Microbiological studies of the corrosive destruction of underground pipelines and assessment of the bio-contamination of reservoir waters of Variogan oil group

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Abstract

The article highlights the scientific and technical aspects of the destruction of underground steel structures due to biocorrosion. The main factors of the biocorrosive environment are considered, a variety of corrosive bacteria is analyzed, including bioelectrochemical interpretations of their metabolic processes, and modern achievements in the development of methods for inhibiting biocorrosion are described. The study also presents the results of scientific research carried out for many years for the Variogan group of deposits, Russia. The oil of the Variogan group is unique – it is low-sulfur and light with a high content of light hydrocarbons (C_1–C_6). The transported medium is characterized by an abnormally high gas content. One of the main reasons associated with high corrosion activity is biocorrosion. It has been proven that sulfate-reducing bacteria (SRB) pose the greatest corrosion hazard among bacteria. They are obligate anaerobes that oxidize organic substances such as pyruvate, lactate, succinate, malate, and alcohols. In some sulfate-reducing bacteria, the ability to oxidize molecular hydrogen has been found. These bacteria are found in rivers, lakes, seas, oceans, and soil, and enter oilfield waters. Effective corrosion inhibitors of the IFKhAN type and the SNPH-1004 R inhibitor with bactericide effect are recommended. The presented material will be of interest to researchers, as well as engineers of organizations that operate underground pipelines.

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1. Introduction

Field pipelines are metal-intensive and technically complex structures, therefore their anticorrosive protection is a very urgent problem.

World experience shows [1] that more than 50% of all corrosion processes in process pipelines are associated with exposure to microorganisms. In Russia [2], up to 80% of oil production wells are infected with various microorganisms. This leads to accidents and enormous economic losses. One of the most famous accidents that occurred due to a significant damage to metal structures due to microbiological corrosion [3] is the rupture of the Trans-Alaska pipeline in 2006: about 1 million liters of petroleum products got into the environment, and the fines of the operator company reached $25 million.

The purpose of this work is to analyze the biosafety of oil wells, nodes, and process equipment and to develop recommendations for protection against biological corrosion for the Variogan group of fields.

2. Experimental

The scope of the work carried out included monitoring the composition of water (6–component analysis, pH, density, dissolved hydrogen sulfide, oxygen, water biocontamination), determination of the corrosion rate directly in the pipeline, laboratory modeling of environments, and the choice of a countermeasure for combatting biological contamination.

The chemical analysis of reservoir water was carried out according to the following methods [4–7] and included the following indicators: iodometry, complexometry for calcium and magnesium content, determination of iron by the photometric method, determination of copper by turbidimetry, compexonometric determination of sulfates, titrimetric determination of sulfides, hydrosulfides and hydrogen sulfide. The results are presented in Table 1.

Corrosion monitoring of the equipment was carried out by the weight method based on the weight loss of the samples, see Table 2.

The technique is based on a gravimetric method for determining the rate of corrosion of metal before and after treatment with the test medium. A reservoir medium containing SRB and samples of the metal under study are used. Reservoir water is sampled in same amounts (250 ml).

Pipe steel samples are cleaned, degreased and placed in reservoir water containing SRB. Then they are kept for 7 days at a constant temperature of 32–34°C in a thermostat. After 7 days, the samples are removed, cleaned from corrosion products and weighed on analytical scales. For reliability of the results, the experiment is repeated 3 to 5 times.

The corrosion rate (p) was determined from the amount of dissolved iron per unit area of the plate per unit time and calculated by the formula:

$$p = \frac{\left(m_1 - m_2\right)}{S \cdot \tau},$$

where p is the corrosion rate ($\mathrm{g/m^2 \cdot h}$); m_1 is the mass of the sample before the test, g; m_2 is the mass of the sample after the test, g; S is the area of the metal plate, $\mathrm{m^2}$; and τ is the exposure time, h. The quantitative content of bacteria and fungi capable of causing metal corrosion in water samples was carried out by seeding water samples on various elective agarized media.

The essence of the method is to determine the minimum amount of the seed material containing one bacterial cell. The calculation of bacterial cells was carried out according to the formula:

$$M = 10^n - \frac{1}{V}$$

where M is the number of bacterial cells in the source water; 10 is the dilution coefficient; n is the serial number of the dilution from which the seeding was made in the last flask where the growth of bacteria was noted; V is the volume of the source water taken for seeding, ml.

The activity index for SRB was determined by the rate of formation of iron sulfide in the seed flask. The activity index is assumed to be equal to 100 units when a black precipitate of iron sulfide is formed in 1 day, 50 – when a precipitate is formed in 2 days, 33 – when a sulfide precipitate is formed in 3 days, *etc.*

The activity index was calculated using the formula:

$$J = \frac{100}{a},$$

where a is the number of days.

Determination of the biocidal properties of the reagents. Bacteria exposed to biocides are passed through membrane filters to separate bacterial cells from the reagent molecules. The cells immobilized on the filter are placed in a Petri dish, filled with agarized Postgate medium, and thermostated at 32°C. The effects of bactericides is determined from the presence or absence of black colonies of SRB.

