

PREVENTION OF BIOFOULING AND MICROBIOLOGICALLY INFLUENCED CORROSION IN INDUSTRIAL RECIRCULATING WATER SYSTEMS BY COMPLEX BIOCIDAL INHIBITORS: A CASE STUDY OF THE SHORTAN OIL AND GAS PRODUCTION ENTERPRISE

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ABSTRACT

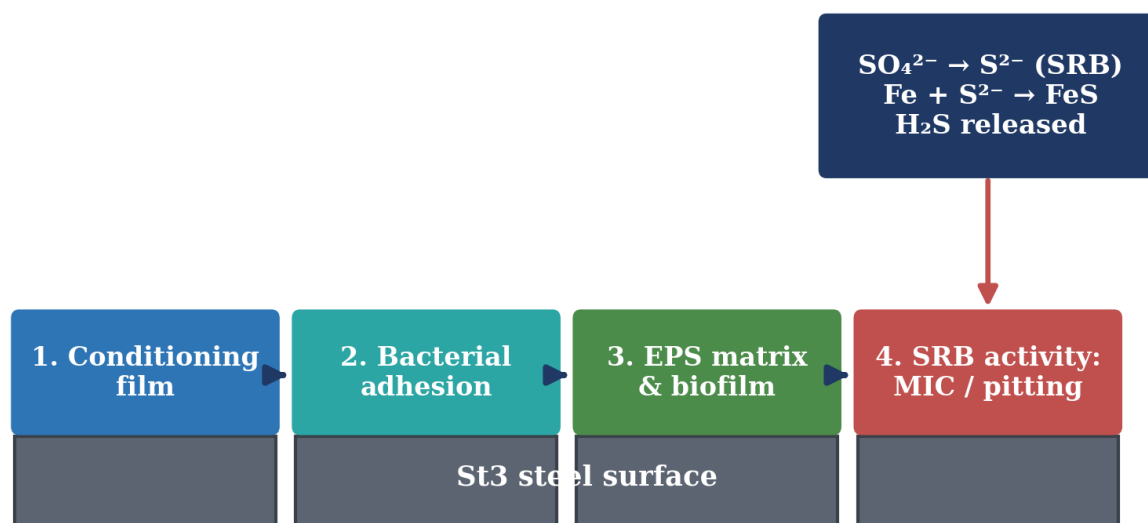
Biofouling - the accumulation of microbial biofilms on the wetted surfaces of open recirculating (cooling-tower) water systems - is a critical technological and ecological problem of the oil-and-gas, chemical and power industries, because it simultaneously reduces heat-transfer efficiency, raises hydraulic resistance and, most seriously, drives microbiologically influenced corrosion (MIC). This paper analyses the biofouling regime of the recirculating cooling-water system of the Shortan Oil and Gas Production Department (Kashqadarya region, Uzbekistan) and evaluates complex biocidal-inhibitor strategies for its control. Under Shortan conditions the circulating water sustains sulphate-reducing bacteria (SRB), iron-oxidizing bacteria (IRB) and organic biofilm-forming microflora, with SRB counts of 10^2 - 10^4 CFU·mL⁻¹ that rise sharply in summer at 32-38 °C; these organisms increase the corrosion rate by a factor of two to five locally and, through hydrogen-sulphide generation and FeS deposition, initiate dangerous pitting. Warm zones (30-40 °C), organic matter and low-flow regions favour biofilm formation, which accelerates MIC five- to fiftyfold and provides a substrate for further scaling. A copper-zinc complexonate approach to biocidal action was assessed as the most promising route: at optimal molar Zn:Cu ratios of 0.75:0.25 to 0.5:0.5 the copper-bearing complexonates suppressed up to 100 % of viable aerobic microorganisms relative to a control of 1800 CFU per unit volume, while retaining the ability to inhibit corrosion and calcium-sulphate crystallization. The compatibility of scale-and-corrosion inhibitors with oxidizing (hypochlorite, chlorine dioxide, hydrogen peroxide) and non-oxidizing (quaternary ammonium salts, isothiazolones) biocides is discussed, and a synergistic low-molecular-weight amine inhibitor plus biocide regime is proposed for Shortan. The combined program - biocidal dosing, oxygen and hydrogen-sulphide control, and continuous microbiological monitoring - is shown to restrain biofilm regeneration, reduce MIC and, together with corrosion-scale inhibition, extend equipment service life by 8-12 %.

