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Corrosion of metal and polymer materials in soil operating conditions

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Abstract:

The object of research is corrosion of metal and polymer materials in soil operating. **Method.** Experimental studies of soil corrosion of samples made from metal piping materials of different manufacturers, as well as polymer composite materials based on an epoxy binder in soil conditions of the Republic of Mordovia (Russia). Metal samples were exposed to various types of soils (chernozem and loam) at a depth of 410 mm and 630 mm. Polymeric materials were located in various soils at a depth of 0.5 m and 1.5 m. During the tests, the samples were kept under conditions of variable temperature and humidity for 12 months. Microbiological studies were carried out to identify microorganisms on the surface of the samples. **Results**. The species composition of microorganisms that settled on the samples during the tests was established, and changes in the mass-strength properties of the composites were revealed. Methods for protecting pipeline materials from biological damage are proposed.

1 Introduction

Biological corrosion of various metallic materials has been studied insufficiently thus far, and primarily it concerns the field of determining the mechanism of destruction. This is due to the fact that in this case, along with the negative effects of microorganisms, complex processes of chemical and electrochemical corrosion occur that overlap each other. The damage from metal corrosion amounts to many tens of billion dollars annually, which includes direct and indirect losses from biocorrosion, capital investments in corrosion protection, increased costs to reduce the aggressiveness of the exploited environment [1]-[6]. Therefore, the study of the operating conditions of structures, the qualitative and quantitative composition of microorganisms corresponding to these conditions, the change in the performance indicators of materials is more than relevant.

It has been established that the impact of microorganisms in soil conditions on metal products and structures initiates and intensifies these processes [7]-[9]. Corrosion processes involve not only nitrifying, thionic acid and sulfate-reducing bacteria, actinomycetes, etc., but also filamentous fungi [10]-[12]. The species composition of microscopic organisms is formed under the influence of microbiota being characteristic of a particular soil-climatic region [4], [13]-[16]. The products of microorganisms' metabolism have a significant impact on the processes of biodeterioration. Such factors as temperature, humidity, light, pressure, acidity, degree of aerobic activity, etc. affect metabolic, morphogenetic and other changes in bacteria and filamentous fungi [17, 18].

The destruction of the metal surface begins with mechanical damage, with the penetration of hyphae in certain areas, then corrosion processes occur as a result of organic acids' effect, products of the metabolite of mold fungi, changing the resistance of the metal surface film or directly participating in electrochemical corrosion processes. It has been established by many authors that the anodic process of metal corrosion is accelerated under the action of micromycetes [19]-[24]. The destruction of structures of miscellaneous purpose proceeds within a short time.

Increasing the durability of building structures in industrial and other enterprises with aggressive environments is of special importance. Improving the above-said durability of building structures is achieved through the use of special means that reduce or completely eliminate aggressive effects on them. One of the ways to extend the service life of structural elements is the use of various protective coatings based on polymer binders. Materials based on epoxy binders are widely used in this capacity. One of the advantages of epoxy resins is the wide possibilities of modifying the structure to improve the performance properties of epoxy polymers and composites based on them. Physicochemical methods of modifying the structure of epoxy polymers (by introducing fillers, plasticizers and other modifiers) are promising, as a result of which it is possible to obtain materials with a given set of operating ability. An important component of these compositions, along with the binder that determines the physical and mechanical properties and durability, is the filler. First of all, this is due to the fact that fillers are actively involved in physico-chemical processes.

The question of protecting construction materials, products and structures made of metal, concrete and wood, operating in underground conditions and in contact with soils, is particularly sensitive. A special vertical profile of the distribution of temperature and humidity of soil air is formed in the ground that varies in time and volume. In addition, soil corrosion of materials is caused by the combined activity of the microbiota. The study of microbiological corrosion features in soils and on the surfaces of underground structures that cause biochemical corrosion is an important task in the field of materials science. However, up to the present moment, this direction has apparently been underdeveloped and only fragmentary information is available on many related issues.

The purpose of the study was to establish the species composition of microorganisms inhabiting the surface of steel pipeline materials and changes in the mass of samples.