3. Results and Discussion

Currently, the problem of protection against internal corrosion of oilfield communications and equipment during extraction, collection, transportation, oil treatment and water disposal is becoming more urgent. Corrosion of the inner surface of pipelines of the oil collection system is caused by the presence of mineralized water in the products of wells being transported, which is released during transport into a separate phase in contact with the metal of the pipe’s lower part. The high gas factor of oil provokes a “cork” mode of media movement, subjecting the linear part of the pipeline to cyclic loads. The unsatisfactory condition of the external insulation and the influence of stray currents from nearby grounding conductors, as well as significant temperature differences of the pipeline wall (up to 100°C during the year) all increase corrosion damage of oilfield communications. The high costs associated with temporary shutdown, replacement and repair of communications encourage fundamental research for finding out the root cause of high corrosion rates. The information obtained in the study will help direct efforts to prevent emergencies, rather than combat its consequences.

3.1. Results of analysis of reservoir water and field oil

To substantiate the processes involved in biocorrosion scientifically, comprehensive information on the composition of reservoir waters and field oils is necessary. An experimental study of reservoir waters used as a working agent to maintain reservoir pressure was conducted. The results are presented in Tables 1–4. The statistical material on the exploitation of deposits is analyzed. When classifying groundwater from oil fields as industrial, it is recommended to analyze the basic composition (carbonates, sulfates, chlorides, calcium, magnesium, sodium, potassium cations) and the content of trace elements (iodine, bromine, boron, strontium, lithium, rubidium, cesium) in the waters. The selection of the list of components in the reservoir waters of oil fields to be analyzed is based on the recommendations of the Ural Branch of the Russian Academy of Sciences [8].

Analysis shows that the characteristics of reservoir water largely depend on how long a field has been in operation, especially when using waters from different development sites as an agent and pumping-in fresh surface waters at the initial stage of development. Reservoir waters separated from oil during its collection and preparation are highly mineralized, and for this reason, discharge into rivers and reservoirs, either intentional or resulting from depressurization, is not allowed, as this leads to the death of freshwater organisms. Therefore, reservoir waters pumped in into productive horizons in order to maintain reservoir pressure are of the greatest scientific interest in terms of investigating the causes of corrosion. Fresh water used in the technological process, from stormwater drainage, waters after washing and steaming equipment and after desalination processes are also pumped in along with reservoir waters.

The use of oilfield wastewater in the reservoir pressure maintenance system in the water drive regime of field development is an important technical and environmental measure in oil production, which makes it possible to implement a closed cycle of circulating water supply according to the scheme: injection well – oil reservoir – producing well – oil and gas collection and treatment system with a water treatment unit.

Oilfield wastewaters are dilute dispersed systems with a density of 1010–1050 kg/m^3, in which the dispersion media are highly mineralized brines of chlorocalcium type (sodium chloride, calcium chloride). The dispersed phases of wastewater are oil droplets and solid suspensions. When a depression is formed in the bottom-hole zone of a formation, intense mixing and gas release occur in the extracted medium in proportion to the pressure gradient, and therefore an emulsion is formed at the phase boundary in the presence of emulsifiers (mechanical impurities, clay, sulfides, *etc.*).

The formation water in emulsified state nearly does not contain any impurities: their amount does not exceed 10–20 mg/l, but after the emulsion is separated into oil and water, the content of dispersed particles in the separated water increases greatly: oil up to 4–5 g/l, mechanical impurities up to 0.2 g/l. This is explained by the fact that as a result of a decrease in the interfacial tension at the oil-water boundary due to addition of a demulsifier reagent into the system and turbulence of the flow, the dispersion of oil in water is intensified, as well as the washing and peptization of various sludge deposits (corrosion products, clay particles) from the inner surface of pipelines. In addition, an intermediate layer accumulates in water separators, which consists of water droplets with undisturbed armor shells, agglomerates of solid particles, mechanical impurities, asphalt-resin substances and high-melting paraffins, microcrystals of salts and other pollutants. As it accumulates, part of the intermediate layer is discharged with water, and a significant amount of pollutants passes into the aquatic environment. In particular, upon mixing of waters with different chemical composition the sulfate equilibrium is disturbed, which also leads to an increase in the amount of solid particles in the water.

Oilfield wastewater is contaminated with sulfate-reducing bacteria up to 102 cells/cm^3 coming from stormwater. They contribute to the precipitation of calcium carbonate and iron sulfide. The presence of residual petroleum products and mechanical impurities in the wastewater leads to a sharp decrease in the intake capacity of injection wells, which subsequently leads to a decrease in reservoir pressure, a drop in oil withdrawals and expensive well repairs.

Tables 1, 2 and Figure 1 present the results of studies on the chemical composition of reservoir water and its corrosion activity toward metal plates. Tables 3, 4 present the results of oilfield oil testing.

3.2. Corrosion monitoring. Analysis of the research results

As noted above, the problem of corrosion resistance and reliability of equipment is currently of utmost importance.

Statistics shows that the service life of pipelines for pumping wastewater into the reservoir can be as short as 1.5–2.5 years instead of the planned 10–15 years. Every year there is a large number of pipeline failures due to internal corrosion. Accidents lead to significant losses in oil production and environmental pollution. Analysis shows that watered oil (90–96%, using the example of the booster pumping station (BPS)), and wastewater used in reservoir pressure maintenance systems are the most aggressive.

