

Influence of soil microorganisms on metal corrosion of underground pipelines

Vliv půdních organismů na korozi podzemních potrubí

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*There have been revealed and summarized the regularities in biocorrosion of steel 17G1S-U, which is traditionally used for manufacturing oil and gas mains. The basic regularities of biocorrosion processes in the 17G1S-U pipe steel under the influence of SRB *Desulfovibrio Sp.* strains Kyiv-10 was obtained by weight-loss testing and surface analysis techniques. Effective inhibitors are proposed, which allow protecting steel 17G1S-U against the development of anaerobic corrosion under the influence of sulfate-reducing bacteria (SRB). The effectiveness of inhibitors is estimated by the degree of their protective effect. The porous structure of the surface film contributes to the initiation of localized corrosion. Damage analysis of the specimen surface corroded under different test conditions was performed.*

*Byly studovány a zhodnoceny trendy v biokorozi oceli 17G1S-U, která je běžně používána pro výrobu petrochemických potrubí. Hlavní metodou studia biokorozních procesů oceli ovlivněné sulfát redukující bakterií *Desulfovibrio Sp.* kmen Kyjev-10 bylo hodnocení hmotnostních úbytků a mikroskopie povrchu. Účinné inhibitory proti účinkům této ananerobní bakterie byly nalezeny. byly vyhodnoceny efektivitu inhibičního účinku. Porozita biofilmu přispívá k lokalizaci napadení. Byla provedena analýza poškození materiálu za různých podmínek expozice.*

INTRODUCTION

Providing reliability and reducing the accidents of underground pipelines in soils with different degrees of mineralization is an important scientific and production task [1,2]. It is known that one of the main factors that cause corrosion damage to metallic structures in soils is the effect of microorganisms (MOs) that use metal as a power source. At the same time, due to their activity, the PH of the medium changes causing fracture of the metal. About 80% of corrosion damage of the oilfield equipment takes place with the participation of MOs, among which the sulfate-reducing bacteria (SRB) play the leading role. At the same time, the use of bactericides to combat them is, as a rule, ineffective, because SRB are firmly fixed on metallic surfaces and form biofilms covered with slurry and products of corrosion [3-5]. It should be emphasized that the kinetics of biocorrosion can be different for different types of steels. This is due to the fact that some doping elements increase biocorrosive stability, but others are potential components of nutrition for bacteria. The grain morphology of steels also affects their corrosion resistance. As a rule, increasing the size of grains intensifies intercrystalline corrosion due to an increase in the length of their boundaries, which traditionally is a "weak point" of steels.

Lithotrophic anaerobic SRB are very often isolated in the H₂S medium, which is the most dangerous of all known corrosion stimulants. In the presence of hydrogen sulfide, the metal is hydrogenated, which reduces its mechanical strength [1-8]. Underestimation of the danger of microbial corrosion causes premature failure of underground pipelines and the occurrence of extraordinary situations with severe environmental consequences [2-3, 10].

Thus, the objective of this research is to establish the basic regularities of biocorrosion processes in the 17G1S-U pipe steel under the influence of SRB *Desulfovibrio Sp.* strains Kyiv-10.

On the outer surface of the gas main "Pasichna – Tysmenytsia" (Fig. 1), multiple corrosive ulcers caused by the influence of biocorrosion are shown. Such defects are typical damage to the metal due to the formation of local sulfide deposits and microorganism colonies in the ground electrolyte in the presence of hydrogen sulfide of biogenic origin on the surface [6, 9]. The unevenness of the surface damage should be noted, which confirms the localization of corrosion processes. This suggests that even small fluctuations in microbiocenosis affect the kinetics of damage to the metalwork.



Fig. 1. Corrosion ulcers found on the wall of the gas main "Pasichna – Tysmenytsia"

Obr. 1. Korozní napadení pod biofilmem na stěně plynového potrubí "Pasichna – Tysmenytsia"

Therefore, in our opinion, it is reasonable to optimize the selection of insulating materials for gas main systems to facilitate the formation of microbiocenosis with high catalase activity, which assists in protection against biocorrosion.