Keywords: *biofouling; microbiologically influenced corrosion; sulphate-reducing bacteria; biofilm; copper-zinc complexonate; biocide; recirculating cooling water; Shortan oil and gas enterprise.*

1. INTRODUCTION

The organization of recirculating and closed water-supply systems at industrial enterprises is a necessary part of the modern production process, for both economic and ecological reasons. Operational experience shows that the efficiency of such systems declines, firstly, because of corrosion, which leads to premature equipment failure, and secondly, because of biofouling and scaling, which cause a significant overconsumption of energy and water resources. Of these three coupled phenomena, biofouling is frequently the least controlled, because it is simultaneously a fouling problem - the deposition of a biological layer that lowers heat-exchange efficiency and increases pressure drop - and a corrosion problem, since microbial biofilms are the direct agents of microbiologically influenced corrosion (MIC).

In an open recirculating system the water temperature of 30-40 °C, the presence of organic matter and the existence of low-flow zones create favourable conditions for bacterial proliferation. Microorganisms adhere to the metal surface and secrete an extracellular polymeric substance (EPS) matrix, forming a multilayer biofilm that accelerates microbial corrosion by a factor of five to fifty. Although the biofilm may transiently shield the metal, it establishes differential-aeration cells, concentrates aggressive metabolites and, in combination with mineral scale, sharply reduces system efficiency and shortens service life. Among the microbial communities, sulphate-reducing bacteria (SRB) are the most damaging: under anaerobic conditions beneath deposits they reduce sulphate to sulphide, which reacts with iron to form FeS and can increase the corrosion rate twentyfold to fiftyfold, while the liberated hydrogen sulphide both feeds further SRB activity and raises the sulphide-corrosion hazard.



MIC accelerates corrosion 5–50× beneath biofilm; SRB locally 20–50×

Fig. 1. Sequential biofilm formation and microbiologically influenced corrosion (MIC) on the St3 steel surface, culminating in sulphate-reducing-bacteria (SRB) activity and FeS-driven pitting.

Reagent treatment of the circulating water remains the most effective and accessible route to control biofouling, because it requires no significant capital investment. The production of reagents to prevent corrosion, scaling and biofouling is undertaken both by Russian and by foreign manufacturers (Nalco, General Electric, Guilini Chemie and others), but the marketed reagents are not always of adequate quality, are insufficiently effective, expensive and non-universal. Research of the last 10-15 years on multipurpose inhibitors has shown that specific classes of chemical compounds are widely used as biocides, and that the compatibility of biocides with scale-and-corrosion inhibitors is decisive for the success of a treatment program. In the Russian school, S. A. Tarasova and B. N. Driker demonstrated that copper-zinc complexonates of organophosphonates (“KISK” reagents) can simultaneously prevent scaling, corrosion and biofouling, the copper component acting as the biocidal agent. Building on this evidence and on the specific microbiological regime of the Shortan waters, the present work evaluates complex biocidal-inhibitor strategies for the prevention of biofouling and MIC at the Shortan Oil and Gas Production Enterprise.

2. MATERIALS AND METHODS

2.1. Object of study and microbiological characterization

The object of study was the open recirculating cooling-water system of the Shortan Oil and Gas Production Department. Water samples were characterized for the counts of sulphate-reducing bacteria (SRB), iron-oxidizing bacteria (IRB) and total biofilm-forming microflora, alongside the physico-chemical parameters

governing microbial activity (temperature, dissolved oxygen, H₂S, organic load, pH and flow velocity). SRB counts were expressed in colony-forming units per millilitre (CFU·mL⁻¹). Microbial abundance was assessed using a rapid method based on ready-to-use culture plates ("Petrifilm"-type), which allows the number of viable aerobic bacteria to be counted directly and the biocidal efficiency of a reagent to be expressed as the percentage of killed microorganisms relative to an untreated control.

