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ROLE OF BIOFILMS IN MICROBIOLOGICALLY INFLUENCED CORROSION OF METALS

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Abstract

Data obtained in the recent years on the effect of biofilms in the development of metal microbiologically influenced corrosion (MIC) are summarized. The main way of sessile cells adaptation and survival on metal surfaces lies in formation of biofilms consisting of living cells surrounded by a multicomponent extracellular polymer substance (EPS). Biosystem created possesses new properties that are different from the properties of individual components. Biofilm ways of formation, growth and survival, functions of the extracellular matrix in regard to the microbial consortium and to the metal surface are presented. Mechanisms of biocorrosion involving the electron transmembrane transition from a metal to the living cell cytoplasm, as well as the extracellular pathways of metal oxidation under aerobic and anaerobic conditions, are considered

Keywords

Microbiologically influenced corrosion (MIC), biocorrosion, biofilms, microorganisms, biocorrosion mechanisms, extracellular polymer matrix, microbial consortium

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Introduction. Microorganisms that exist in the environment are exerting great influence on the corrosion of metals and structural materials. Contact with a biologically active medium (microorganisms and products of their metabolism) leads to the so-called microbiologically influenced corrosion (MIC) (biocorrosion, microbial induced corrosion or biodegradation), which is one of the main causes of corrosion damage, equipment failures, financial losses in billions and environmental disasters. Variety of microorganisms, complicated mechanisms of their functioning, survival and interaction among them under altering conditions of the outer world create serious problems in understanding the mechanisms of biocorrosion, selecting a protection strategy and evaluating the efficiency of the applied anticorrosive agents.

Microbiological corrosion is a type of corrosion destruction caused by the vital activity of living microorganisms of various taxonomic groups present in the environment (in fresh and sea water, soil and in the air), where there appear

conditions for their existence, and it includes various processes, which are used by living microorganisms directly or indirectly to affect metals and alloys [1] causing their destruction. MIC was first discovered more than 100 years ago [2]. Problems associated with microbial corrosion are being aggravated every year due to an increase in the technogenic factor; therefore, more and more attention is being paid to material and environmental issues.

Microbiological corrosion is not a new type of corrosion [3] and develops in parallel with its other types (for example, soil, marine, atmospheric, chemical, etc.). Other corrosion processes contribute to the MIC development amplifying the destructive effect, for example, stress corrosion cracking [4], crevice corrosion, hydrogen embrittlement, corrosion induced erosion [1], corrosion fatigue intensification, and under-deposit corrosion [5], etc. As a rule, microbial corrosion is localized forms of corrosion, such as rill corrosion, crevice corrosion and pitting [6].

Economic losses caused by microbial corrosion are very high. Let us consider several examples that prove participation of microorganisms in the development of equipment corrosion. It is traditionally believed that approximately 20–40 % of the entire corrosion damage to metals is caused by microbial exposure [1, 7], which causes corrosion of metal equipment, including pipelines, tanks, water distribution systems, railway systems, ships, medical equipment and devices, nuclear waste storage facilities [1], etc. *Ontario Hydro* (Canada) reported on the pitting corrosion development due to microbiological deposits in the pipelines of heat exchangers in nuclear power plants [8]; the cost of replacing pipelines amounted to several billion dollars. *Escom*, i.e., the national energy company in South Africa, which provides 90 % of the country's electricity needs, discovered the effect of microorganisms on carbon steel in water cooling systems at all of its power plants. According to the authors of [9], biocorrosion is the cause of more than 25 % of failures in the oil and gas industry. Economic losses associated with equipment repair and downtime constitutes millions of dollars a year. In the UK alone, GBP 250 million a year is spent on replacing bio-corroded gas pipelines [10]. An important part of capital costs is the use of corrosion resistant alloys, which reduce the probability of materials' damage by MIC, but their price is 3 or more times higher than carbon steels.

Many types of microorganisms appear to be the active corrosive agents and are involved in the corrosion process in metals that are resistant to corrosion in various environment (copper, aluminum and their alloys). A special place within the metal microbial corrosion problem is occupied by *aluminum alloys*

corrosion. Most scientists connect the problem of aircraft wear to microbial contamination of fuel storage tanks and wing tanks; correlation is observed between the number of microorganisms and the acceleration of corrosion processes. Cell viability maintenance is facilitated by fossil fuels, which are the source of carbon required for nutrition and functioning of the microorganisms that enter the fuel tanks from air and water [3]. Cells are adsorbed at the metal — fuel — air phases interface and destabilize the aluminum protective oxide film causing local biocorrosion. The most common pollutant is the *Hormoconis resinae* fungus [11]. When studying microorganisms in the fuel tanks of the US Air Force aircraft, 12 types of pollutants were found, including four types of *Bacillus* and two types of *Staphylococcus* bacteria [12]. In samples obtained from the corroded sections of seven aircraft, 208 microorganisms were identified, including 158 species of bacteria, 36 species of yeast and 14 species of fungi. *Micrococcus, Enterococcus, Staphylococcus, Aerococcus, Bacillus, Aspergillus* and *Penicillum* microorganisms caused severe corrosion of the AA7075 alloy [13].