Research objectives:

1. Selection of test samples.
2. Identification of the species composition of filamentous fungi in the samples.
3. Identifying changes in the mass of the samples during exposure in various environments.
4. Establishing the operational reliability of metal pipeline materials in a corrosive environment (ground conditions).
5. Assessment of the durability of polymer materials having been kept in loamy soils.

2 Materials and Methods

Two types of steel samples were considered as the objects of research: zinc-coated steel samples and steels samples without zinc coating. During the tests, metal piping materials were used: 1) electric-welded straight steel pipes according to GOST 10704-91 (Vyksa Metallurgical Plant, Russia) [25], steel grade St20 GOST 1050-2013 “Metal products from nonalloyed structural quality and special steels. General specification” [26]; 2) galvanized water and gas pipes according to GOST 3262-75 “Water-supply and gas-supply steel pipes. Spesifications” [27] (Vyksa Metallurgical Plant), steel grade St3sp GOST 380-2005 [28].

In St20 steel, the main part of the metal is constituted by iron. The concentration of carbon is 0.2%, it has a large concentration of magnesium and silicon. All the elements included in the composition determine the performance characteristics of steel. 3sp steel refers to carbon steels of commercial-quality general-purpose types, designed for the manufacture of hot-rolled products, as well as pipes, tapes, wires, hardware items, etc.

The studies of biocorrosion of metal materials were carried out in the soil conditions of the Republic of Mordovia (Russia). It should be noted that the representatives of various microorganisms grow on the surface of pipeline materials depending on the type of soil and the depth of samples' laying. The samples were exposed to various types of soils (chernozem and clay loam soil) to a depth of 410 mm and 630 mm. During the tests, the samples were kept in variable temperature and humidity conditions for 12 months. The influence of weather conditions and soil-climatic factors was monitored during the tests. The average monthly values of hydrothermal humidification coefficients in the territory of the republic were 1.0-1.4. The average annual relative humidity was in the range of 75-76%. It reached maximum values equal to 83-85% in the winter months, minimum values (61-63%) in May and June. The average annual precipitation was 500-550 mm. The average annual air temperature was within the range of +4.1...+4.4 ^{o}C. The soil freezing was below normal.

Epoxy composites with various fillers were considered as polymer materials. Powdered thermolith, diatomite, container glass, and slag were taken as fillers. The filler content was taken in optimal quantities by ensuring high strength values. Epoxy-diane resin of ED-20 grade acted as a binder in the compositions, polyethylene polyamine was in the capacity of a hardening agent. The compositions of the test composites are shown in Table 1.

Table 1. Quantitative content of components in compositions

Component	Content of components, in weight parts				
	Composition number				
	1	2	3	4	5
ED-20	100				
PEPA	10				
Filler	-	80	100	40	90
		thermolith	glass	diatomite	slag

The polymer materials exposure sites were located in various soils at a depth of 0.5 m and 1.5 m.

The resistance of polymer materials and their components to fungi can be performed under laboratory conditions. However, laboratory studies do not allow us to take into account the impact of climatic factors on polymer construction materials, to determine the degree of interrelation of biodeterioration processes intensity with climatic aging. It is known that the effect of climatic factors causes a change in the composition and structure of polymer materials and, as a result, changes the species composition of microorganisms involved in destructive processes.

Identification of microorganisms from the surface of the samples was carried out by the impression method. This method provides for direct contact of a dense nutrient medium with the object under study, while reducing a number of intermediate operations that can lead to inaccuracies and errors.

For the materials used in the manufacture of protective coatings, physicochemical and biological resistance, high adhesion to the substrate, etc. are of great significance. In the course of the conducted studies, the relative change in the tensile strength under bending and compression of filled epoxy composites aged for 6 months in soil at depths of 0.5 m and 1.5 m were the indicators monitored. At the next stage, the identification of the type of micromycetes spawning on the surface of polymer composites with various fillers was performed under laboratory conditions. The identification of micromycetes was carried out on the basis of their morphological and cultural features, using determinants: Raper, Thorn, 1949; Raper, Fennell, 1965; N.M. Pidoplichko, 1971; M.A. Litvinov, 1967; A.A. Mil'ko, 1974; T.S. Kirilenko, 1977; Donch, Gams, 1980; A.Yu. Lugauskas, A.N. Mikulskene, D.Yu. Shlyauzhene, 1987; V.I. Bilai, E.Z. Koval, 1988.

