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INCREASING THE EFFICIENCY OF MICROBIOLOGICAL PROTECTION OF UNDERGROUND FACILITIES

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ABSTRACT

Highlight important aspects of microbiological protection of underground facilities. It is shown that an important environmental and technological problem is the protection of underground oil and gas pipelines from microbial corrosion by soil corrosion-hazardous microorganisms, including the crucial role played by sulfatvosstanovitelnye (SRB) and thione (TB) bacteria. The influence of the nature of the inhibitor and the hydrophobicity of the electrolyte composition of basic and modified mastics. The influence of heterotrophic bacteria isolated from the damaged asphalt blocks pipeline, the stability of modified bitumen-polymer sealant. The effect of nitrogen-containing corrosion inhibitors on the growth and enzyme activity of the bacteria and the sulfur cycle, the mechanism locks thiobacteria and gidrogenaznoi reaction korozionnoaktivnih SRB. The efficiency of the derivatives dioksodekagidroakridina the rate of microbial corrosion of steel under the ISF and thiobacteria. A comparative evaluation of the effectiveness of these inhibitors in industrial inhibitor. These inhibitors provide a high degree of protection from corrosion in the presence of SRB (90%), which indicates their antibacterial properties and offers the prospect of their use in industrial applications of anaerobic corrosion caused by SRB.

KEYWORDS

Temperature measurements;
Measurement error;
Thermal energy;
Thermodynamics;
Metrology.

Introduction

During the operation of underground structures, the most important of which are oil and gas pipelines, damage to pipes, and mechanical corrosion, also includes a biological component, which consists of the destruction of the protective coating under the influence of associated soil microorganisms. This leads to the formation of corrosion cracks, leakage of the transported product, and, as a result, the emergence of environmental hazards and environmental pollution.

To date, among a wide, constantly updated range of insulating materials [1], despite the presence of modern types of insulation (polyurethane, poly epoxy, three-layer polyethylene), the dominant positions in the oil and gas complex of Ukraine have retained less effective ones in terms of anticorrosion and technical and operational parameters, but much cheaper mastic and mastic-tape coatings based on oil bitumen (fig. 1).

As a result of microbial destruction of the protective coating due to the impact of a heterotrophic block of aerobic and anaerobic bacteria: VOB, ZVB, DNB, SVB, the physical and mechanical properties of protective materials change [2-3], their strength, elasticity, adhesive characteristics decrease, and, therefore, they are lost The main function of coatings is to protect the metal from corrosion.

Biodamage of insulating materials used for anticorrosive protection of underground structures is the result of the interaction of microorganisms and the surface of insulating materials and it starts with adhesion. On the protective material, which acts as a substrate, the adhesion, and growth of cells of microorganisms that form a biofilm occur. As a result of the impact of living cells of microorganisms that form a biofilm occur. As a result of the impact of living cells and their metabolic products on the protective material, its aging occurs, the operational characteristics of the coatings change, which leads to their destruction. This is eloquently evidenced by the data on economic losses.

Thus, the annual (not fully taken into account) losses from damage in the United States are about 1.5 billion dollars, in Japan - up to several billion yen, in England - about 10 million pounds sterling [4].

Although in most European countries and the USA the share of oil-bitumen insulation does not exceed 10%, in addition, the scope of application is limited to pipes with a diameter of up to 600 mm and operation in environments of low corrosive activity.

During the long-term operation of pipelines with bitumen coating in the pipeline conditions, the degradation of the insulating coating occurs with the loss of its dielectric properties. Over time, cracking of the protective coating is possible. When operating pipelines in saline, highly mineralized soils containing soluble CO_2 and H_2S, the amount of salt is 3-4 percent or more; In the cracks of the

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coating, corrosion processes occur, which are the result of an accelerated transition of iron into solution in the presence of hydrogen sulfide, as well as the formation of H_2 from hydrogen ions. The penetration of hydrogen to the steel surface leads to a sharp decrease in the strength of the metal structure and, as a result, corrosion processes.