MATERIALS AND METHODS

The objects of research were the model specimens from the 17G1S-U pipe steel in the initial state, with the size of 10×30×1 mm. The specimens were cut from the pipe, their working and lateral surfaces were milled. The specimen surface was not polished, since the gas main surface contains micro-roughness. In general, the preparation of specimens for the experimental research is similar to that described in [11].

SRB cells *Desulfovibrio Sp.* strains Kyiv-10 were grown in Postgate's B liquid medium [12] in a thermostat at a temperature of 28 °C for 14 days. Pure colonies of sulfate reducers were obtained in a semi-liquid Postgate's B medium by inoculating a ten-fold dilution.

The schemes of experiments with additional introductions into the test system of inhibitors such as organic nitrogen-containing compounds were also investigated:

Inhibitor # 1 – 1,8-dioxo-3,3,6,6,9-pentamethyl-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine;

Inhibitor # 2 – hexamethyldodecylammonium chloride.

The control medium was Postgate's B sterile nutrient medium for the cultivation of SRB bacteria. The exposure period of steel specimens was 62 days. Upon completion of the research, the metallic specimens were subjected to the mechanical and chemical treatment to remove corrosion products from their surface.

The corrosion rate of metallic specimens was determined by the gravimetric index of the corrosion rate (K_{gr}):

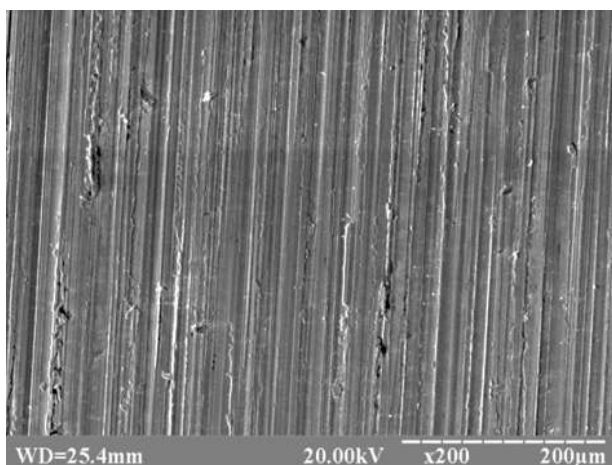
$$K_{gr} = (m - m_0) / (S \cdot \tau) \text{ [mg dm}^{-2} \text{ day]}, \quad (1)$$

where m is the final mass of the specimen, mg; m_0 is the specimen mass before corrosion, mg; S is the surface area of the specimen, dm²; τ is the exposure period, day.

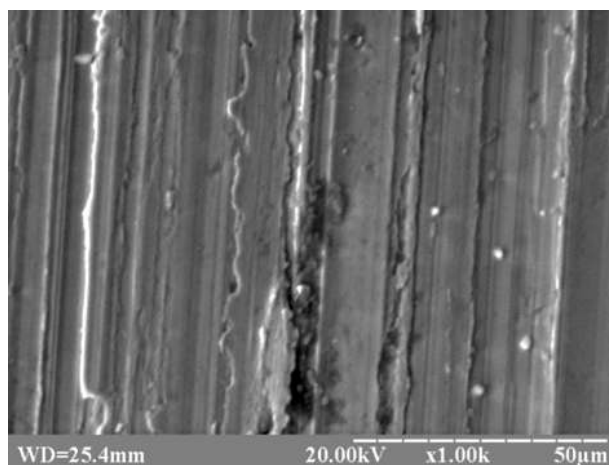
The bactericidal properties of the inhibitors studied were determined according to the DSTU 3999-2000 [13]. The concentration of inhibitors was 0.5% and 1.0%. The effectiveness of the inhibitors studied was characterized by the degree of protective action of inhibitors (Z), calculated by the formula:

$$Z = [(K_{gr} - K_{gr1}) / K_{gr}] \cdot 100 \text{ [%]} \quad (2)$$

where K_{gr} is the corrosion rate in the uninhibited medium, mg dm⁻² day; K_{gr1} is the corrosion rate in the presence of inhibitors, mg dm⁻² day.