Corrosion of metals occurs as a result of their oxidation by environmental components and is described by the anode process equation:

$$Me \rightarrow Me^{n+} + ne$$

Abiotic (chemical) and biotic (microbiological) corrosion are distinguished, and they are inextricably linked with each other. Oxygen (O_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), acids, etc. [14], which play the role of an oxidizing agent, are considered to be the main abiotic agents causing chemical corrosion. Many of them contribute to the maintenance of vital activity of microorganisms. Oxygen is a strong cathodic agent that is usually present in water and at the boundary with the aerial environment ensuring existence of the aerobic bacteria. Periodic supply of oxygen from the outside to anaerobic systems also contributes to an increase in the microbiological activity and significantly affects the corrosion rate [15]. Carbon dioxide is used by methanogens to generate methane [16].

The rate of microbial corrosion is determined by the species composition of biogeocenosis, physical and chemical properties of the medium at the phases interface, such as oxygen, salts, metal ions and pH concentrations, redox potential of the system, conductivity, as well as by properties of the metal surface itself. An important parameter is the presence of hydrocarbon impurities, such as lubricants, oils, oil, fuels, etc., which appear to be a nutrient medium for many microorganisms contributing to preservation of their viability.

Various microorganisms, including bacteria, fungi and archaea, are involved in the MIC [17]. *Various classifications* (Fig. 1) of microbiological corrosion are proposed depending on the type of microorganism, mechanism of action, type of corrosion destruction, etc. Depending on the microorganism affiliation to a particular taxonometric group, bacterial, fungal (micromycelic), enzymatic and mixed groups are distinguished [18].

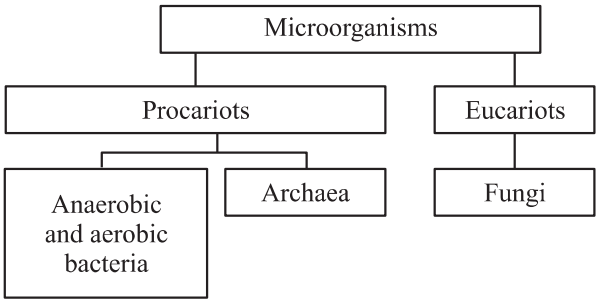

Fig. 1. Taxonometric groups of microorganisms that cause MIC

Species composition in the microbial community. This composition could differ, which is determined by environmental conditions. Under extreme operating conditions (for example, in tanks, where the temperature could easily reach 70 °C or higher), archaea are able to play an important role in corrosion acceleration processes [18]. In warm and humid climates such as in Southeast Asia, fungi could become the main cause of biocorrosion. Literature generally describes bacterial corrosion [19] caused by aerobic and anaerobic bacteria as the most destructive. The danger of bacterial corrosion is explained by a high degree of survivability and ease in adaptation to various adverse living conditions in water, soil and fuel. Bacteria could exist in a wide range of not only the temperature, but also of pH medium (1.0–10.5). Most intense corrosion in soil is observed in marshy areas (pH = 6.2–7.8, the optimum existence for most bacteria) rich in organic residues and with a low oxygen content.

Sulfate-reducing bacteria (SRB) and sulfate-reducing archaea (SRA) for several decades were considered as the main cause of microbial corrosion, since sulfates are widely spread in seawater, wastewater [20] and in oxygen-free environments [21]. However, corrosion damage to metals (cast iron, structures made of soft steel and corrosion resistant steel, copper, aluminum and alloys) could be caused not only by SRB [22] and SRA [23], but also by other bacteria, including thionic [24], nitrate-reducing (NRB) [25], metal oxidizing/reducing bacteria (such as iron- (FeOB) [26] or manganese-oxidizing bacteria (MnOB) [27], as well as by bacteria and fungi that secrete organic acids and exopolymers or mucus [28].

Sulfate-reducing bacteria (SRB) and archaea (SRA) (*Desulfovibrio* and *Desulfotomaculum*), as well as obligate anaerobes are oxidizing organic substances (pyruvate, lactate, succinate, formiate, malate, choline, amino acids, carbohydrates, alcohols, etc.) and are able to reduce the sulfates to H_2S:

$$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow S_3O_6^{2-} \rightarrow S_2O_3^{2-} \rightarrow S^{2-}$$

Thionic bacteria (*Tiobacillus*) are able to oxidize the sulfides:

$$S^{2-} \rightarrow S^0 \rightarrow S_2O_3^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$$

Nitrate-reducing bacteria (NRB) are involved reduction to ammonia:

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2 \rightarrow NH_3$$

Metal oxidizing bacteria (FeOB and MnOB) (*Proteobacteria Gallionella* and *Leptothrix*) oxidize iron or manganese compounds followed by generation of insoluble oxides:

$$Fe^{2+} \rightarrow Fe^{3+} \text{ or } Mn^{2+} \rightarrow Mn^{4+}$$

Acid producing bacteria (APB) (*Streptococcus*) in the process of vital activity are producing metabolites — acids. Fungi, i.e., eukaryotes (*Aspergillus, Penicillium, Fusarium* and *Cladosporium*), retain moisture on the surface of metals and secrete organic acids. Methanogens (Met) (*Methanococcus, Methanosarcina, Methanospirillum* and *Methanobacterium*) being the strict anaerobes carry out the synthesis of methane:

$$CO_2 \rightarrow CH_4$$

It should be noted that the species composition of microorganisms, some of which are listed above, is very diverse, and each microorganism has its own functioning features, which is reflected in the mechanism of their effect on metals.