Microbiological corrosion also leads to the destruction of underground pipelines, which is one of the reasons for the formation of pitting and ulcers under corrosion products in soils of increased corrosive activity (salt marshes, swampy, silty soils).

Given this, the problem of improving oil-bitumen insulation in order to give it qualitatively new properties remains relevant both in scientific and practical aspects.

Methodology

One of the ways to solve this problem is the modification of oil-bitumen mastics with corrosion inhibitors, which would simultaneously inhibit electrochemical corrosion and exhibit biocidal properties, increasing the physical and mechanical properties of the resulting insulating coatings. An integrated approach to the modification of oil-bitumen coatings has significant prospects and will improve their reliability and service life.

Since the main metabolite of sulfate-reducing bacteria is hydrogen sulfide, which is a stimulant for both corrosion and hydrogenation of steels, the task of suppressing the vital activity of SRB is especially urgent. Today and in the near future, among the various methods of combating the corrosion of underground metal structures, the leading place is given to inhibitor protection, which does not require significant investments.

Organic corrosion inhibitors provide a high degree of metal corrosion protection at low concentrations in a corrosive environment. Inhibitors are fast-acting and their use is cost-effective.

The main advantages of inhibitor protection are its simplicity, economy, and the possibility of replacing an existing inhibitor with a more efficient one, without violating the process scheme.

In previous works [5-6], we have shown that the introduction of corrosion inhibitors, which are organic substances of various classes, into the composition of the base polymer-bitumen mastic makes it possible to obtain modified polymer-bitumen-based mastics with increased physical and mechanical properties and plasticity. The base was bituminous-polymer mastic of the MBPID-1

One of the important indicators of the quality of bitumen-polymer mastics is water saturation, which determines the hydrophobicity and, as a result, the dielectric properties of the insulating coating, so it was advisable to monitor the change in water saturation of the base and modified mastics in a wide range of inhibitor concentrations from 0.05% to 2.0% wt.

Three series of experiments were carried out to study the water saturation of the base and modified mastics with inhibitors "Ing.3" (from the class of amines) and "Ing.6" (quaternary ammonium salt) in distilled and seawater. For commercial reasons, the names of the inhibitors are not disclosed. Figure 2 shows the results of studies on the effect of the nature of the inhibitor on the hydrophobicity of mastics. The analysis of the obtained results showed that the water saturation of the modified mastics is significantly lower than for the base mastics, while the nature of the kinetic dependences is also excellent. So, for the base mastic, a monotonous increase in water saturation is observed throughout the entire study period, while for modified mastics, after reaching optimal values, water saturation practically does not change. The fact that the water saturation of the modified mastics is significantly lower than the water saturation of the base mastic suggests that the nature of the inhibitor introduced into the composition of the base polymer-bitumen mastic affects the hydrophobicity of the modified mastics. In this case, the inhibitor adsorbed on the surface of the bitumen-polymer base probably forms a new structure with increased hydrophobicity. The results obtained should be taken into account when using modified mastics in swampy, silty soils.

It is also important to note that after soaking in distilled water, a base mastic sample becomes brittle, and a brown coating forms on its surface. At the same time, samples of modified mastics remain plastic under the same conditions, and no deposits are observed on their surface.

The brown coating on the surface of the base mastic sample may be due to the desorption of water-soluble mastic components.

The nature of the dependences of water saturation in seawater (fig. 3) is similar to those obtained for distilled water. It should be noted that the water saturation of the base and modified mastics in seawater is much lower than in distilled water. The linear nature of the kinetics of changes in the mass of mastics is typical only for base mastic, while for mastics modified with Ing.3 and Ing.6 inhibitors, water saturation reaches its maximum value, after which it practically does not change.

The results obtained are important from a practical point of view since they open up another facet for the use of modified bitumen-polymer mastics both in seawater and in highly mineralized soils, the salt content of which exceeds 4% [7]. Visual analysis of the mastics samples showed that the modified mastics in seawater remain plastic and no deposits are observed on their surface.