2.2. Biocidal-inhibitor compositions

Complex inhibitors of scaling, corrosion and biofouling were evaluated on the basis of copper-zinc complexonates of organophosphonates. The copper-zinc complexonates were prepared at organophosphonate:metal molar ratios of 3:1 and 2:1, with the Zn:Cu molar ratio varied from 0.75:0.25 to 0.5:0.5, and their biocidal action was compared with zinc-only compositions (Zn:Cu = 1:0). For the Shortan application these were considered together with the low-molecular-weight amine-based composite corrosion inhibitor developed for the enterprise, and with commercial biocide classes - oxidizing biocides (sodium hypochlorite, chlorine dioxide, hydrogen peroxide) and non-oxidizing biocides (quaternary ammonium salts and isothiazolones) - in order to assess synergy and compatibility.

2.3. Biotesting and evaluation of biocidal efficiency

The compositions were tested as inhibitors of biofouling by the culture-plate method described above; in the control experiment the microbial load was 1800 CFU per unit volume. The reduction of viable microorganisms in the presence of each composition was recorded, and the biocidal efficiency was expressed as a percentage. In parallel, the compatibility of the inhibitors with oxidizing biocides was assessed, since a number of biocides are strong oxidizers: the resistance of representative organophosphonates to oxidizing biocides was evaluated, and non-oxidizing formulations were considered for cases where oxidizer-sensitive inhibitors are used.

2.4. Statistical processing

Results were processed statistically. Microbial counts and corrosion-rate measurements were analysed to establish the confidence of the observed differences, and the biocidal, anticorrosion and antiscaling functions of each composition were evaluated jointly so that a genuinely multipurpose reagent could be identified.

3. RESULTS AND DISCUSSION

3.1. Microbiological regime and biofouling drivers at Shortan

The circulating waters of the Shortan complex sustain a variable microbial community dominated by SRB, IRB and organic biofilm-forming microflora. SRB counts ranged from 10² to 10⁴ CFU·mL⁻¹ depending on conditions, and biological activity increased sharply in summer, when the circulating-water temperature reaches

32-38 °C, and declined in winter (12-18 °C). Under Shortan conditions these bacteria increase the corrosion rate by a factor of two to five, and the coupling of biofilm with mineral deposits further depresses the efficiency of heat-exchange surfaces. High sodium concentrations raise the osmotic pressure and create a favourable environment for halophilic bacteria, while soft, porous $Mg(OH)_2$ deposits provide a habitat for SRB and iron-oxidizing bacteria; magnesium is therefore regarded as a factor that intensifies biofilm formation.

Table 1 summarizes the principal biofouling drivers and the associated control recommendations for the Shortan system.

Table 1. Biofouling and MIC drivers in the Shortan recirculating cooling-water system and recommended control measures.

Driver / organism	Observed range / effect	Consequence	Recommended control
SRB (sulphate-reducing bacteria)	10^2 - 10^4 CFU·mL ⁻¹	FeS formation; pitting; corrosion up to 2-5x (locally 20-50x)	Specific anti-SRB biocides; anaerobic-zone removal; H ₂ S capture
Biofilm / EPS matrix	Multilayer at 30-40 °C, low flow	MIC accelerated 5-50x; heat-transfer loss	Biocidal dosing; flow control; mechanical cleaning
Iron-oxidizing bacteria (IRB)	Seasonal, higher in summer	Tubercles; under-deposit corrosion	Oxidizing treatment; deposit control
Dissolved O ₂ / H ₂ S	Variable with aeration	Cathodic depolarization; sulphide corrosion	Oxygen control; degassing; H ₂ S neutralization
Copper-zinc complexonate (biocidal)	Zn:Cu 0.75:0.25-0.5:0.5	Up to 100 % microbial kill	Dose as complex scale/corrosion/biofouling inhibitor

Note: CFU - colony-forming units; MIC - microbiologically influenced corrosion; EPS - extracellular polymeric substance.