Biofilms and its main components, properties and functions. Planktonic microbes in the liquid phase volume (planktonic cells) are usually not critical in corrosion; microorganisms attaching to the surface (so-called sessile cells) pose the maximum danger [18]. As a substrate, cells could use inorganic materials (metal structures, water pipes, soil particles, etc.) or materials of organic nature. Once on the surface of metals and in the pores of material, living cells do not lose their viability and ability to divide generating around them a biofilm that protects them against external influences [29]. Microbial biofilms are a combination of microbial cells and extracellular matrix (EPS) localized at the phase interface. It is namely the formation of biofilms that causes biofouling, biodegradation and

biocorrosion in structures; biofilms are able to influence the electrochemical processes through cooperative metabolism of microorganisms, which is missing with individual species [30]. Synergistic effect produced by various microorganisms in biofilm consortia could cause severe metal corrosion. For example, DSS duplex steel corrosion is explained by the symbiosis of sulfate-reducing and sulfur-oxidizing bacteria [1, 24]. It should be noted that biofilms do not always lead to damaging the metal; on the contrary, often their presence protects the metal against corrosion. Thus, biofilms generated by the *Pseudomonas aeruginosa* bacteria increased corrosion rate of the nickel–copper alloy, but protected the nickel–zinc alloy [31]. Corrosion resistance was increasing in the presence of *Escherichia coli* and *Geobacter grayreducens* biofilms [32].

A biofilm is a three-dimensional structure, complex in its chemical and species composition, which ensures the existence of microorganisms and their communities created at the phase interface (metal–air, metal–liquid). Most biofilms appearing in the environment are attributed to the multi-species biofilms, which could contain dozens of microorganisms, including bacteria, yeast and mold fungi, protozoa, viruses, etc. Biofilms have different lifespans ranging from several days to many years; in the course of time their composition regenerates and mutates [10].

Biofilm consists of a matrix or extracellular polymer substances (EPS), and of living cells that pass through the entire life cycle from division to destruction. EPS is a complex multifunctional system that combines microorganisms into a single whole and ensures increase in their survivability. The matrix main function is to maintain the chemical constancy of the microbial community microenvironment. Matrix is a complex of biopolymers synthesized by cells of microorganisms or captured from the outside [3, 10]; it contains polysaccharides, proteins, lipids, nucleic acids, and other components (Table 1). Due to the formation of polymer three-dimensional structures, matrix performs a structure generating function combining microbial cells into a unified system. Matrix provides mechanical stability of a biofilm creating a protective barrier for the microbial community. Matrix architecture and density are of heterogeneous type, i.e., a biofilm is penetrated by channels supplying cells with nutrition and diverting metabolic products. Matrix components are also backup power sources, which allow the cells that make up a biofilm to survive under the adverse conditions.

Due to the matrix rheological properties (matrix viscosity is ensured mainly due to the polysaccharides included in its composition), a biofilm is held on the metal surface; matrix is involved in the cells adhesion process on the surface and

their aggregation. Matrix possesses significant sorption properties with external substances, organic compounds and inorganic ions necessary for the cells functioning and nutrition, and exports the cell components. At the same time, matrix reduces the diffusion rate of substances unfavorable for cells (disinfectants and biocides) into the biofilm ensuring maintenance of the microorganisms' viability. In addition, presence of polysaccharides contributes to maintain the exoenzymes' activities, which are contained in the biofilm. Matrix generates a special microenvironment for cells retaining water and preventing the loss of fluid. Finally, it helps to maintain the system redox potential and provides the intercellular electron transfer [10]. Thus, microorganisms are able to attach to the surface and stay on it, then to create an extracellular matrix, which plays a major role in cell adhesion [33], biofilms generation [34] and protection of adsorbed microorganisms against the environment [35].

Table 1

Biofilm extracellular matrix (EPS) components and their main functions

Matrix components	Main functions	Source
Exopolysaccharides	Biofilm generation, ensuring mechanical stability	[36]
Proteins	Biofilm structure stabilization and maintenance, polysaccharide networks generation, connection with microorganism cell surface	[36, 37]
Exoenzymes	Biopolymer degradation, redox potential maintenance	[38]
Amyloids	Cell adhesion	[39]
Extracellular DNA(eDNA)	Cell aggregation	[40]
Hydrophobic components, lipopolysaccharides	Cell adhesion and biofilm generation	[41]
Water	Biofilm preservation against alteration in water potential	[42]

Biofilm mechanical properties are determined by interaction of the matrix components with each other due to intermolecular and intramolecular interactions, i.e., hydrogen bonds, electrostatic and ionic interactions, and Van der Waals forces [37]. Biofilm mechanical stability is ensured by exopolysaccharides that fix cells on the surface. In this case, micro colonies could move around the surface without mechanical damage [43]. In the process of

biofilm matrix strengthening, interaction of its components with multivalent ions plays an important role. For example, calcium ions are able to interact with the *P. aeruginosa* alginate by crosslinking the polyanionic alginate chains [44].

Matrix is a biochemically active system. In response to environmental exposure, a biofilm could adapt to new living conditions either by activating intracellular processes that contribute to the synthesis of specific matrix components by cells, or by intensive cell division, or by transition of the biofilm components into the environment in searching for new habitats. Matrix protects cells against various types of stress, including thermal, osmotic, acid-base, etc. The study of biofilms rheological characteristics demonstrated that cohesion processes (so-called strain strengthening) are significantly enhanced as a result of external stress effects on biofilms [45]. Due to the matrix viscoelastic properties, biofilms exhibit the ability to reversible deformation, which allows them to survive exposed to short-term stress effects. Depending on the nature of the forces acting on the biofilm matrix, both reversible and irreversible deformation of the structure could appear. Thus, *S. aureus* biofilms demonstrate elastically resilient properties during short-term impacts and viscous liquid properties during prolonged exposure [43].