Statistical analysis of the causes of failures of oilfield equipment shows that:

- emergencies occur in pipelines through which oil is transported with a water content of more than 50–60% and a flow rate of 0.1–1.0 m/s;
- ruptures of oil pipelines occur in areas with a stratified flow regime of the oil emulsion, *i.e.*, under conditions where the aqueous phase is separated from it;
- the localization of corrosion damage in the lower part of the pipeline is characterized by the complex effect of many factors: concentrations of microbacteria, Cl^-, HCO_3^-, SO_4^{2-}, and Ca^{2+} ions; pH; pressure in the pipeline; content of mineral particles, CO_2, H_2S, and O_2; flow rates; the presence of inhibitors in the medium; degree of water content in oil, *etc.*

The development of deposits using methods of flooding oil reservoirs with river and lake waters at the initial stage of development leads to the intense development of microbiological processes. Subsequently, as the microorganisms get into ground communications facilities with stagnant zones such as reservoirs, settling tanks, and pipeline sections with low reservoir fluid velocities (~0.5–2 m/s), they develop intensely and cause bacterial corrosion of ground equipment.

Table 1. Results of formation water studies at the Zapadno-Varyogansk field.

pH	**Units of measurement**	**Water hardness, total**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}+K^{+}**	**ΣK**	**Cl^{-}**	**HCO_3^{-}**	**SO_4^{2-}**	**ΣA**
5.0	mg-equiv/L	133.0	125.0	8.0	290.5	423.5	415	8.50	<10	423.5
	mg/L	–	2550	97.28	6972	9619.28	1472	518.5	–	15230.2
	equiv. %	–	14.75	0.945	34.30	50	49	1.003	–	50

Table 1 (continued).

Units of measurement	**Mineralization**	**Characteristics**					**Water density g/cm^3**	**Type of water**
		by Palmer			**by Sulin**			
		S₁	**S₂**	**A₁**	**Na^{+}+K^{+}** **Cl^{-}**	**$Cl^{-}$$Na^{+}$+$K^{+}$** **$Mg^{+}$**		
mg-equiv/L	–	–	–	–	0.7	15.562	1.022	IV (chlorocalcium)
mg/L	24849.53	–	–	–				
equiv. %	100	69	29	2				

Table 2. Corrosion monitoring of steel plate.

Sampling location	Exposure, days	Starting weight, g	Weight after removal, g	Plate area, m^2	$V_{cor.}$, $g/(m^2 \cdot hr)$	$\mathrm{V}_{cor.}$, mm per year
BPS*	65	21.83	18.69	0.003	0.67	0.75
	65	21.96	18.91	0.003	0.65	0.73
BPS	34	26.20	23.89	0.003	0.94	1.05
	34	20.92	18.96	0.003	0.80	0.89

* booster pumping station.

Figure 1. Metal plates – samples for corrosion rate measurements by the weight loss method.

Table 3. Fractional composition of oil.

Fractional composition (temperature of the start and end of boiling of the oil fraction), °C	Volume of oil fractions, ml
T (start of boiling) – 60	3.0
60 – 90	6.0
90 – 120	8.0
120 – 150	9.0
150 – 180	10.0
180 – 210	6.0

Fractional composition (temperature of the start and end of boiling of the oil fraction), °C	**Volume of oil fractions, ml**
210 – 240	7.0
240 – 270	7.0
270–300	10.0
300–330	14.0
T (end of boiling) 330–357	20.0

Table 4. Field oil test results.

oil fractions, °C	**Kinetic viscosity at 20°C, mm^3/s (cSt)**	**Flash point in a closed crucible, °C**	**Mass fraction of sulfur, mg/kg**	**Density at 15°C, kg/m^3**	**Turbidity temperature, °C**	**Solidification temperature, °C**
Start of boiling – 60	–	–	none	>700	–	–
60–90	–	–	none	>700	–	–
90–120	–	–	none	712.2	–	–
120–150	0.76	–	45	742.6	<35	<–40
150–180	0.98	–	95	765.9	<35	<–40
180–210	1.27	30	239	787.2	–34	<–40
210–240	1.90	52	528	809.9	–24	<–40
240–270	2.85	74	1017	827.9	–15	–25
270–300	4.99	91	1862	847.0	–3	–7
300–330	–	–	4520	–	–	–
330–360	–	–	8287	–	–	–

It can be concluded that a significant fraction of all losses of the transported medium that result from corrosion of pipelines operated in the West Siberian region occur due to biocorrosion (Tables 5, 6).

In order to account for the quantitative content of bacteria and fungi capable of causing metal corrosion in reservoir water, water samples were seeded on various elective agarized media. The results are presented in Table 5.

Table 5. Results of sowing on various media in order to take into account the quantitative content of bacteria and microscopic fungi.

Test	Quantity CFU, quantity CFU/ml							
	MPA	King's medium	Beyerinka thiosulfate agar	Tayler's medium	Chapeka-Doxa's medium	Kali-nenko's mediun	Vino-gradsky's medium (I)	Vino-gradsky's medium (II)
1	$3.1 \cdot 10^4$	$4.45 \cdot 10^2$	60	none	none	none	none	none
2	$5.92 \cdot 10^5$	$6.1 \cdot 10^3$	10	none	none	none	none	none
3	$7.4 \cdot 10^4$	$9.6 \cdot 10^2$	$1.1 \cdot 10^2$	33	none	none	none	$7.3 \cdot 10^2$
4	$7.2 \cdot 10^4$	none	none	none	none	none	none	none

Analysis of the amount of Colony Forming Unit (CFU) per meat-peptone agar (MPA) showed the presence of aerobic heterotrophic bacteria in all samples.