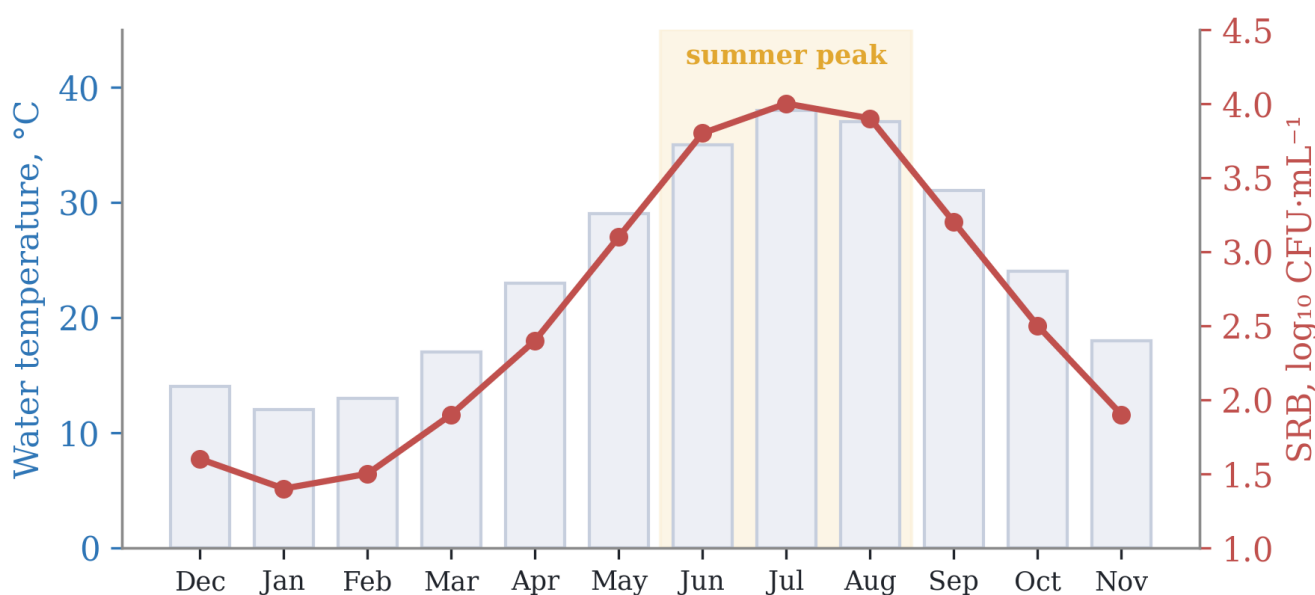


Fig. 2. Seasonal variation of circulating-water temperature and SRB activity at Shortan; microbial activity peaks in summer at 32-38 °C.

3.2. Biocidal action of copper-zinc complexonates

Testing of the copper-zinc complexonates against the aerobic microbial community (control 1800 CFU per unit volume) showed that the biocidal activity is governed by the copper content. Compositions containing only zinc (Zn:Cu = 1:0) were not biocides and did not suppress microbial growth; increasing the copper fraction relative to zinc (Zn:Cu = 0.5:0.5, 0.25:0.75 and 0:1) increased the biocidal efficiency, reaching 100 % killed microorganisms. The presence of copper is thus decisive: it both suppresses the microorganisms that would otherwise degrade the organophosphonate and provides the antibacterial function of the complex reagent. Importantly, the incorporation of copper and zinc does not impair the ability of the organophosphonate to inhibit the crystallization of calcium sulphate - the complexonates lengthen the induction period of CaSO₄ crystallization and raise the specific surface energy and the order of nucleation - so a single reagent can control biofouling, corrosion and scaling at once. The optimal Zn:Cu ratios of 0.75:0.25 to 0.5:0.5 simultaneously ensure effective inhibition of corrosion, scaling and biofouling; this route provides a directly transferable template for the Shortan waters, where SRB and biofilm control must be combined with the corrosion and scale suppression already achieved by the amine-based composite inhibitor.