Main stages of biofilm generation. Biofilms generation by microorganisms is a complex process, where many structures and systems of microorganism cells are involved. Five main stages of a biofilm existence are distinguished (Table 2).

Table 2

Stages of biofilm generation and characteristics thereof

Biofilm generation stages	Characteristic feature
Adhesion	Transition process with cells from a mobile to the attached existence mode
Cell monolayer generation and cell co-aggregation	Cell diffused monolayer generation on a surface due to the cells' motion, structural and functional restructuring processes start [46]
Microcolony formation	Cell aggregation and launch of the matrix biosynthesis mechanism
Biofilm maturation	Biofilm matrix components synthesis and its architecture formation [47], microorganisms intercellular communication
Biofilm decay	Biofilm matrix degradation, cells destruction and/or transfer to the state-at-ease condition to generate a new biofilm [45, 48]

Adsorption of living cells, macromolecules (proteins, polysaccharides and humic acids) and smaller molecules (fatty acids and lipids) is taking place on metal surfaces at the first stage of a biofilm generation. A reversible stage is distinguished depending on contact time, flow rate, stage of cell development, surface characteristics and other factors, as well as the irreversible stage of sorption, when cells and molecules are strongly fixed on the surface and continue their functioning. In the absence of cytotoxic agents in the system, adsorbed cells grow and multiply creating colonies, growth and development of biofilms is observed, which leads to formation of local cathodic and anodic sections and, as a result, to biodegradation of any surface. Characteristics of the metal matrix (chemical composition, roughness, wettability and polarization) significantly affect the rate of microorganisms' accumulation and their distribution over the surface, especially, in the early stages of a biofilm generation [49]. Chemical composition of the surface is especially important at the stage of living cells attachment. For example, metal ions influence the surface colonization by microorganisms [10], and the presence of metal ions on the surface could either promote adsorption [50] or inhibit it (for example, the chromium ions [3]). Surface topography could provide a strong effect on the adhesion rate of microorganisms. The paper [51] indicates correlation between surface roughness of various nature (for example, copper, silicon, 316 steel and glass) and adsorption of microorganisms [51]. Higher surface roughness significantly increased the number of attaching microorganisms due to better adhesion.

Attached cells create a microlayer and then form micro colonies simultaneously synthesizing an extracellular matrix around them, which colloidal structure contributes to the capture of new microorganisms and molecules that are involved in vital activity of the resulting microbiological community. Matrix qualitative and quantitative composition could vary significantly depending on the type of microorganisms creating the biofilm, the stage of biofilm formation and the conditions of its habitat. As a result, a biofilm is generated that functions as a unique organism. At the same time, separate microorganisms are able to leave it to colonize new surface areas [18]. In laboratory conditions, the process of monospecific biofilms complete maturation takes an average of 24–48 hours; and then during their life span practically no serious structural rearrangements are observed, but their functional activity is significantly increasing. In natural multi-species biofilms, boundaries between the stages are erased and are not determined in time. Microorganisms constituting multi-species and mono-species biofilms are involved in the intercellular communication processes. Using the *Quorum Sensing* (QS) system, they are able to interact with each other creating a unique

organism and regulating many vital activity processes, including secondary metabolism, life support, division and much more.

Let us consider the basic mechanisms of microbial corrosion that occur in presence and absence of oxygen.

Microbiologically influenced corrosion under aerobic conditions. *Corrosion as a result of differential aeration.* Inhomogeneous bacterial colonization leads to formation of local anodic and cathodic zones with differential aeration. In an aerobic condition, zones with reduced oxygen concentration (or anode sections) are generated beneath the colonies, where metal oxidation (its dissolution) is taking place. Surrounding areas, where oxygen concentration is higher (oxygen is reduced from O_2 to OH^-) become the cathodic regions [3]. Even in the absence of the microorganisms' vital activity and only by creating a gradient of oxygen concentration in the biofilm, pitting corrosion would be developing, as a result of potential difference generation on different parts of the metal surface [17]:

extracellular anode (beneath the biofilm): $Me - ne \rightarrow Me^{n+}$

extracellular cathode (outside the biofilm): $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

This mechanism does not depend on the microorganisms' species diversity and on the presence of exogenous products resulting from their metabolic activity, and is determined only by the biofilm characteristics, i.e., surface area, thickness and gas permeability.

Corrosion mechanism in the presence of metal-oxidizing bacteria. MIC in the presence of aerobic microorganisms oxidizing a metal (iron or manganese) appears to be a more complex process [52]. In the presence of iron oxidizing bacteria (FeOB), the $Fe^{2+} - e \rightarrow Fe^{3+}$ oxidation is taking place accompanied by the heterogeneity zones formation on the metal surface consisting of $Fe(OH)_3$. As a result, corrosion current appears due to formation of the differential aeration pairs with various values of electrode potentials in sections covered with a layer of insoluble products of iron oxidation (anode) and aerated areas with a higher potential (cathode):

extracellular anode (beneath the biofilm): $Fe - 2e \rightarrow Fe^{2+} \rightarrow Fe^{3+}$

extracellular cathode (outside the biofilm): $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