a)



b)

Fig. 2. Surface morphology of steel 17G1S-U at various magnifications in the initial state

Obr. 2. Morfológie povrchu oceli v původním stavu

For microstructural and fractographic studies, the electron microscope REM-106I and raster electron microscopy methods were used.

RESULTS AND DISCUSSION

The analysis of findings of the experimental research into the growth suppression of SRB bacteria *Desulfovibrio sp.* strains Kyiv-10 in the course of model laboratory experiments showed that in the sterile Postgate's B medium, in the case of steel 17G1S-U, no corrosion traces were detected. The relative corrosion activity, Fig. 3b, was calculated by the formula:

$$\lambda = [(K_{gr0} - K_{grb}) / K_{gr0}] \cdot 100 [\%] \quad (3)$$

where K_{gr0} and K_{grb} is the corrosion rate in the A medium and in the studied B,C,D,E,F media, respectively.

An increase in the corrosion rate in the case of test schemes B, C was found, indicating their significant biocorrosion activity: $\lambda_B = 193.75\%$ and $\lambda_C = 206.25\%$. For the test schemes D, E, F, a decrease in the corrosion rate was observed: $\lambda_D = 31.25\%$, $\lambda_E = 87.50\%$, and $\lambda_F = 81.25\%$, respectively. The sign “-“ in this case indicates that the biocorrosion rate of the steel 17G1S-U in these media was lower than in the control A medium.

Without inhibitors

In Postgate's B medium inoculated by SRB, the latter act as stimulators of the SRB growth activity, as evidenced by greater metal losses. The surface of the steel specimens was covered with a black precipitate, and the cloudiness of the corrosive medium was observed, indicating the development of biocorrosion with the

participation of SRB, which caused the formation of biogenic sulfide of iron. When the specimens were dosed into the solution of hydrochloric acid, the sulfide film was destroyed with the release of hydrogen sulfide. As a result, specimens from the 17G1S-U steel were corroded under the action of SRB.

Effect of inhibitors 1 and 2

For steel 17G1S-U, the addition to the medium of inhibitor # 1 at a concentration of 0.5% caused the largest mass losses. This inhibitor at a concentration of 0.5% did not show the inhibitory effect, but, on the contrary, acted as a stimulant of the biocorrosion processes caused by SRB. By the end of the experiment, the growth rate of corrosion for the steel 17G1S-U was observed to be 4-5%. At the same time, an increase in the number of SRB cells was found, which may be due to the adaptation of SRB bacteria to the action of the toxicant (in particular, due to the adsorption of MOs on the steel surface with the formation of a protective biofilm), which led to the intensification of corrosion processes. A gradual increase in the number of SRB bacteria is probably due to the formation of metabolites, which are less toxic as compared to the initial inhibitor. It was found that an increase in the concentration of inhibitor # 1 to 1.0% leads to the suppression of the sulfate-reducing activity. At the same time, the degree of metal protection against biocorrosion for steel 17G1S-U amounted to 76,6%.

At a concentration of 0.5%, inhibitor # 2 almost completely suppressed the growth of SRB. The degree of metal protection against corrosion, at the same time, was 95.74%. With an increase in the concentration of inhibitor # 2 in the nutrient medium up to 1.0%, the effectiveness of inhibiting the growth activity of SRB somewhat