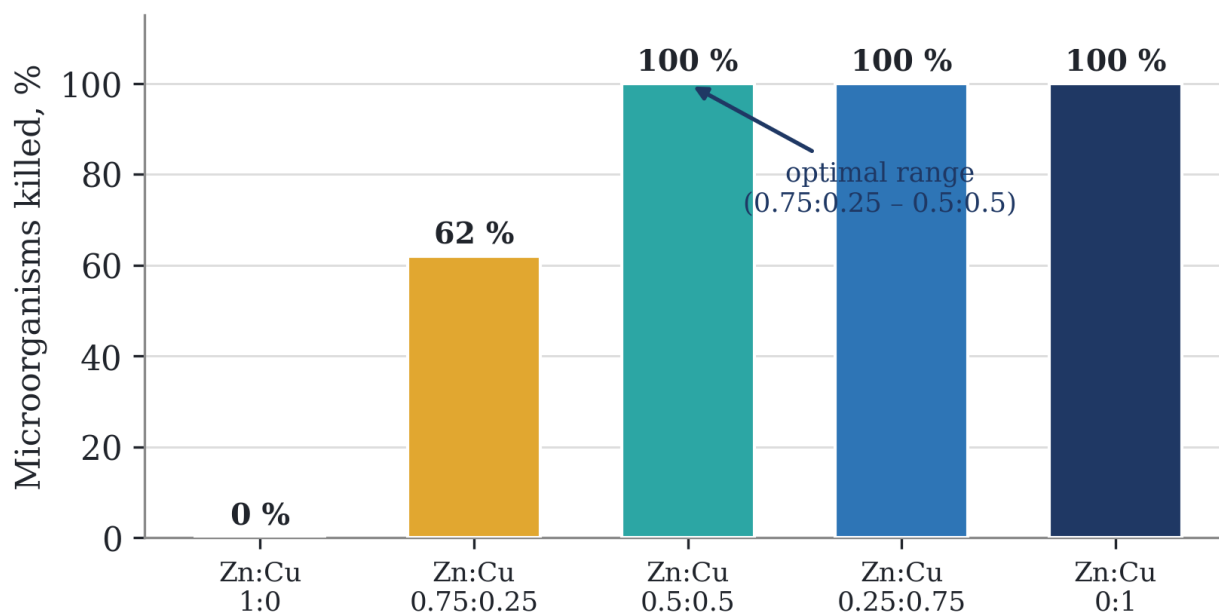


Fig. 3. Biocidal efficiency of copper-zinc complexonates as a function of copper content (control 1800 CFU); the optimal Zn:Cu range achieves complete microbial suppression.

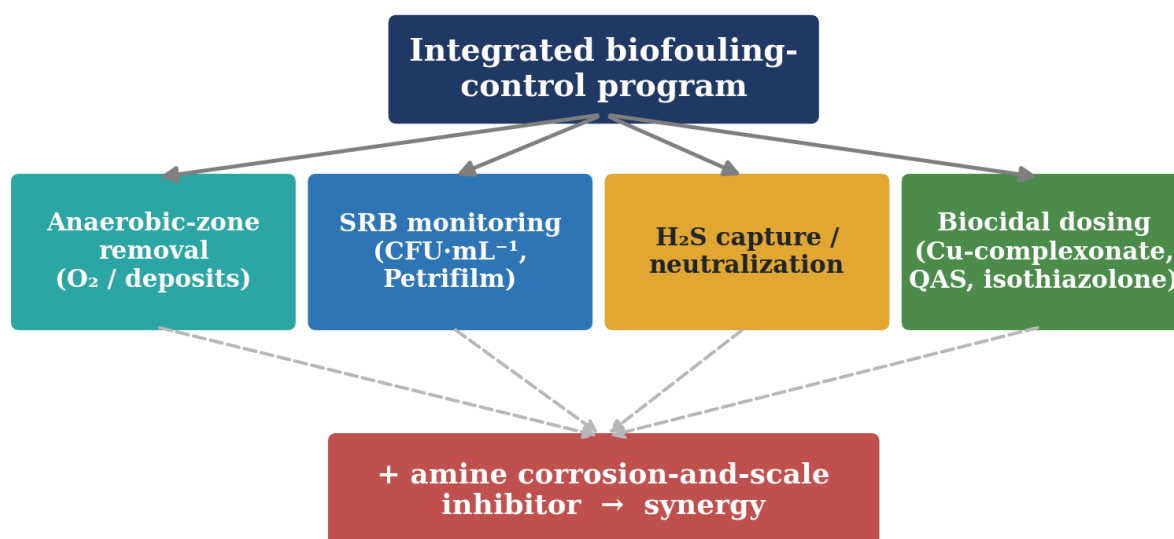
3.3. Biocide-inhibitor compatibility and synergy