Table 6 shows the data we obtained on the content of coliform bacteria, *Ecsherichia coli*, *Pseudomonas aeruginosa* and sulfate-reducing *Clostridium* in water samples.

Table 6. CFU bacteria, 100 ml.

Type of bacteria	Sample 1	Sample 2	Sample 3
Common *Coliform* bacteria	not detected	100	200
Thermotolerant *Coliform* bacteria	not detected	100	200
Pseudomonas aeruginosa	not detected	not detected	not detected
Spores of sulfate-reducing bacteria CFU/20 ml	200	200	200
Ecsherichia coli	not detected	100	200

Analysis of the results shows that the highest content of CFU bacteria capable of participating in corrosive processes (*Coliform* and *Ecsherichia coli*) was found in the water of sample 3, and such corrosive objects as spores of sulfate-reducing bacteria were also isolated from this sample. The results obtained allow us to unequivocally assert the possibility of the participation of microorganisms in metal corrosion.

Under the influence of microbiological processes, corrosion occurs primarily in sections of pipelines and oil and gas equipment where water is collected and settled. Biogenic studies indicate that sulfates and sulfides are converted to hydrogen sulfide upon oxidation, under the action of SRB, of either molecular hydrogen or hydrogen released as a result of a cathodic reaction. It should be noted that hydrogen sulfide-containing media enhance the hydrogenation of the metal, which leads to its embrittlement and corrosion cracking. Hydrogen is especially dangerous in this regard when welding pipe joints under field conditions at low air temperatures.

Based on the analysis of the results of our experiments, the following conclusions were made:

1. Local (pitting) corrosion of carbon and low-alloy steels of oil pipelines on the inner surfaces of pipes is initiated in places favorable for the vital activity of microorganisms, in particular SRB and heterotrophic bacteria. At the same time, microbiological corrosion begins to develop, forming colonies of germinal pits, i.e., local corrosion sites.
2. In the subsequent stages, the electrochemical mechanism of chloride-carbon dioxide corrosion manifests itself.
3. Local corrosion of the pipe wall is accompanied by the hydrogen absorption by the metal around the nuclei of pits, leading to its embrittlement, which facilitates the origination and propagation of cracks.
4. Selective local destruction of the metal in the lower part of oil pipeline pipes (groove corrosion) is explained by the peculiarities of the hydrodynamics of the flow of gas-liquid flows (three-phase oil emulsions) through pipelines. At the same time, carbon dioxide corrosion occurs under the condition of constant exposure of the metal from the protective film shielding it and transition of the metal to the electrochemically active state, as well as formation of an active macrogalvanic pair between the exposed metal section and the rest of the pipe surface covered with a protective layer.
5. Microorganisms in the supply water stimulate corrosion of pipe steel, including that protected by an epoxy coating, while microbes are capable of feeding on epoxy resin.
6. Corrosion damage at microscopic level begins mainly in the areas where microorganisms are accumulated: in zones bordering grains and around “nests” formed in place of carbide grains that fell out as a result of chemical “etching” of austenite around the matrix.

The diffractograms of petroleum product deposits on the inner surfaces of the pipe (Figure 2) contain diffraction reflections of a number of compounds. The most intense ones belong to carbon compounds with graphite structure, *i.e.* the deposits studied are solid hydrocarbons. Iron sulfides FeS are also present there, along with salts – $CaCO_3$ and $CaSO_4$.

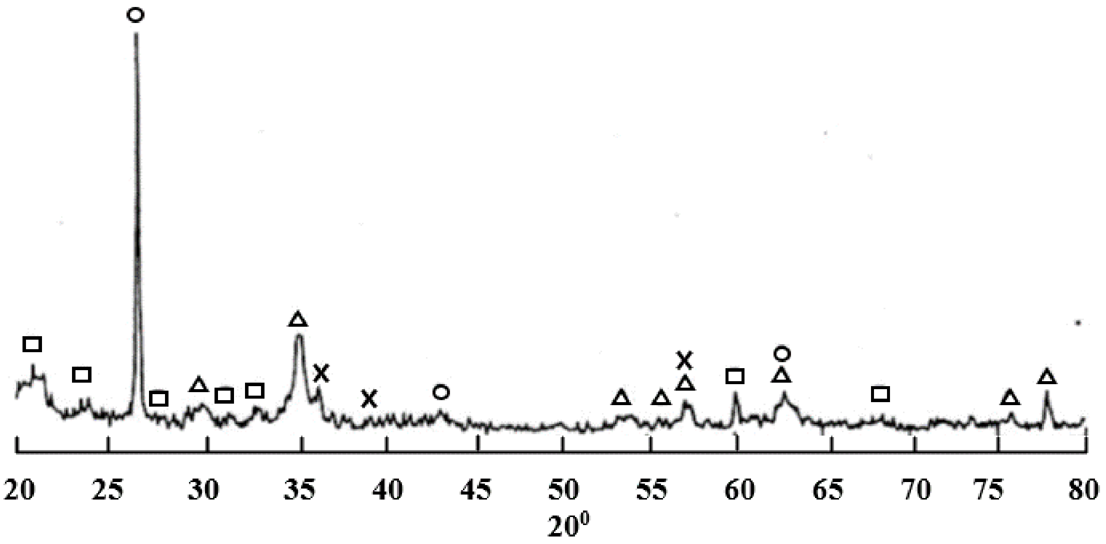

Figure 2. Diffractogram of oil deposits on the inner surface of the pipe: □ – $CaSO_4$, ○ – C, × – $CaCO_3$, △ – FeS.