An important factor of the insulating coating, which determines its effectiveness, is bio resistance to the action of soil microorganisms. In order to test microbial resistance, samples of bitumen-polymer mastics developed by us were transferred for research to the Institute of Microbiology and Virology of the National Academy of Sciences of Ukraine. The stability of samples of modified bitumen-polymer mastics in relation to corrosive microorganisms was evaluated according to the described methods [8]. The essence of the method for determining biostability is to quantify the growth of bacteria in the presence of a coating as the only source of carbon. After a three-month exposure of prototypes in appropriate nutrient media, it was found that the developed mastics are bio resistant to the effects of corrosive microorganisms and they can be used for re-insulation of pipelines in such problematic sections of the route as marshy, silty soils, solonchaks, soils with high humidity, where the highest risk of microbial corrosion. The proposed inhibitors "G" and "J", belonging to the class of amines and quaternary ammonium salts, turned out to be polyfunctional, as they combined an inhibitory effect on electrochemical metal corrosion and a bactericidal effect on corrosive microorganisms.

The qualitative and quantitative composition of bacteria isolated from damaged bituminous coatings taken from the surface of the main gas pipeline "Pasechnaya - Dolina" was determined. The number of bacteria was determined by the

method of tenfold limiting dilutions according to DSTU 3999-2000. The results of microbiological analyzes are presented in the table 1.

The results obtained showed that a high content of sulfate-reducing and iron-reducing bacteria is characteristic of swampy soils.

In the underground environment, the vital activity of sulfur cycle bacteria - sulfate-reducing and thionic - leads to the intensification of corrosion damage to the metal of main oil and gas pipelines. Therefore, we considered it expedient to study the effect of dioxodecahydroacridine derivatives as corrosion inhibitors and compare it with the activity of inhibitor (J) from the class of quaternary ammonium salts on these groups of microorganisms. The study was carried out using two concentrations of inhibitors 0.2 and 0.5 g/l of nutrient medium.

Inhibitor "J" turned out to be the most effective in relation to SRB (fig. 4), which, already at a concentration of 0.2 g/l, suppressed the growth of microorganisms by 93.3%, and with an increase in concentration to 0.5 g/l, the corresponding indicator was 95.9%.

Close to the given values was the effectiveness of suppressing the growth of SRB inhibitors 1/0 and 3/0, which at a concentration of 0.5 g/l blocked growth by 93.8% and 97.7%, respectively. The efficiency of inhibitors 6/0 and 7/0 was significantly lower and did not exceed 80% at a concentration of 0.5 g/l.

Another indicator characterizing the activity of corrosion inhibitors is their effect on the rate of corrosion processes. The corrosion rate of metal samples under the influence of the studied inhibitors decreased in accordance with the previously determined SRB growth blocking activity (fig. 5). A high level of blocking of biocorrosion processes was revealed by inhibitors 1/0, 3/0, and (J). The corrosion rate in their presence decreased from 29.6 mg/dm^2 day to 3.8; 1.7 and 2.4 mg/dm^2 day, respectively. The effectiveness of inhibitors 6/0 and 7/0 was 3-4 times less.

Since not only the intensity of suppression of bacterial growth and corrosion rate is important for the reliability of blocking microbial corrosion, but also the mechanism by which this blocking occurs, we determined the type of inhibition and the inhibition constants for all the studied inhibitors - derivatives of dioxodecahydroacridine. It was found that inhibitors 1/0, 3/0, and 7/0 blocked the growth of SRB activity by a competitive mechanism, while inhibitors 6/0 and (J) - by a non-competitive mechanism.

Based on the obtained results, we can conclude that the most effective means of anticorrosion protection among the studied quaternary nitrogen-containing compounds is an inhibitor (I), which acts on SRB by a non-competitive mechanism and exhibits the lowest inhibition constant, i.e. maximally meets the requirements for biocide corrosion inhibitors.