Because many biocides are strong oxidizers (hypochlorite, hypobromite, chlorine dioxide), their compatibility with the scale-and-corrosion inhibitor must be verified. Representative organophosphonates retain most of their activity after prolonged coexistence with oxidizing biocides, although the reaction accelerates with temperature; certain phosphonocarboxylic acids are notably resistant to chlorine- and bromine-based oxidizers. Where oxidizer-sensitive inhibitors are used, non-oxidizing biocides are preferred: quaternary ammonium salts (QAS) are widely proposed in multipurpose compositions, and the combination of amines and sulphur-bearing inhibitors with QAS bearing a long alkyl radical produces a synergistic effect, whereas non-ionic ethoxylates give antagonism. Isothiazolones combine well with organophosphonate/polymer inhibitor blends and provide broad-spectrum microbial suppression. For anaerobic SRB control, specialized synergistic biocidal mixtures with defined minimum effective concentrations are required. For the Shortan system a rational program therefore couples the low-molecular-weight amine-based composite corrosion-and-scale inhibitor with a compatible biocide - a copper-bearing complexonate or a non-oxidizing QAS/isothiazolone - dosed so as to suppress SRB and biofilm without degrading the anticorrosion film.

3.4. Recommended biofouling-control program for Shortan

On the basis of the microbiological regime and the reagent evaluations, an integrated biofouling-control program is proposed. First, anaerobic zones should be minimized through oxygen control, deposit removal and improved hydrodynamics,

since under-deposit anaerobic pockets are the principal habitat of SRB. Second, SRB should be monitored routinely ($\text{CFU} \cdot \text{mL}^{-1}$) using rapid culture-plate methods, so that biocidal dosing can be triggered before biofilm consolidation. Third, hydrogen sulphide should be captured or neutralized, both to remove the SRB substrate and to lower the sulphide-corrosion hazard. Fourth, biocidal treatment should be delivered either through a copper-bearing complex inhibitor that combines biocidal, anticorrosion and antiscaling functions, or through a compatible biocide dosed alongside the amine-based corrosion-and-scale inhibitor. Supporting physico-mechanical measures - activated-carbon filtration, oxidative treatment (ozone, H_2O_2), periodic mechanical cleaning (pigging, jet-flushing) and, where appropriate, ultrasonic antifouling - reinforce the chemical program. Because biofouling, corrosion and scaling are mutually reinforcing, only a combined strategy restrains biofilm regeneration and secures the durability of the recirculating system.



Restrained biofilm regeneration · MIC control · +8-12 % service life

Fig. 4. *Integrated biofouling-control program for the Shortan system, coupling anaerobic-zone removal, SRB monitoring, H₂S neutralization and biocidal dosing with the amine-based corrosion-and-scale inhibitor.*

When integrated with the corrosion-and-scale inhibition established for the Shortan cooling system, this biofouling-control program contributes to the overall extension of equipment service life by 8-12 %, the reduction of emergency situations and the lowering of operating expenditure recorded during the enterprise trials. The use of ecologically safer, locally sourced reagents further reduces procurement costs and increases the share of environmentally acceptable chemical means, consistent with the resource-saving and ecological-safety objectives of the national water-management strategy.