It was demonstrated that the *Acidithiobacillus ferrooxidans* cells accelerate pitting corrosion of carbon steel [53, 54]. In addition to iron, microorganisms are also able to use other metals as an electron donor, manganese (MnOB) [55], for example, which catalyzes the $Mn^{2+} \rightarrow Mn^{4+} + 2e$ oxidation accompanied by manganese dioxide (MnO_2) deposition. It was shown in paper [57] that the ACE4 *Bacillus cereus* cells are able to oxidize Fe^{2+} and Mn^{2+} up to Fe^{3+} and Mn^{4+}

and to accelerate pitting corrosion of the 5LX API steel due to uneven aeration. Final reaction products in the presence of oxygen include the precipitates, i.e., iron oxide (Fe_2O_3) and manganese oxide (MnO_2), which are increasing the surface heterogeneity. As a result of oxygen intense consumption by iron-oxidizing bacteria and growth in $Fe(OH)_3$ deposits, the oxygen level beneath the $Fe(OH)_3$ layer is decreasing, which leads to an increase in the potential difference between cathode and anode due to differential aeration, and, consequently, to acceleration in the corrosion process. Thus, if FeOB or MnOB cells appear on a metal surface containing the Me^{2+} metal oxidation products, the pitting corrosion rate would increase.

Another function of the iron-oxidizing bacteria is that they, as part of a biofilm, create conditions for the growth of anaerobic microorganisms, since a local anaerobic environment is generated under the thick layer of iron-oxidizing bacteria and oxide deposits. Indeed, FeOB are the early soft steel colonizers followed by anaerobic SRB sulfate-reducing bacteria and other microorganisms [53]. It was established that a mixed culture causes more severe iron corrosion, than monocultures of FeOB or SRB strains [58]. However, the theory of differential aeration is not applicable to most oil and gas systems that are strictly oxygen-free, and an anaerobic habitat is created for the accompanying micro-flora.

Microbiologically influenced corrosion under anaerobic conditions. Three different types of microbial corrosion in the absence of oxygen are distinguished [59].

1. MIC of the first type (direct effect of microorganisms on the metal) appears, when corrosion reactions are involved in the metabolic cycle of microorganisms [11, 60]. Corrosion is caused by microorganisms that fill the intracellular electron deficiency by establishing a direct contact of cells with the reducing metal. In this case, anode and cathode are separated by a cell wall and electrons are transported through the cell membrane. As a rule, these are sulfate-reducing and nitrate-reducing anaerobic bacteria that are using sulfates and nitrates as electron acceptors for respiration.

Out of the six most studied species of anaerobic heterotrophic sulfate-reducing bacteria of the genus *Desulphovibrio*, at least four cause biocorrosion, including *D. desulfuricans, D. vulgaris, D. africans* and *D. salexigenes*. Metal structures corrosion by SRB is characteristic for underground facilities and structures located in dense clay and aquifer soil layers [10]. SRB are the most common bacteria involved in MIC due to the sulfates' wide availability in various aquatic environments, for example, in the sea water [14]. Bacteria use

sulfate as the electron acceptor to obtain the hydrogen sulfide. To ensure metabolism, the cells need a source of electrons, which are usually the oxygen-containing hydrocarbons (formiate, pyruvate, acetate, methanol, lactate, etc.). A classic redox reaction of the SRB metabolism in the presence of a carbon source (for example, lactate) is as follows:

oxidation: $CH_3CHOHCOO^- + H_2O - 4e \rightarrow CH_3COO^- + CO_2 + 4H^+$

reduction: $O_4^{2-} + 9H^+ + 8e \rightarrow HS^- + 4H_2O$

Gibbs energy for the overall reaction is $\Delta_r G° = -164$ kJ/mol, which indicates the thermodynamic advantage of the process considered above. With the presence of organic carbon available, SRB cells do not require an alternative electron source, as the redox process is taking place directly in the bacteria cytoplasm.

However, cell layers and components of the biofilm matrix prevent the mass transfer of organic carbon to cells in the biofilm lower layer, and they experience carbon starvation. Iron could become an alternative electron donor (Table 3), since the values of the redox potential in Fe^{2+} / Fe and CO_2 + acetate / lactate pairs are close. In this case, biofilms provoke severe corrosion of the metal [1].

Table 3

Standard values of redox potentials [1]

Redox pair	$E°$, B
Fe^{2+}/ Fe	–0.447
CO_2 / formiate	–0.432
CO_2 + acetate / lactate	–0.430
CO_2 / methanol	–0.370
CO_2 / CH_4	–0.244
SO_4^{2-} / HS^-	–0.217
$2H^+$ / H_2	0
NO_2^- / NH_3	0.330
NO_3^- / NH_3	0.360
$2NO_3^-$ / N_2	0.760

According to the theory of cathodic sulfate biocatalytic reduction, the reducing agent (iron) electrons penetrate through the SRB cell wall into the cytoplasm, where sulfate is reduced to the HS^- ion [61]:

extracellular anode: $Fe - 2e \rightarrow Fe^{2+}$ ($E° = 447$ mV);

intracellular cathode: $SO_4^{2+} + 9H^+ + 8e \rightarrow HS^- + 4H_2O$ ($E° = 217$ mV).

The difference in the standard potential values is ΔE° = 230 mV (at pH = 7), which corresponds to the Gibbs free energy alteration value, i.e., $\Delta_r G^\circ$ = = −178 kJ/mol [61]. Such electron transfer through the cell wall is known as the extracellular electron transfer (EET) [14]. The theory of transmembrane electron transfer could explain the enhanced corrosion with carbon steel in the presence of *Archaeoglobus fulgidus* archai (SRA) under conditions of carbon starvation at the temperature of 80 °C [62]. It is obvious that carbon steel corrosion in the presence of sulfate-reducing microorganisms is complicated by parallel secondary corrosion processes connected to generation of highly active products, in particular, to increased corrosion by the acid reaction product (H_2S). Corrosion behavior of copper-containing Cu/Ni (70 % Cu and 30 % Ni) and brass (76 % Cu, 22 % Zn and 2 % Al) alloys in sea water was described in paper [63]. It was shown that sulfide and acid metabolic products lead to destruction of the passivating protective layer and accelerate corrosion; and matrix components are binding the copper ions reducing their toxic effect on the living cells.