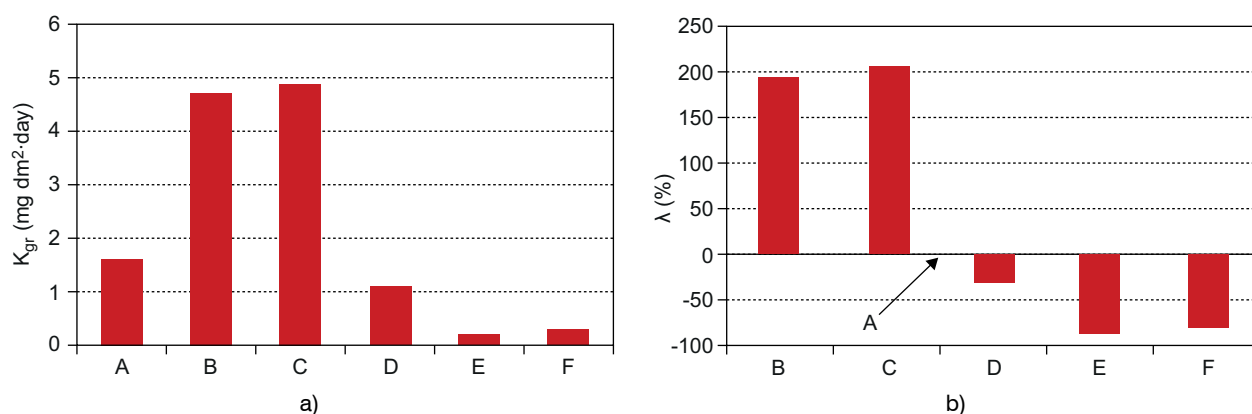


Fig. 3. Corrosion rate of specimens from steel 17G1S-U in the presence of *Desulfovibrio sp.* strains Kyiv-10 in the following media: A – control A medium; B – Postgate's B medium + SRB; C – Postgate's B medium + SRB + inhibitor # 1–0.5%; D – Postgate's B medium + SRB + inhibitor # 1–1.0%; E – Postgate's B medium + SRB + inhibitor # 2–0.5%; F – Postgate's B medium + SRB + inhibitor # 2–1.0%

Obr. 3. Korozní rychlost vzorků v různých prostředích: A – kontrolní medium A; B – Postgate B medium s přidavkem SRB; C – Postgate B medium s přidavkem SRB a 0,5% inhibitoru 1; D – Postgate B medium s přidavkem SRB a 1,0% inhibitoru 1; E – Postgate B medium s přidavkem SRB a 0,5% inhibitoru 2; F – Postgate B medium s přidavkem SRB a 1,0% inhibitoru 2

decreased, as evidenced by a decrease in the protective effect of the inhibitor to 93.62%. Visual analysis of the specimen surface after the experiments showed that in the presence of inhibitor # 2 at a concentration of 0.5% and 1.0% in the medium on the metal surface, no traces of corrosion were detected. In the presence of the investigated inhibitor, no cloudiness of Postgate's B medium was observed, no sulfide film was formed on the steel specimens, and a gray-black precipitate dropped to the bottom of tubes, indicating the death of a significant number of SRB cells and a slowdown in the process of biocorrosion of the steel. A high degree of the metal protection against the influence of SRB indicated the bactericidal properties of the investigated inhibitor. The results obtained are consistent with the results presented in [11].

Table 1 summarizes the data on the influence of the inhibitor nature on the degree of protection of steel 17G1S-U against biocorrosion caused by SRB.

Tab. 1. The influence of the inhibitor nature on the degree of protection of steel 17G1S-U / *Vliv typu inhibitoru na biokorozi oceli*

Steel	Inhibitor	Concentration of inhibitor (%)	Protective action Z (%)
17G1S-U	–	–	4.70
	1	0.5	absent
		1.0	76.60
	2	0.5	95.74
		1.0	93.62

Sem-analysis of the surface of corroded specimens

Without inhibitors

It is found that for the test schemes A and B, the surface of specimens from the 17G1S-U steel was corroded, which is confirmed by the data on the mass loss of specimens. The surface of steel specimens acquired a black color due to biocorrosion with the participation of SRB.