The study of the effect of dioxodecahydroacridine derivatives and quaternary nitrogen-containing derivatives on thionic bacteria Thiobacillus sp showed that inhibitors 1/0 among dioxodecahydroacridine derivatives and inhibitor "J" among QAS turned out to be the most effective in relation to the group of microorganisms, which showed a degree of growth blocking of 95.8 and 97.1 %, respectively (fig. 6) and almost 90% reduced the corrosion rate under the influence of thionic bacteria.

Dioxodecahydroacridine derivatives - 1/0; 3/0; 6/0; 7/0; QAS - Inhibitor "J" Inhibitor 1/0 will quickly and efficiently neutralize most of the dangerous bacteria, inhibitor (J) will ensure the impossibility of microbial colonization of the surface of gas and oil pipelines for a long time of operation of underground structures.

The results of experimental studies are important from a scientific point of view since they open the prospect of modeling polyfunctional inhibitory systems.

Obtaining biostable modified mastics with the participation of nitrogen-containing corrosion inhibitors with increased hydrophobicity and the development and practical implementation of biostable modified insulating coatings on a bitumen-polymer basis is one of the ways to solve an important environmental and technological problem of microbiological protection of underground gas and oil pipelines in order to prevent the occurrence of environmental disasters.

Table 1

Qualitative and quantitative composition of bacteria isolated from damaged samples of bituminous coating

Sample No	Sampling location	DNB	VOB	ZVB	SVB
1	Turyanka river	10^4	10^4	10^6	10^{2-3}
2	Forest line	10^4	10^2	10^5	10^{2-3}
3	Angle of rotation	10^2	10^3	10^6	10^{2-3}
4	Swamp area	10^4	10^1	10^7	10^4

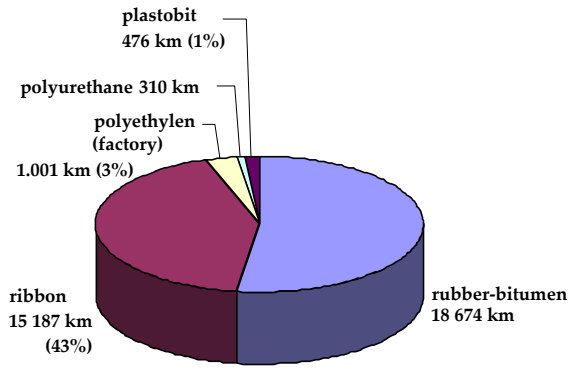

Fig.1. The structure of insulated roofs in the gas sector of the economy

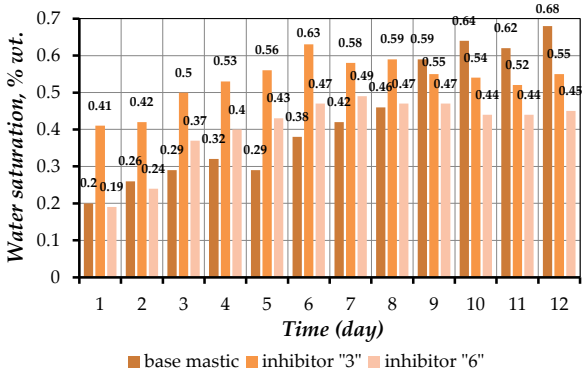

Fig.2. Influence of the nature of the inhibitor on the water saturation of bitumen-polymer mastics in distilled water

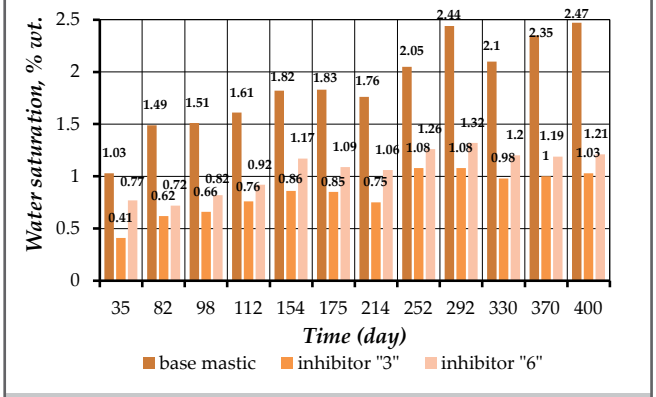

Fig.3. Influence of the nature of the inhibitor on the water saturation of bitumen-polymer mastics in seawater