Due to the high wettability of metals, hydrocarbons form a hydrophobic film of adsorbed active petroleum compounds on their surfaces. This layer is an activating and adhesive element that captures crystals of salts, agglomerates of iron sulfide and inclusions. The accumulation and compaction of visco-solid ARP (asphalt-resin-paraffin) oil deposits favor the origination and development of multiple ulcerative corrosion of internal surfaces, up to through holes. The water present in oil accumulates in closed spaces such as lenses between and under layers of solid deposits. Under these conditions, it is permanently saturated with chemically reactive sulfur and chlorine compounds, as a result of which it turns into an electrolyte, and this contributes to the intense corrosion destruction of internal surfaces.

It is known that the process of biocorrosion occurs where a metal contacts bacteria, which form a biofilm on the surface. The mechanism of depolarization under the action of bacteria was proposed by Booth G.H. [9–12]. The conversion of Fe into soluble divalent Fe^{2+} ions takes place at the anode. Atomic hydrogen accumulates at the cathode [13] and is used by sulfate-reducing bacteria to reduce sulfates SO_4^{2-} to H_2S. Fe^{2+} reacts with H_2S to form insoluble iron sulfide, FeS (Figure 3).

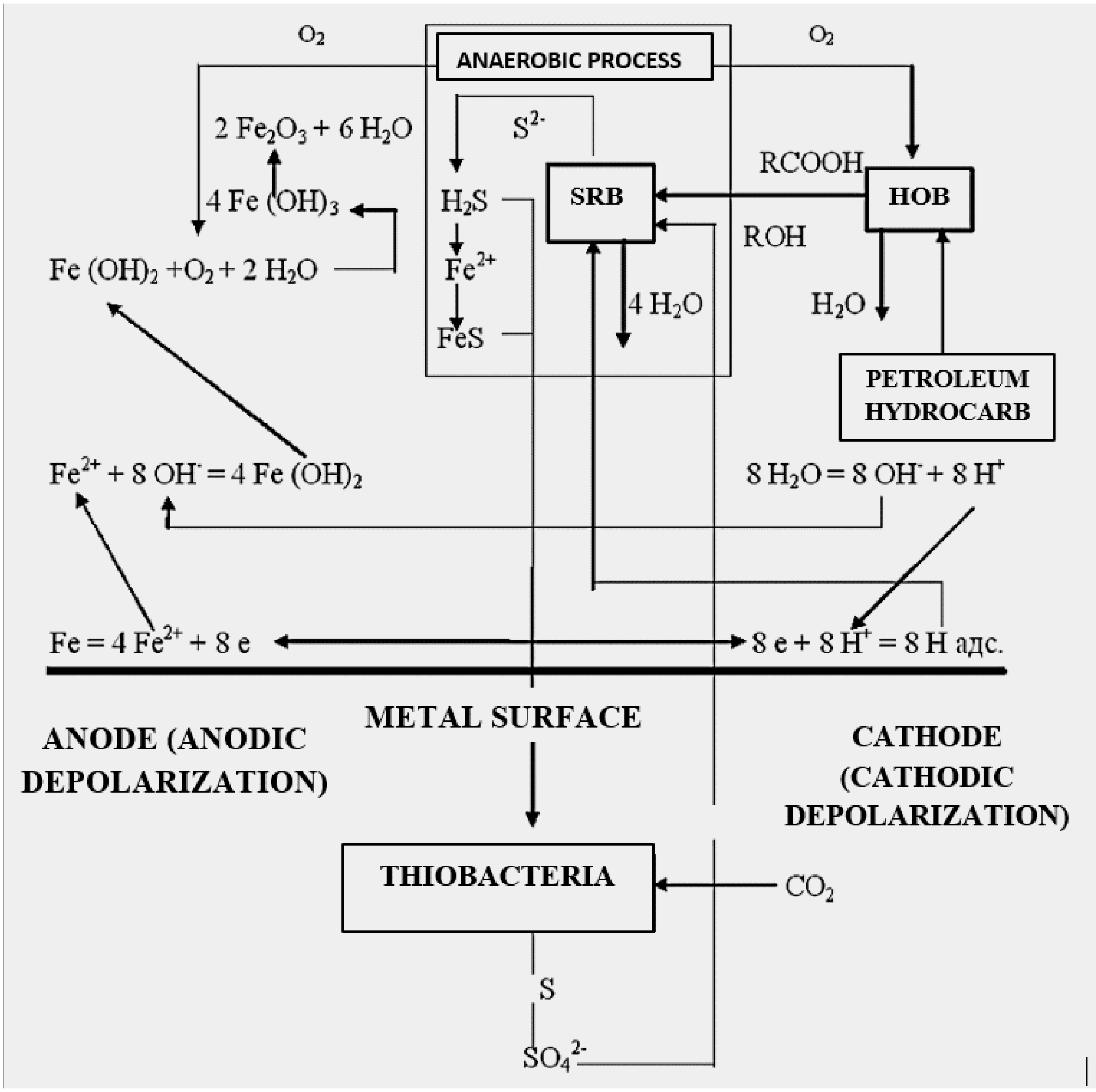

Figure 3. Scheme of biocorrosion of metals [9, 10]. SRB – sulfate reducing bacteria; HOB – hydrocarbon-oxidizing bacteria.