Transfer to an alternative source of electrons is also known for other types of bacteria using the redox reactions. Metal vulnerability to the action of a biofilm would depend on the potentials difference value or, in other words, whether it could be used by cells as an electron donor to maintain metabolism (see Table 3). For example, reduction of nitrates (and nitrites) could also lead to MIC. The authors of paper [64] proposed a similar mechanism of biocatalytic cathodic reduction of nitrate in the NRB cells:

extracellular anode (beneath the biofilm): $Fe - 2e \rightarrow Fe^{2+}$ (E° = 447 mV);

intracellular cathode: $2NO_3^- + 12H^+ + 10e \rightarrow N_2 + 6H_2O$ (E° = 760 mV).

Thus, the *Bacillus licheniformis* microorganism cultivated as NRB under carbon starvation conditions created a dimple of 14.5 μm in one week on the C1018 carbon steel [64]. Similar results were obtained in regard to the *P. aeruginosa*, which were cultured as NRB [1]. Unlike sulfate reduction, the E° standard electrode potential value in nitrate reduction is high enough to make even copper a reducing metal [65].

It should be noted that electron transport from the anode to the cathode is possible only in the case of direct interaction of the microorganism cell wall with a metal. Plankton cells (freely moving in the cell suspension) do not cause corrosion due to the absence of contact with the metal surface.

Transport of electrons through the microorganisms' cell walls into the cytoplasm could be carried out in several ways (Fig. 2). Electrons from the metal surface are able to enter the cell using either the cytochrome C of the cell wall, or

through the conductive pills [66, 59]. In addition, indirect electron transfer is possible through the electron transfer mediators (for example, riboflavin and adeninflavin), which are absorbing electrons from the metal surface and transmit them to the cytochrome C connected to the cell wall [14]. It was experimentally proven that in the presence of a biofilm, the *P. aeruginosa* mediator dinucleotide (FAD) accelerates corrosion in the 304 corrosion-resistant steel and in carbon steel [14, 67], while riboflavin and FAD accelerate corrosion in the C1018 carbon steel [68].

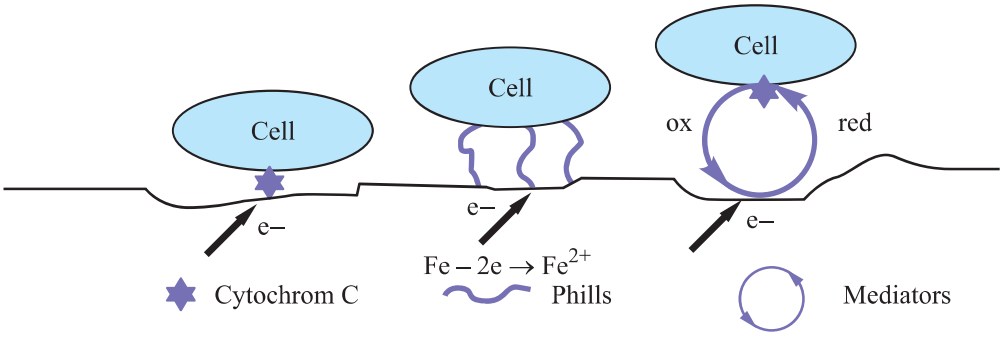

Fig. 2. Ways of electrons' transmembrane transport into the cytoplasm of living microorganisms

2. MIC of the second type is determined by the oxidizing effect of the microorganisms' secreted metabolites that create a corrosion-active aqueous medium to develop the abiogenic corrosion [69]. In the process of vital activity, microorganisms secrete metabolic products, and the main are acids ranging from sulfuric and nitric to organic acids, including formic, acetic, lactic, oxalic, malic, and even polyhydric (humic and pyruvic) acids. This contributes to development of the pitting corrosion due to reducing the local pH value, which could appear by 3 units lower. This is an option of thermodynamically favorable electrochemical corrosion ($\Delta_r G° < 0$), when protons are used as the oxidizing agent:

extracellular anode (beneath the biofilm): $Me - ne \rightarrow Me^{n+}$

extracellular cathode (beneath the biofilm): $2H^+ + 2e \rightarrow H_2^-$

In the presence of water, corrosion is developing according to the standard laws of electrochemistry, and the influence of acid metabolites increases at the biofilm — metal phases interface. Acid-producing bacteria (APB) create an acid environment beneath the biofilm. Thus, sulfuric acid appears as the product of the denitrifying bacteria vital activity. Alginic acid produced by the *Ps. aeruginosa* bacterium significantly reduces the pH at the metal — biofilm interface and facilitates the pitting corrosion development. APB is the only

group of microorganisms, whose number correlates with the corrosion rate [10]. Proton reduction itself does not require biocatalysis, unlike sulfate or nitrate reduction. Thus, the MIC of the second type is developing extracellularly and is an analogue of abiotic corrosion; however, it could be complicated by parallel processes. Presence of fuels, oils and lubricants on the surface of structures contributes to the microorganisms' reproduction, since it is a source of carbon, sulfur, nitrogen and microelements. Formation of soluble complex metal ions compounds (for example, aluminum) with anions of organic acids increases the corrosion rate [3] preventing the process of repeated passivation due to deposition of the oxidation products on a metal surface. For example, *A. niger* secretes organic acids that cause corrosion in the 2024 aluminum alloy [70].

