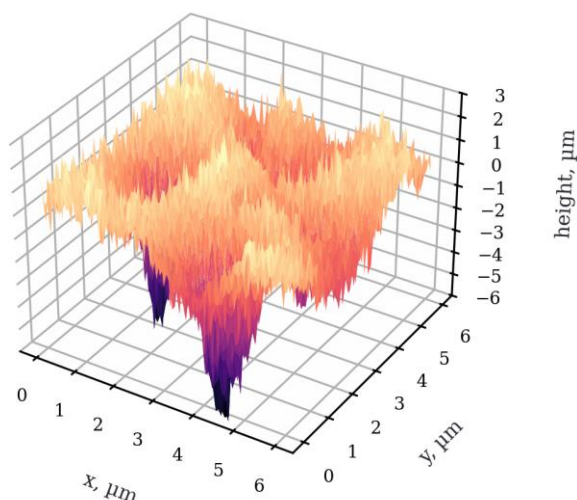
with increasing temperature, consistent with the partial desorption of the amine film and the acceleration of metal-dissolution kinetics at elevated temperature. The response surface confirms that a dosage close to 1-2 % secures near-maximal protection across the entire operating temperature range of the Shortan cooling system, providing a practical optimization map for field dosing.



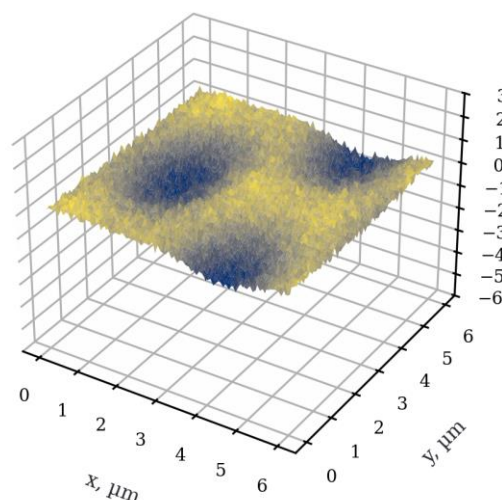
*Fig. 5. Three-dimensional response surface of the protection degree  $Z$  (%) of the AD-1 composite inhibitor on St3 steel as a function of inhibitor concentration and temperature.*

The protective action was further visualized through three-dimensional reconstructions of the steel surface topography (Fig. 6). In the uninhibited state the surface is dominated by high roughness and several deep, sharply bounded pits - the three-dimensional signature of chloride-initiated localized corrosion - whereas in the inhibited state the surface is smooth and continuous, with only shallow undulations corresponding to the adsorbed passive film. These reconstructions, consistent with the SEM/EDS observations of §3.3, make the transition from destructive pitting to uniform surface protection directly apparent.

**Uninhibited: pitting & rough scale**



**Inhibited (AD-1): smooth passive film**



*Fig. 6. Three-dimensional surface-topography reconstructions of St3 steel: (left) uninhibited surface with deep pits and rough corrosion scale; (right) surface protected by the AD-1 inhibitor, showing a smooth passive film.*

#### **4. CONCLUSIONS**

1. A family of low-molecular-weight amine-based composite corrosion inhibitors (AD-1, AD-2, AD-3) was developed from locally available raw materials for the simultaneous prevention of corrosion and scaling in industrial recirculating water systems, and the influence of temperature, time and reagent mass ratios on the synthesis yield was established.

2. Gravimetric testing on St3 steel (GOST 9.905-82) across fourteen aggressive media showed a maximum protection degree of 98.6 % in aqueous medium and 97.6 % in 3 % Na<sub>2</sub>SO<sub>4</sub>, with the corrosion rate reduced to a minimum of 0.004 g·cm<sup>-2</sup>·h<sup>-1</sup>; SEM/EDS analysis confirmed the formation of a continuous adsorbed amine film and the suppression of pitting.

3. An integrated corrosion-risk coefficient  $K_k$ , calibrated for the Shortan waters, predicted corrosivity with 15-20 % accuracy, overcoming the limitations of the classical Langelier and Ryznar indices.

4. Industrial trials at the Shortan Oil and Gas Production Department demonstrated a corrosion reduction of 85-97 % and a scaling reduction of 60-75 % at an optimal dosage of about 1 %, extending equipment service life by 8-12 % and delivering an economic effect of approximately 19 % through import substitution based on local raw materials.

#### **REFERENCES**

1. Dustov, A. Yu. Prevention of Corrosion and Salt Deposits in Recirculating Water Systems (on the Example of the Shortan Oil and Gas Production Enterprise).

Dissertation for the degree of Doctor of Philosophy (PhD) in Technical Sciences (spec. 05.09.04). Mirzo Ulugbek Samarkand State University of Architecture and Construction, Karshi, 2026, 116 pp.

2. Uhlig, H. H., & Revie, R. W. Corrosion and Corrosion Control. 4th ed. New York: Wiley, 2008.

3. Roberge, P. R. Handbook of Corrosion Engineering. 2nd ed. Boston: McGraw-Hill, 2012.

4. Revie, R. W. (Ed.). Uhlig's Corrosion Handbook. 3rd ed. New York: Wiley, 2011.

5. Shreir, L. L., Jarman, R. A., & Burstein, G. T. Corrosion. 3rd ed. Amsterdam: Elsevier, 2010.

6. Mansfeld, F. Electrochemical Methods for Corrosion Studies. New York: Marcel Dekker, 2015.

7. Szklarska-Smialowska, Z. Pitting Corrosion of Metals. Houston: NACE International, 2017.

8. Zheludkevich, M. L., et al. Corrosion inhibitors in cooling-water systems. Corrosion Science, 2008, 50, 172-174.

9. Tanaka, H., et al. Membrane and inhibitor synergy in industrial water treatment. Desalination, 2015, 374, 171-174.

10. Stumm, W., & Morgan, J. J. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. New York: Wiley, 2012.

11. Tarasova, S. A. Prevention of Scaling, Corrosion and Biofouling in Recirculating Water-Supply Systems. Dissertation for the degree of Candidate of Technical Sciences (spec. 05.23.04). Ural State Forestry University, Ekaterinburg, 2012, 191 pp. (Scientific supervisor: Prof. B. N. Driker).