Thus, SRBs are the primary factor of biocorrosion in such a technogenic niche as soils, transported watered media, as well as the inner and outer surfaces of metal pipelines (Figure 4).

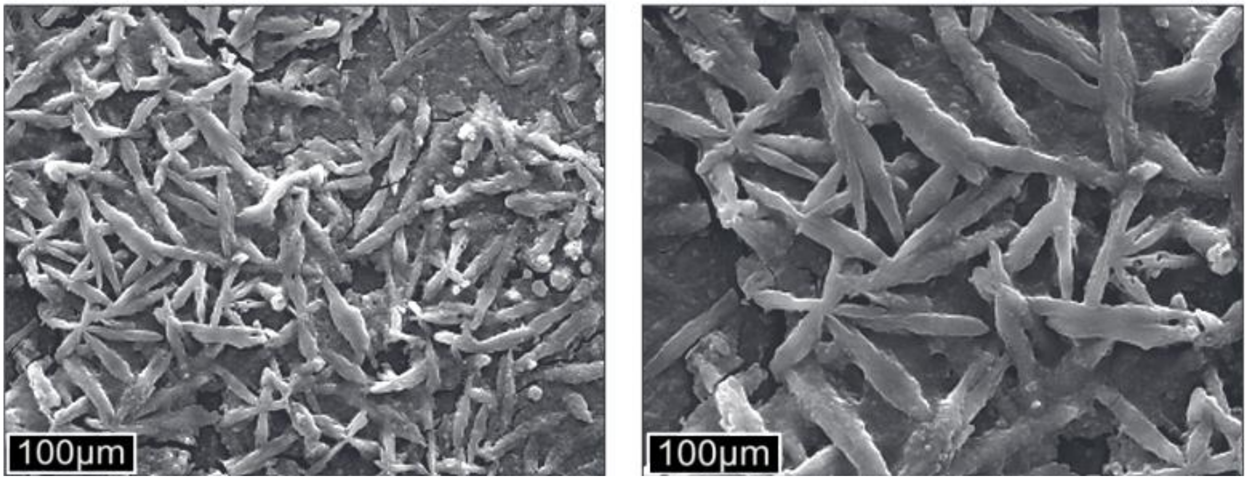

Figure 4. Micrographs of the surface of tubular steel in SRB media obtained using a scanning electron microscope.

It should be noted that, despite the great diversity in the physiology of corrosive bacterial microflora, some groups of microorganisms are not only non-adversaries against each other, but even, on the contrary, create a biocenosis that supports their vital activity (Figure 3). The most striking example of such a biocenosis is the mutual existence of HOB, SRB and thion bacteria. The role of HOB in this community is to consume oxygen in the process of vital activity and form an anaerobic environment, oxidize petroleum hydrocarbons with formation of intermediate products of incomplete oxidation – alcohols, aldehydes, which under the anaerobic conditions thus created are consumed by SRB in the course of nutrition. SRB development takes place in the production of many oil fields. The effect of SRB on a metal is one of the main factors of biocorrosion. Thionic bacteria (*Tiobacillus*) can oxidize sulfur to sulfuric acid (the local concentration of which reaches 10%) and thus contribute to the formation of acidic aggressive media.

3.3. Inhibitors and bactericides of microbiological corrosion

An effective method of combating microbiological corrosion is to use corrosion inhibitors in combination with bactericides. We will conduct a brief analysis of the most effective biocides and corrosion inhibitors, according to the authors. In [15], using the example of the SNPH-1004P inhibitor reagent, it was shown that the only effective method of combating microbiological contamination of oil fields and protecting ground equipment from internal corrosion is the use of bactericidal inhibitors using integrated protection technology, which includes antibacterial treatment of all links of the technological chain: producing wells – booster pumping stations – cluster pumping stations – injection wells, combined with a permanent supply of the reagent in effective concentrations. The results of the analysis of the bactericidal activity of SNPH-1004P are presented in Figure 5 and in Table 7 [15].