3 Results and Discussion

The results of the microbiological study are shown in Table 2.

Table 2. Findings of microbiological study

No	Test samples	Species composition of fungi on samples
1	Galvanized sample aged in	Fusarium moniliforme, Penicillium chrysogenum +

	chernozem soil at a depth of 410 mm	bacteria
2	Steel sample aged in chernozem soil at a depth of 410 mm	Fusarium moniliforme, Chaetomium globosum, Mucor corticola + bacteria
3	Galvanized sample aged in loam soil at a depth of 630 mm	Mucor corticola
4	Steel sample aged in loam soil at a depth of 630 mm	Chaetomium globosum, Aspergillus ustus, Mucor corticola + bacteria

The results obtained, given above in Table 1, show the fouling of the surface of steel and galvanized water and gas pipes samples with filamentous fungi, which belong to representatives of mesophilic and psychrophilic species of the genera Penicillium, Fusarium and Chaetomium.

The representatives of filamentous fungi were found on all the samples embedded in ground. Most often, we found fungi of the genus Fusarium, mold fungi from the family Chaetomiaceae which live almost everywhere. Chaetomium is a genus of filamentous fungi that are common in soil, air, seeds, and plant waste. Fungi of the genus Fusarium moniliforme are widespread mold fungi. The spores of this fungus spread through the air mainly in warm and humid weather. Penicillium chrysogenum is a saprophytic species, widespread everywhere. Mesophyll fungi grow at temperatures from +5 to 37 ^{o}C. Aspergillus ustus fungi grow like mold on the surface of many substrates. They grow rapidly in humid warm environments, using organic substances for their vital activity. For most microorganisms, the decisive factor for vital activity is the presence of water that promotes rapid development, growth, physiological activity, and, accordingly, the creation of biomass in a short time.

One of the indicators demonstrating the destruction of samples out of the studied pipeline materials is the change in their mass content. The results obtained are shown in Figure 1.

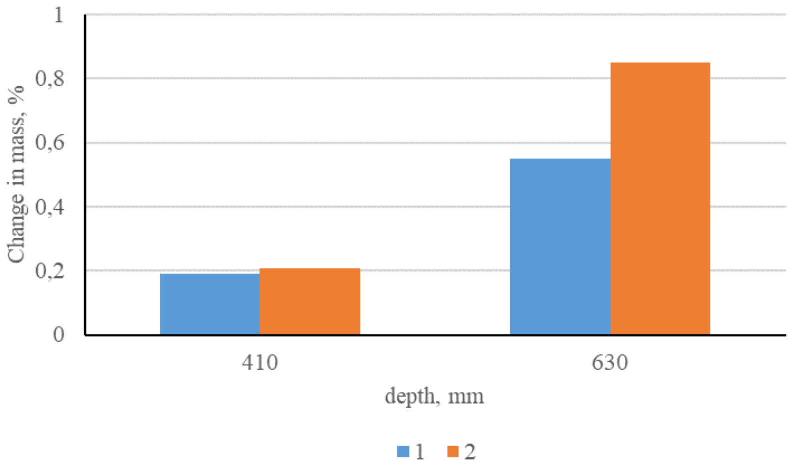


Fig.1 - Change in the mass content of samples being sunk into ground: 1– galvanized sample, 2 – steel sample

The exposure of the samples to soil has shown that the changes in mass were mainly found in the steel samples. At the same time, the values of the construction materials' hardness change, hence the durability of building structures decreases. It was also revealed that the surface of the steel pipe samples was subjected to uneven corrosion. The presence of a zinc coating reduces the spread of corrosion.

The results of studying the species composition of micromycetes contaminating various components of polymer composites that have been in soil conditions for a long time have revealed 2 classes of micromycetes: ascomycetes and zygomycetes.

The class of ascomycetes was distinguished by the following genera of micromycetes *Verticillium, Fusarium, Chaetomium, Alternaria, Cladosporium, Trihoderm, Gliocladium, Stachybotrys, Aspergillus u Penicillium*.