Aerobic and anaerobic microorganisms are found among the APB [71]. Acids are capable of destroying a film passivating the metal, i.e., a thin and dense metal oxide. The *Acetobacter spp* bacteria oxidizing ethanol to the acetic acid during aerobic fermentation cause pitting corrosion in steel and copper alloys [72]. Bacteria of the *Acidithio bacillus* genus accelerate the rate of corrosion in metals and alloys due to generation of sulfuric acid during the thiosulfate oxidation [73].

Anaerobic microorganisms are also able to generate protons. For example, copper corrodes in the SRB presence precisely due to the sulfides formation, despite the fact that the sulfate reduction potential $E^{\circ}_{SO_4^{2-}/HS^-} < E^{\circ}_{Cu^+/Cu}$ and $E^{\circ}_{Cu^{2+}/Cu}$, and copper is unable to provide cells with energy using direct electron supply for intracellular sulfate reduction [74]. However, copper corrosion in the presence of H_2S produced by SRB is well known accompanied by generation of the Cu_2S corrosion product [1]. Thus, both corrosion mechanisms could appear depending on the metal in contact with SRB, and these mechanisms are connected to both the direct consumption of electrons from the metal for the oxidizer intracellular reduction and the release of proton oxidizing agents by the cells for its extracellular reduction. It should be noted that hydrogen is the product of proton reduction, which could also be involved in physical/electrochemical corrosion processes, such as fatigue cracking and hydrogen embrittlement. Local decrease in pH would contribute to an increase in the rate of crack growth [1, 10].

Mucous bacteria are secreting extracellular acid polysaccharides in the process of functioning, which enhances metal corrosion. *Ps. paucimobilis*, *Ps. solanacearum* and polysaccharides secreted by them accelerated the copper tubes corrosion rate [10].

Fungi are the eukaryotic microorganisms that are widespread in the atmosphere and in the aquatic environments, and they convert the organic substrate accompanied by generation of organic acids (oxalic, lactic, formic, acetic and citric). *A. niger* fungi secrete oxalic acid, which causes MIC of the second type [10].

Mycological corrosion is destruction of metals and metal coatings exposed to aggressive media generated as a result of the mycelial (imperfect, mold) fungi vital activity. Holding moisture on the surface of metals and producing organic acids, fungi cause corrosion of ferrous and non-ferrous metals and contribute to corrosion of components made of brass, copper, steel, aluminum and their alloys. Biocorrosion under exposure to fungi is developing in places with limited air exchange, high humidity, pH values close to neutral and optimal temperature. Temperature range of the fungi vital activity is quite wide (0–45 °C), and each type of mycelial fungi has its temperature optimum. Fungi species diversity and their high adaptability to living conditions lead to the fact that the damage caused by the fungi vital activity is comparable in its volume to the damage caused by bacteria. Typical representatives of fungi that cause biocorrosion in different climatic zones include fungi of the *Aspergillus, Penicillium, Fusarium, Cladosporium* genera and others [10]. Mycelial fungi according to their type of nutrition belong to heterotrophs, i.e. they consume carbon from ready organic compounds; therefore, they are unable to develop on the surface of clean and uncontaminated metal. However, presence on a metal surface of organic substances (oil, grease, paint, etc.) leads to generating conditions for the colonization by fungi, and then mycelium causes metal corrosion by metabolite acids. Strong acid-generating agents include fungi of the *Aspergillus* genus. It was established in paper [75] that *A. niger*, as well as *Trichoderma harzianum*, reduce pH of the medium by several units, which significantly accelerates corrosion of the AZ31B magnesium alloy. Mass losses from corrosion after testing for 12 days in the presence of *A. niger* reached for 4 g/m^2 with aluminum, 18 g/m^2 with copper and 33 g/m^2 with iron, which was 4 times higher than the loss of each metal from standard corrosion.

3. MIC of the third type is caused by microorganisms that are using enzymatic catalysis for biodeterioration [3]; corrosion is developing through generation of products that could act as depolarizers or catalysts in corrosion reactions. Enzymes produced (catalase, superoxide dismutase, alkyl hydroperoxidase) are limiting accumulation of the active oxygen forms by cells, such as H_2O_2, catalyzing its decomposition [3] into water and oxygen, which is being sorbed on the surface of a metal substrate and is involved in the electron transfer reactions.

Methods of microorganisms' study in biofilms. Various approaches, methods and tools are used to study MIC and to evaluate the efficiency of reducing microbial corrosion. Traditional microbiological methods based on the cultivation of microorganisms constituting a biofilm in a nutrient medium in order to determine the qualitative composition and number of living cells are far from being always effective and reliable. It is much more difficult to implement them methodically than to cultivate planktonic microorganisms. This is mainly due to two reasons. Firstly, there appears a multicomponent extracellular matrix, which complicates separation of mixture into separate cells for inoculation. Secondly, it is the presence of altered metabolism with the living cells functioning under anaerobic medium conditions in the thickness of a biofilm. Qualitative identification of living microorganisms and determination of their metabolic activity could be conveniently carried out using the highly sensitive and specific bioluminescent method for determining the ATP using the luciferin-luciferase system [76]. It is based on the fact that all living organisms contain ATP, which is required to maintain the energy status of a cell. When a cell dies, ATP production stops and it disappears. Thus, ATP presence in a sample indicates the presence of exactly the living, but not the defunct microorganisms.