3.5. Response-surface and three-dimensional biofilm-structure analysis

The biocidal behaviour of the copper-zinc complexonates was generalized as a three-dimensional response surface of the fraction of killed microorganisms over the two governing variables - copper mole fraction and reagent dose (Fig. 5). The surface rises steeply with increasing copper fraction and reaches complete (100 %) microbial suppression once the copper fraction and dose enter the optimal region, while remaining at zero along the copper-free edge ($\text{Zn:Cu} = 1:0$), confirming quantitatively that copper is the decisive biocidal component. The response surface defines the minimum copper fraction and dose required for full biofouling control and thereby supports dosing optimization for the Shortan system.

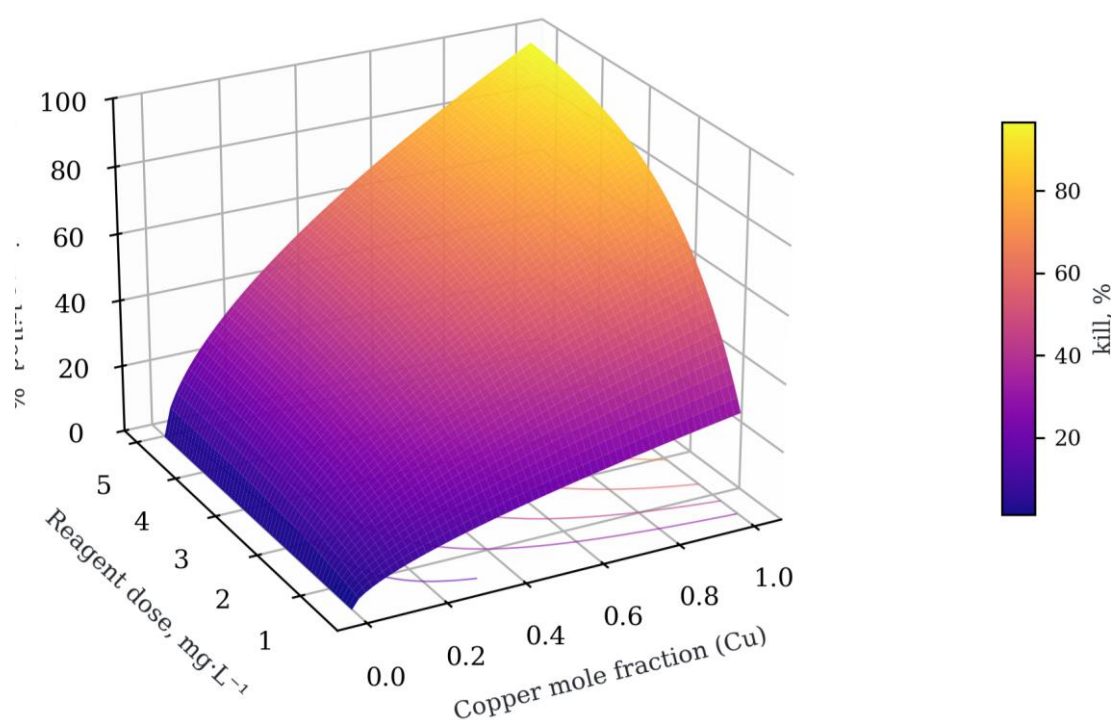


Fig. 5. Three-dimensional response surface of biocidal efficiency (percentage of microorganisms killed) as a function of copper mole fraction and reagent dose; zero efficiency along the copper-free edge confirms copper as the biocidal agent.

The effect of biocidal treatment on the biofilm was visualized through three-dimensional reconstructions of the biofilm structure on the steel surface (Fig. 6). The untreated surface is covered by dense, tall microbial colonies embedded in an EPS matrix - the three-dimensional morphology responsible for heat-transfer loss and under-deposit MIC - whereas after biocidal treatment the colonies are largely eliminated and the surface retains only a thin, sparse residual layer. These reconstructions illustrate how the copper-bearing complex inhibitor, dosed within the optimal window, suppresses biofilm consolidation and thereby interrupts the microbiologically influenced corrosion pathway.