The class of zygomycetes from microorganisms detected on the surface of epoxy composites includes fungi of the genera Rhizopus and Mucor.

As part of the study, it was also found that at different depths, the species composition of micromycetes growing on the surface of the polymer composite is different. It is possible to distinguish repeating fungi, but there are also species that are characteristic only for a certain depth.

On the surface of the control samples without filler, aged in the ground at a depth of 0.5 m for 6 months, there were found 3 species of fungi of the genus Aspergillus (Aspergillus ustus, Aspergillus terreus, Aspergillus cryroe), 1 species of the genus Rhiropus (Rhiropus cohnii), 1 species of the genus Fusarium (Fusarium moniliforme), 1 species of the genus Penicillium (Penicillium cyclopium), 1 species of the genus Mucor (Mucor corticola) 1 species of the genus Cladosporium(Cladosporium elotum) 1 species of the genus Stachybotrys (Stachybotrys chertarum) and many bacteria. At a depth of 0.5 m, a fungus of the species Mucor corticola grows on the surface of composites with various fillers, and fungi of the species Fusarium moniliforme, Aspergillus ustus and Aspergillus terreus were also found on most composites.

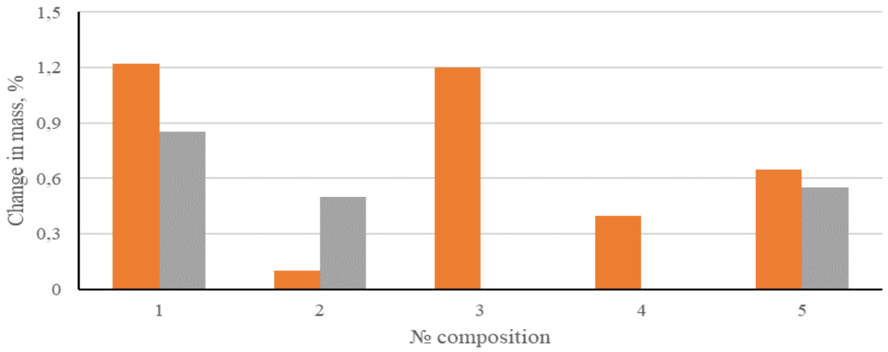
After keeping the samples at a depth of 1.5 m on the surface of an unfilled epoxy composite, the following species composition of microorganisms was revealed: 1 species of fungi of the genus Aspergillus (Aspergillus ustus),1 species of the genus Rhiropus (Rhiropus cohnii), 1 species of the genus Fusarium (Fusarium moniliforme), 3 species of the genus Penicillium (Penicillium cyclopium, Penicillium lonosum, Penicillium chrys), 1 species of the genus Mucor (Mucor corticola), 1 species of the genus Cladosporium (Cladosporium elotum), 1 species of the genus Alternaria (Alternaria bross).

Fusarium moniliforme was found at a depth of 1.5 m on all composite samples, the micromycetes of the species Aspergillus ustus were also found most frequently.

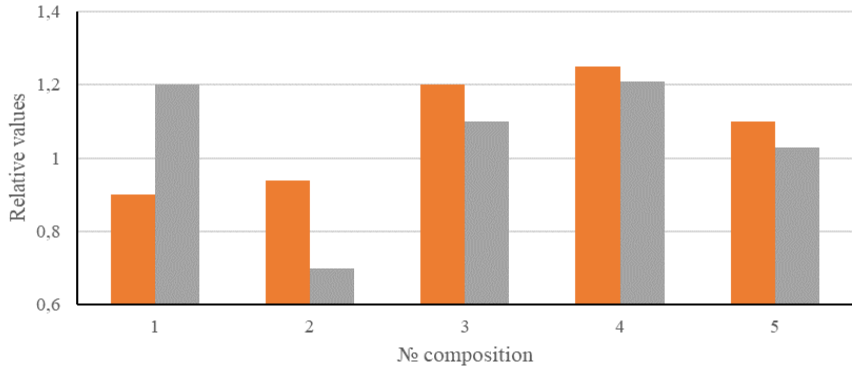
The results of the microbiological study have shown that the species and quantitative composition of microflora on the polymer composites samples placed at a depth of 1.5 m in soil decreases slightly compared to the data obtained on the samples operated at a depth of 0.5 m.