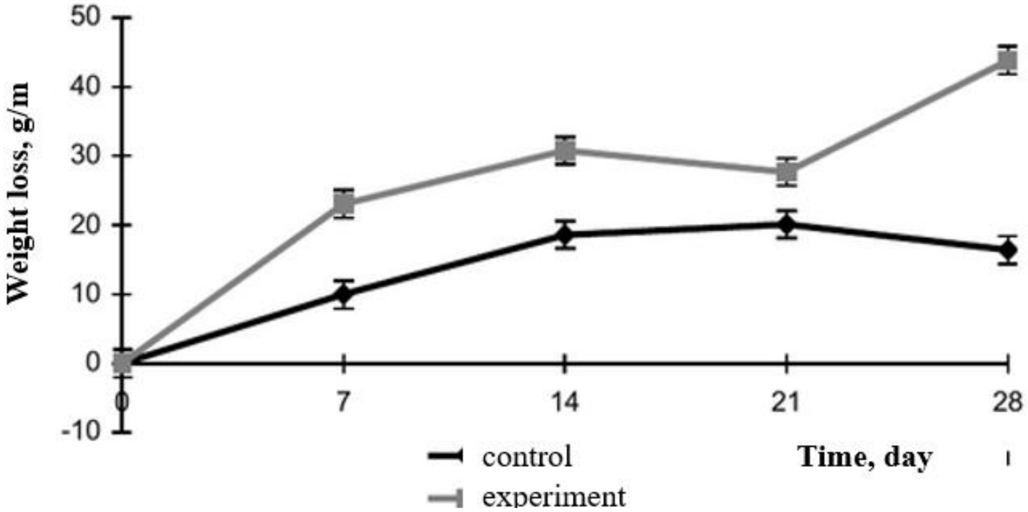

Figure 5. Change in plate mass loss in oilwater with bacteria (experiment, without bactericide) and (control, with bactericide).

The concentrations of the bactericide inhibitor, which effectively suppress the vital activity of SRB, are presented in Table 7.

Table 7. Comparison of the effectiveness of bactericidal concentrations of SNPH-1004P and NAPOR-1007 reagent relative to SRB.

Bactericide inhibitor	Concentration causing 100% suppression of SRB cells, mg/l	
	Planktonic SRB	**Planktonic SRB**
SNPH-1004P	25	400
NAPOR-1007	75	1200

The data show that the SNPH-1004P reagent, in the studied concentrations, has an excellent biocidal effect on bacterial cells, *i.e.* it completely destroys the structure of the bacterial cell, which prevents the formation of reagent-resistant SRB cells.

The characteristics of the bactericidal inhibitor SNPH-1004P are clearly presented in Table 8.

Table 8. Characteristics of the inhibitor bactericide SNPH-1004P.

Characteristic	Standard
Appearance	liquid from light yellow to brown color
Kinematic viscosity, mm^2/s:	
at 20°C, no more than	50
at −45°C, no more than	500
Specific consumption, g/m^3:	

Characteristic	Standard
corrosion protection SRB 90%	15–25
corrosion protection SRB 100%	150
Density, g/cm^3	0.89
Solubility:	
in water	dissolves (disperses)
in oil	dissolves

A technological regulation as of 2017 has been developed for the use of a corrosion inhibitor, the bactericide SNPX-1004P, at the Variogan field in order to combat corrosion.

It should also be noted that IFKhAN series reagents (for example, IFKhAN-90, 91) are effective inhibitors for protection against hydrogen sulfide corrosion and hydrogen absorption by steel pipelines and apparatuses in the oil and gas production and processing industries [16].

Yu.I. Kuznetsov *et al.* were the first to study the effect of the chemical structure of quaternary ammonium compounds (QAC) with general formula $[C_6H_5CH_2NR_1(R_2)(R_3)]^+Cl^-$ on their protective inhibitory properties. The ways of purposeful selection and synthesis of effective inhibitors of corrosion and hydrogenation of steel in H_2S-containing media based on QAC have been determined. A new effective inhibitor based on diphenylguanidine (DFG), IFKhAN-91, in combination with a QAC has been developed, which has a high protection efficiency and significant aftereffect in acidic hydrogen sulfide-containing media, which opens up a good prospect for their practical application in the protection of oil refining and oil production equipment [17].

The author [17] also investigated the aftereffect of the protective ability of DFG, IFKhAN-91 and QAC-9 and their mixtures for 1–24 hours. A noticeable aftereffect is demonstrated by the mixed composition QAC-9+IFKhAN-91 (2:1) at 24 hours of exposure and an inhibitor concentration of 100 mg/l. The protective effect against corrosion was Z=97% and that against hydrogen absorption was P=51%, which makes the composition QAC-9+IFKhAN-91 (2:1) promising for applications for protection against hydrogen sulfide corrosion of primary oil refining plants. Taking into account the conditions of interphase transfer of inhibitors in a heterogeneous corrosive environment of petroleum distillates, a solubilizer was proposed for dissolving the composition QAC-9+IFKhAN-91, based on the residues of butyl alcohol distillation.

4. Conclusions and Recommendations

Thus, in this study it was proved that the internal corrosion of pipelines of in-field oil collection and transportation systems of the Variogan field is due, among other things, to the presence of a bacterial background, the presence of a mineralized aqueous phase and carbon dioxide dissolved in water and oil. The rate of internal corrosion of pipelines in terms of corrosion depth is up to 1.0 mm/year. For a more accurate calculation of the corrosion rate based on the loss of metal mass and for tracking local corrosion, the time of exposure of samples for corrosion control by the weight method should be at least 60-90 days.

The degree of aggressive effect of the aqueous phase of pipelines of in-field oil collection and transportation systems on the metal of pipes is characterized as "highly aggressive" [Table 2 in the Working Documentation (RD) 39-0147103-362-86 (on the rate of corrosion), and Table 4 in RD 39-0147103-362-86 (on the chemical composition of the aqueous phase)]. In accordance with the requirements of [RD 39-132-94 (Section 7.7) and RD 39-0147103-362-86 (Section 5)], corrosion inhibitors must be used to protect pipelines of in-field oil collection and transportation systems.