With inhibitors

As noted above, inhibitor # 1 intensified the corrosion process (test scheme C). On the surface of the specimens, Fig. 4a,b, "islets" with a length of 40-100 μm and a width of 50 μm were found.

They have a random orientation that intersects the initial deformation relief at various angles. These islets have no clearly defined orientation and are merged into the network. The depressions between the islands were the sites of macrolocation of the corrosion process. Despite such "islet", corrosion developed quite uniformly in the depressions. According to the test scheme (D), uniform corrosion damage was detected on the specimen surface along with several macro-ulcers with a length up to 100 μm and a width 20-30 μm . Visually their depth varies slightly, the bottom is practically flat and covered with traces of corrosion, Fig. 4b.

The maximum inhibitory effect with suppressing the growth of SRB on specimens from the 17G1S-U steel was caused by inhibitor # 2. Even when added at a concentration of 0.5% (test scheme E), this inhibitor caused a reduction in corrosion, the specimen surface had only minor corrosion damage. The deformation relief of the analyzed surface, due to mechanical treatment, remained virtually in its original state, Fig. 4c.

According to the test scheme (F), the corrosion resistance of the 17G1S-U steel was insignificant. The surface is virtually in its initial state with individual microcorrosion damages, which manifested itself only in large increments, Fig. 4c. The results of the conducted studies indicate that an effective inhibitor of microbial corrosion of steel under the influence of SRB was inhibitor # 2. The high protective effect of inhibitor # 2, which is associated with quaternary ammonium salts, is probably due to the fact that, under microbial corrosion, a thin sulfide film is formed that is coated with a monomolecular layer of the inhibitor, which stops its further growth and inhibits the anodic dissolution of the metal [14 -15].

Inhibitor # 2 can be considered as a promising component in the development of new inhibitory compositions for the protection of metals against biocorrosion caused by SRB. Sulfur reducing bacteria (SRB) are environmentally hazardous because they have the strongest corrosion properties among soil microorganisms. As a result of their high activity, growth and multiplication, the metal fracture can begin suddenly and lead to the formation of through perforations with the leakage of transported products and the pollution of the environment. To prevent such emergencies, it is necessary to use insulating coatings modified by corrosion inhibitors with biorefractory properties that resist SRB in soil locations. To protect the gas pipelines from microbial corrosion caused by SRB, the following design of the insulating coating is proposed: primer - modified mastic - insulating tape. Primer that contains an inhibitor is applied to the cleaned surface of the pipeline. After the primer dries up, a mastic modified with an inhibitor, which exhibits bactericidal properties against SRB, is applied on top of it. And an insulating tape is applied above the mastic.