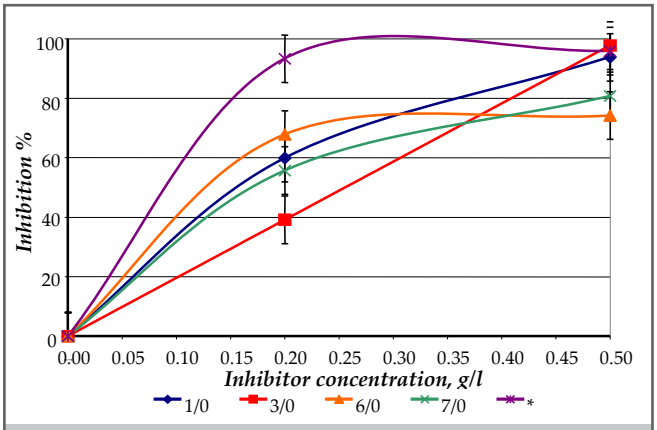

Fig.4. The intensity of SRB growth inhibition by nitrogen-containing corrosion inhibitors

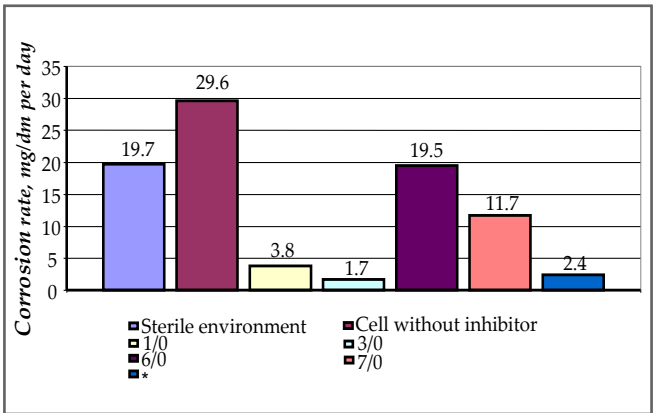

Fig.5. Inhibition of the corrosion rate of metal samples in the presence of SRB nitrogen-containing inhibitors

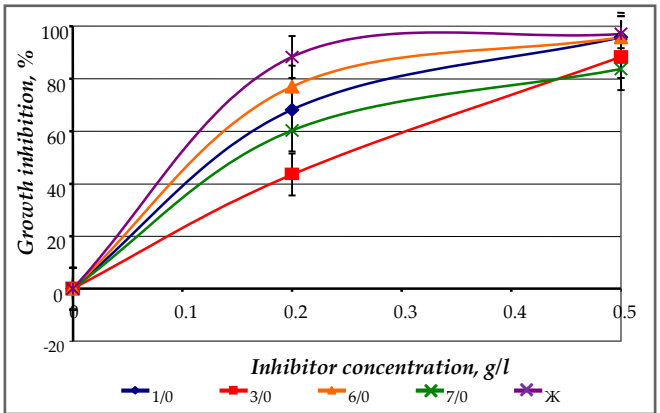

Fig.6. Inhibition of growth of thionic bacteria by nitrogen-containing corrosion inhibitors

Conclusion

1. An important environmental and technological problem is the protection of underground oil and gas pipelines from microbiological corrosion under the influence of soil corrosive microorganisms, among which sulfate-reducing (SBR) and thionic (TV) bacteria play a decisive role.

2. The effect of the nature of the inhibitor and the composition of the electrolyte on the hydrophobicity of the base and modified mastics were studied.

3. The influence of heterotrophic bacteria isolated from the damaged bituminous coating of the main gas pipeline on the stability of modified bitumen-polymer mastics has been studied.