Wastewater contains dissolved gases: oxygen, hydrogen sulfide, carbon dioxide, which intensify their corrosive activity, leading to rapid wear of oilfield equipment and pipelines and, consequently, secondary contamination of wastewater with corrosion products. The wastewater contains iron (II), the oxidation of which leads to the formation of sediments and carbon dioxide.

Oilfield wastewater is contaminated with sulfate-reducing bacteria coming from stormwater, contributing to the precipitation of calcium carbonate and iron sulfide.

Biocorrosion is among the main reasons causing high corrosion activity.

Sulfate-reducing bacteria pose the greatest corrosion hazard among bacteria. These are obligate anaerobes that oxidize organic substances such as pyruvate, lactate, succinate, malate, as well as alcohols. Some sulfate-reducing bacteria have shown the ability to oxidize molecular hydrogen. These bacteria are found in rivers, lakes, seas, oceans, soil, and oilfield waters.

The optimal pH values for the development of SRB are in the range from 5.5 to 9, those of the redox potential are within 115–450 mV.

Under the conditions of formations infected with SRB, hydrogen absorption by the metal is observed, which leads to pitting corrosion. In our case, the mechanism of destruction is as follows: atomic hydrogen is embedded in the crystal lattice and "knocks out" metal atoms from it. A change in the lattice structure begins, and an electrochemical pair arises. As atomic hydrogen is accumulated and the pressure increases, the microhardness of the metal decreases and its brittleness increases [13].

The main reason for the occurrence of biocorrosion in oil fields where conventional flooding is used (or was used) is due to lack of special treatment of the river or lake water injected underground where the SRB found favorable temperature, chemical and, in general, environmental conditions for the intense development and reproduction. First of all, the underground equipment of wells suffers from biocorrosion, as well as above-ground equipment and pipelines, since the water extracted with oil contains hydrogen sulfide and is corrosive. Water is separated from oil, immediately pumped back into the reservoir at the field and is further enriched with aggressive components.

In relation to the microbiological problem, oil fields can be divided into 3 groups:

- 1st, new fields where the intensification of oil production is at an initial stage, and the production of oil wells does not contain hydrogen sulfide (does not apply to our case);
- 2nd, deposits in the late stage of operation, developed using flooding of productive formations, where the appearance of hydrogen sulfide is caused by flooding;
- 3rd, deposits where the extracted products contain hydrogen sulfide since the beginning of development.

For the 3rd group of deposits, only anticorrosive measures with the use of corrosion inhibitors and bactericidal inhibitors can be recommended.

For the 2nd group of deposits, where hydrogen sulfide and SRB are found both in the productive reservoir and in the extracted products, the fight against sulfate reduction is carried out in two directions: suppression of SRB in the reservoir and protection of oilfield equipment from corrosion. The suppression of SRB in the reservoir must be carried out by treating injection wells with bactericides in a shocking dosage. To protect the equipment from corrosion, it is recommended to treat the media with complex reagents – bactericide inhibitors, introducing them into various points of the protected medium.

Combating microbiological corrosion is mist effectively done by chemical methods, *i.e.*, treatment of microbially infected media with bactericidal inhibitors that cause the death of microorganisms.

Bactericidal inhibitors should have the following properties:

- when combined with mineralized oilfield media, they should not produce precipitation that can lead to a decrease in the permeability of productive formations;
- processability (liquid state, low viscosity, low pour point);
- stability during long-term storage;
- low toxicity to maintenance personnel, no pungent odor;
- availability of the raw material base.

In addition to the listed general requirements, bactericidal inhibitors are subject to special requirements that take into account the technical characteristics of the protected materials and structures, their operating conditions, *etc.* Thus, bactericides used to protect drilling equipment from corrosion must be compatible with the components of drilling fluids and not change their physicochemical properties; inhibitors-bactericides used in oil fields should not be dissolved in oil and petroleum products, so as not to cause the failure of catalysts at refineries.

Currently, considerable experience has been accumulated in the development and recommendation of effective bactericidal inhibitors for oil reservoir flooding systems, including the bottom-hole zone of injection wells. To date, a wide range of biocide inhibitors has been developed, including nitrogen-, oxygen-, sulfur-, halogen-containing organic and inorganic compounds. Nitrogen-containing compounds with long hydrocarbon chains have become the most popular among these. According to their chemical properties, they are divided into:

- derivatives of aliphatic fatty acids (primary, secondary and tertiary monoamines, diamines and amides; polyethoxylated amines, diamines and amides); the salts of these compounds include derivatives of acetic, phosphoric, oleic, naphthenic and other fatty acids of natural (acids of coconut, soy and tallow oils, natural fats and other oils) or synthetic origin,
- corrosion inhibitors based on organophosphorus complexes of d-metals,
- imidazolines and their derivatives,
- quaternary ammonium bases and their derivatives,
- pyridine derivatives,
- and other nitrogen-containing compounds.

As a recommendation for corrosion protection, corrosion inhibitors of the IFKhAN series [18, 19] are proposed, as well as a complex inhibitor, SNPH-1004R bactericide, to protect oil collection systems, oil pipelines transporting watered oil where the structural flow shape is stratified or varies along the length of the pipeline, from contamination with sulfate-reducing bacteria.

5. References

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