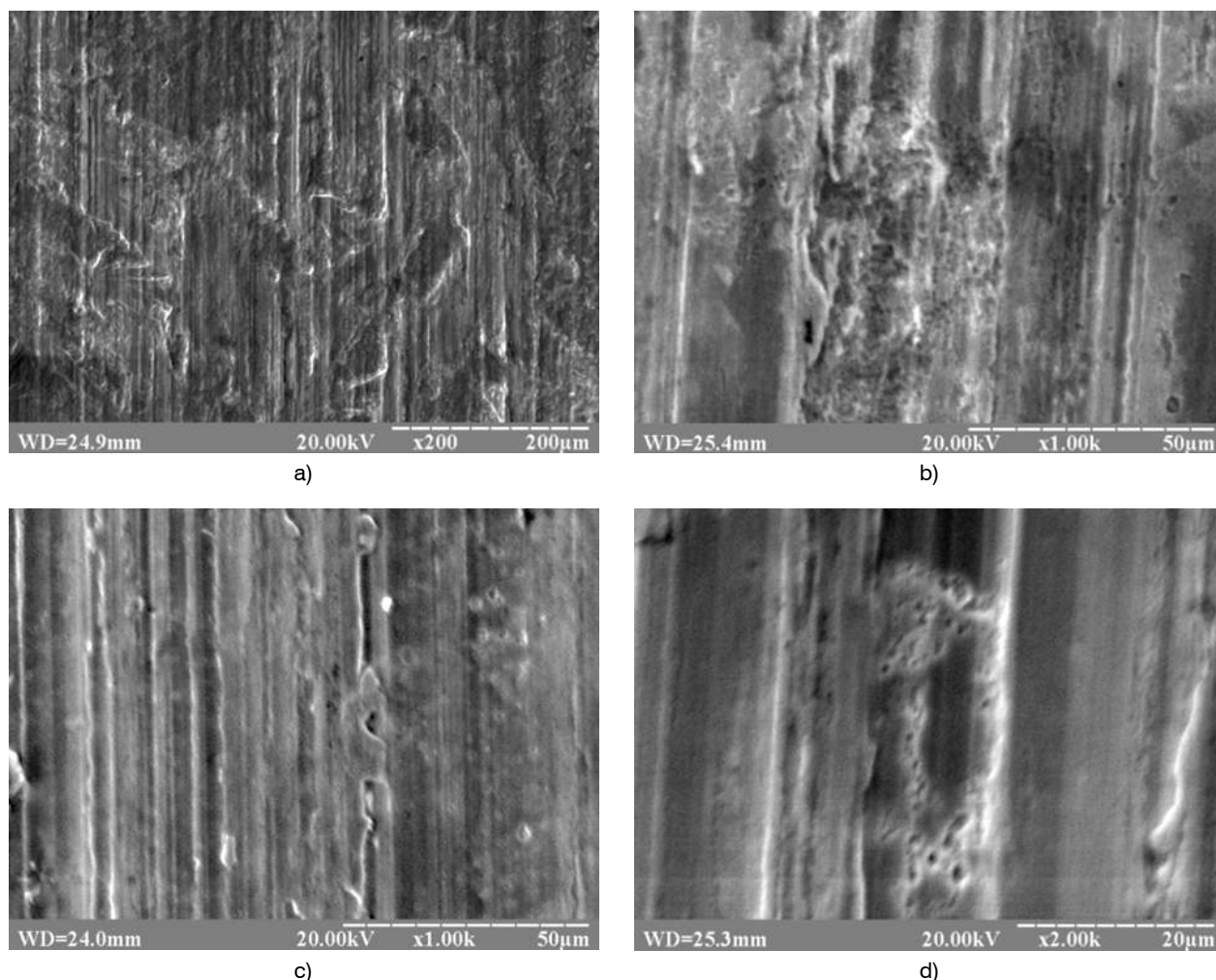


Fig. 4. Morphology of the surface of specimens from steel 17G1S-U subjected to the effect of biocorrosion in different media: a) Postgate's B medium + SRB + inhibitor # 1-0.5%; b) Postgate's B medium + SRB + inhibitor # 1-1.0%; c) Postgate's B medium + SRB + inhibitor # 2-0.5%; d) Postgate's B medium + SRB + inhibitor # 2-1.0%

Obr. 4. Morfologie napadení vzorků v různých prostředích: a) Postgate B medium s přidavkem SRB a 0,5% inhibitoru 1; b) Postgate B medium s přidavkem SRB a 1,0% inhibitoru 1; c) Postgate B medium s přidavkem SRB a 0,5% inhibitoru 2; d) Postgate B medium s přidavkem SRB a 1,0% inhibitoru 2

CONCLUSIONS

The basic regularities are established in the variation of the corrosion rate of specimens from steel 17G1S-U in the presence of organic inhibitors in the sterile Postgate's B medium, which were inoculated with SRB bacteria. The influence of the inhibitor nature on the degree of protection of steel specimens with the development of anaerobic corrosion under the influence of SRB is evaluated. The bactericidal properties of inhibitor # 2 and the high protective effect from microbial corrosion caused by SRB are established. The physical-mechanical interpretation of the relief morphology of the investigated specimens under different modes of biocorrosion effect was proposed.

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