4. The effect of nitrogen-containing corrosion inhibitors on the growth and enzymatic activity of sulfur cycle bacteria was studied, and the mechanism of blocking thionic bacteria and the hydrogenase reaction of corrosive SRBs was established.

5. The effectiveness of dioxodecahydroacridine derivatives on the rate of microbial corrosion of steel under the influence of SRB and tone bacteria was studied. A comparative evaluation of the effectiveness of these inhibitors with the industrial inhibitor "J" was carried out. caused by SVB.

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Повышение эффективности микробиологической защиты подземных сооружений

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Реферат

Отмечены важные аспекты микробиологической защиты подземных сооружений. Показано, что важной экологической и технологической проблемой является защита подземных нефтегазопроводов от микробной коррозии почвенно-коррозионно-опасными микроорганизмами, в которой решающую роль играют сульфатредуцирующие (СРБ) и тионовые бактерии (ТБ). Исследовано влияние природы ингибитора и гидрофобности электролитного состава базовых и модифицированных мастик и гетеротрофных бактерий, выделенных из поврежденного трубопровода, стабильность модифицированного битумно-полимерного герметика и воздействие азотсодержащих ингибиторов коррозии на рост активность ферментов бактерий и серного цикла, механизм блокировки тионовых бактерий и гидрогеназной реакции коррозионно-активных СРБ, эффективность производных диоксида декагидроакридина на скорость микробной коррозии стали под воздействием СРБ и тионовых бактерий. Проведена сравнительная оценка эффективности этих ингибиторов по сравнению с промышленным ингибитором. Эти ингибиторы обеспечивают высокую степень защиты от коррозии в присутствии СРБ (90%), что свидетельствует об их антибактериальных свойствах и открывает перспективу их использования в промышленных применениях от анаэробной коррозии, вызванной СРБ.

Ключевые слова: нефтегазопроводы; микроорганизмы; ингибитор; механизм; коррозия.

Yeraltı qurğuların mikrobioloji mühafizəsinin səmərəliliyinin artırılması

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Xülasə

Yeraltı qurğuların mikrobioloji mühafizəsinin mühüm aspektləri qeyd olunmuş, göstərilmişdir ki, mühüm ekoloji və texnoloji problem yeraltı neft və qaz kəmərlərinin həlledici rol oynayan sulfat reduksiyaedici (SRB) və tion bakteriyaları (TB) daxil olmaqla, torpağın korroziyaya uğradan mikroorqanizmlərin mikrob korroziyasından qorunmasıdır. İnhibitorun təbiətinin və zədələnmiş boru kəmərindən təcrid olunmuş əsas və dəyişdirilmiş mastikaların və heterotrof bakteriyaların elektrolit tərkibinin hidrofobikliyinin təsiri, dəyişdirilmiş bitum-polimer mastikasının dayanıqlığı və azot tərkibli korroziya inhibitorlarının böyüməsinə təsiri, bakteriyaların fermentlərinin aktivliyi və kükürd dövranı, tion bakteriyalarının bloklanması mexanizmi və korroziyada fəal SRB-nin hidrogenaz reaksiyası, deka hidroakridin dioksid törəmələrinin SRB-nin və tion bakteriyalarının təsiri altında poladın mikrob korroziya sürətinə təsir effektivliyi tədqiq edilmişdir. Bu inhibitorların sənaye inhibitoru ilə müqayisəli effektivliyinin qiymətləndirilməsi aparılmışdır. Bu inhibitorlar SRB-nin (90%) iştirakı ilə korroziyaya qarşı yüksək dərəcədə qorunma təmin edir ki, bu da onların antibakterial xüsusiyyətlərini göstərir və SRB-nin yaratdığı anaerob korroziyaya qarşı sənaye tətbiqlərində istifadə perspektivini açır.

Açar sözlər: neft və qaz kəmərləri; mikroorqanizmlər; inhibitor; mexanizm; korroziya.