The results of physical testing are shown in Figure 2.

It follows from the test results (Fig. 2 a) that a greater change in the mass of samples equal to 1.2% is characteristic of compositions without filler and the ones filled with ground tar glass, aged at a depth of 0.5 m. A smaller change in mass up to 0.15% is characteristic of composition samples No. 2, driven to a depth of 0.5 m below the earth's surface. When the samples were kept at a depth of 1.5 m, the compositions filled with ground glass and diatomite have not changed their mass after 6 months of testing.



(a)



(b)

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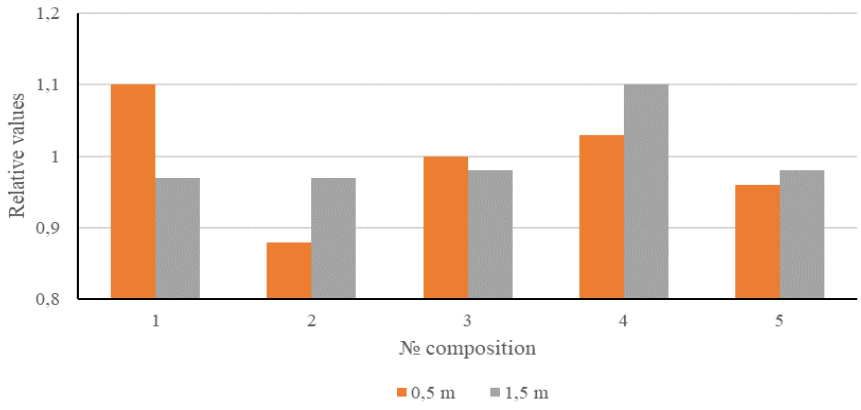

(c)

Fig. 2 - Dependences of changes in mass content (a), bending strength (b) and compression (c) of epoxy compositions on the type of filler after 6 months of keeping samples in the ground at depths of 0.5 m and 1.5 m

It can be seen from the research data that when the samples were kept at a depth of 0.5 m for 6 months, an increase in bending strength was observed in compositions No. 3-5. It is equal to 10-22%. The maximum change (22%) is characteristic of composition No. 4 with diatomite in the amount of 40 weight parts per 100 weight parts of resin ED-20. Also, the compressive strength of composition No. 4 has increased by 4%. In composition No. 1 without filler, the compressive strength has also increased to 10%, but the bending strength has decreased by 10%, relative to the control values. A decrease in strength values up to 12% is typical for composition No. 2 which was filled with powdered thermolite.

When keeping composites at a depth of 1.5 m, a decrease in compressive strength of less than 2% was observed in compositions No. 1, 2, 3, 5. For composition No. 4 with diatomite, the compressive strength increases up to 10% when keeping composites at a depth of 1.5 m relative to the initial values. The tensile strength in bending increases by more than 20% in compositions No. 1 and 4. Low results for this value were shown by composition No. 2 with thermolite. Strength reduction in bending was 30% after 6 months of keeping the samples in soil at a depth of 1.5 m.

Thus, composition No. 4 filled with powdered diatomite, appeared to be the most resistant one in terms of strength figures in soil conditions, regardless of the depth of keeping the composites considered.

4 Conclusions

1. As a result of the conducted studies, the biological resistance of the samples made of metal and polymer materials when being kept in ground conditions has been established.
2. The change in the species composition of microorganisms on the surface of the samples when they are kept in chernozem and loamy soils has been shown.
3. It has been revealed that various types of filamentous fungi, as well as bacteria that contribute to the development of corrosion processes grow on the surface of the samples.
4. The change in the mass of samples due to the formation of corrosion products has been determined.
5. It has been revealed that zinc coatings contribute to increasing the biological resistance of pipeline materials.
6. The corrosion resistance of polymer epoxy composites with various fillers kept in soil conditions at different exposure depths has been studied.
7. Filled polymer composites, which are the most resistant in terms of strength characteristics, have been identified.

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