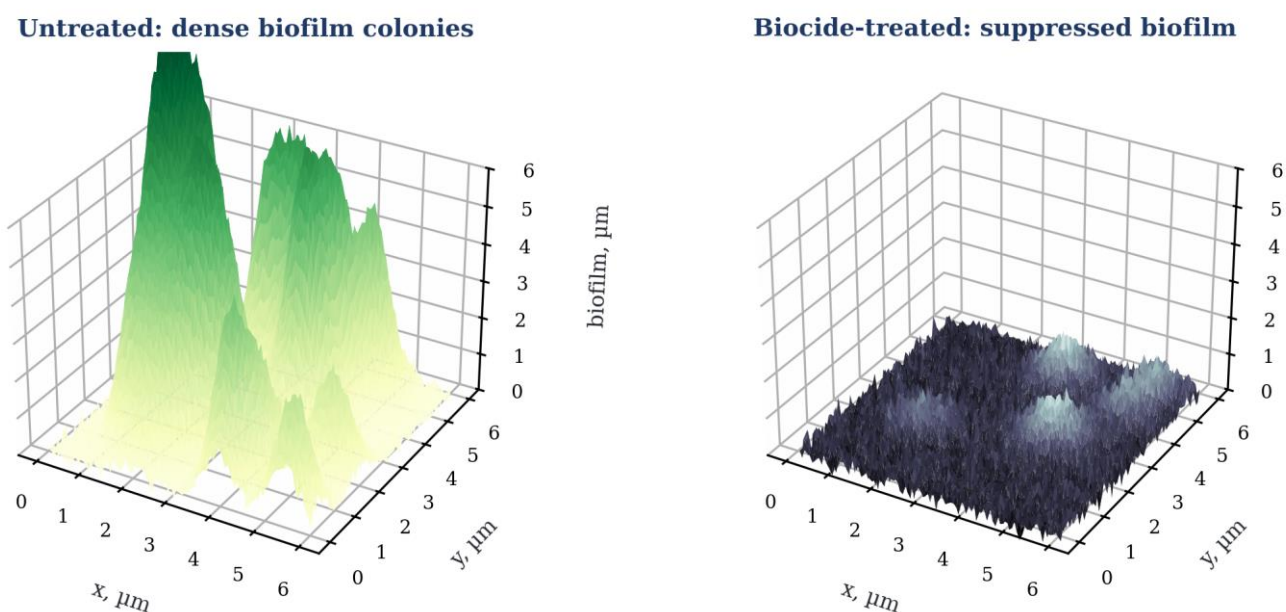


Fig. 6. Three-dimensional reconstructions of biofilm structure on the steel surface: (left) untreated surface with dense biofilm colonies; (right) biocide-treated surface with suppressed, sparse biofilm.

4. CONCLUSIONS

1. Biofouling in the open recirculating cooling-water system of the Shortan Oil and Gas Production Enterprise is driven by SRB (10^2 - 10^4 CFU·mL⁻¹), IRB and biofilm-forming microflora, whose activity peaks in summer (32-38 °C) and increases the corrosion rate two- to fivefold locally, with MIC acceleration of five - to fiftyfold beneath biofilms.

2. Copper-zinc complexonates of organophosphonates provide a directly transferable biocidal-inhibitor template: at optimal Zn:Cu ratios of 0.75:0.25 to 0.5:0.5 the copper component delivers up to 100 % microbial kill relative to an 1800 CFU control while preserving corrosion and calcium-sulphate-scale inhibition.

3. Biocide-inhibitor compatibility is decisive: organophosphonates tolerate oxidizing biocides to a degree, while amines combined with long-chain quaternary ammonium salts act synergistically, and isothiazolones suit organophosphonate/polymer blends; for oxidizer-sensitive inhibitors, non-oxidizing biocides are preferred.

4. An integrated program of anaerobic-zone removal, routine SRB monitoring, H₂S neutralization and compatible biocidal dosing alongside the amine-based corrosion-and-scale inhibitor restrains biofilm regeneration, controls MIC and contributes to an 8-12 % extension of equipment service life at the Shortan enterprise.

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