In recent years, genomic testing methods are being actively developed, and they include quantitative polymerase chain reaction (qPCR), analysis of 16S and 18S ribonucleic acid (16S RNA with bacteria and archaea and 18S RNA with fungi and other eukaryotic cells) and analysis of the entire genome, which allows to identify more than 90 % of all microorganisms present in the environmental samples [18]. However, due to the high stability of DNA and RNA molecules, results of the analysis could be overstated, since they include both living and already defunct cells. Transcriptomic analysis make it possible to identify active and inactive genes. Complementary genomic testing in combination with transcriptomic methods could solve the problem of overstating the number of microorganisms. Understanding genomics, transcriptomics and metabolomics with complex microbial populations could provide valuable new information about the relationship between environment, microbial community and biocorrosion processes.

To study the microorganisms' influence on structural materials, various spectral analysis methods are used, including atomic force, infrared, surface, Auger electron, X-ray photoelectron and Mössbauer spectroscopies, Fourier transform spectroscopy, etc. (Fig. 3). Methods of optical and electron microscopy provide information on the morphology of microbial cells, their distribution on the surface, EPS presence and nature of crystalline or amor-

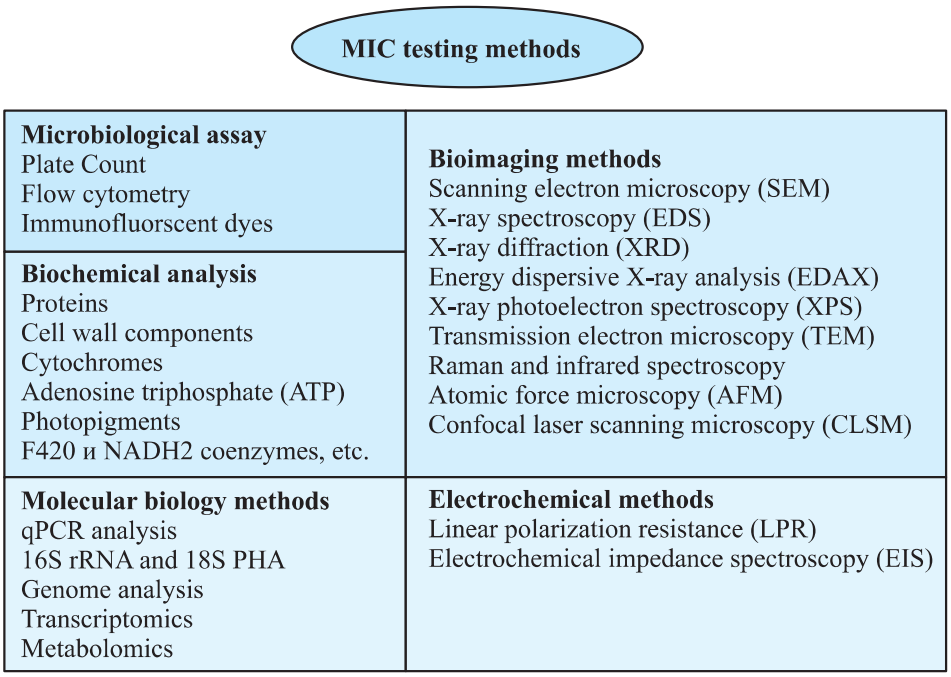

Fig. 3. MIC testing methods

phous corrosion products, and these methods make it possible to identify the type of a corrosion attack, whether it is a pitting or a uniform attack. The authors of paper [10] in studying the influence of biofilms' generation on corrosion processes used environmental scanning electron microscopy (ESEM), atomic force microscopy (AFM) and confocal laser scanning microscopy (CLSM) allowing to obtain 3D images of hydrated biofilms in real time and to demonstrate localization of cells and matrix. Methods such as X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDAX) provide information on corrosion products on the metal surfaces. Auger electron microscopy (AES) makes it possible to create a map of corrosion products on a metal surface, for example, in the capacitor tubes, and draw conclusions about nature of the corrosion foci distribution. Using the X-ray photoelectron spectroscopy (XPS), chemical composition of corrosion products could be predicted. It should be noted that AES and XPS methods are suitable for evaluating only thin deposits; laser Raman spectroscopy (LRS) in combination with optical microscopy could be used to analyze deposits with a thickness of more than 1 μm, which significantly expands the scope of the method introduced [10]. Combination of different methods is used to explain the mechanisms of the microorganisms' corrosive influence. For example, energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS), X-ray distraction (XRD), electron microprobe analysis

(EPMA), scanning electron and atomic force microscopy (SEM) were used in paper [77] to study composition and structure of sulfide films generated on the surface of carbon steel in the presence of *Disulfovibrio alaskensis* SRB.

To assess the risks of the MIC occurrence, attempts are made to develop qualitative and quantitative integrated prognostic models that allow evaluating probability of corrosion and predicting the rate of the process development. The authors of paper [78] suggested that a reliable forecast could be made if the following factors affecting the MIC are taken into consideration:

- biofilm development kinetics, i.e., living cells transport from a liquid to the metal surface, attachment, accumulation (biofilm growth) and separation thereof;
- diffusion of chemical substances (for example, of substrate, metabolites and buffer particles) from a liquid through a biofilm to the biofilm-metal interface;
- set of basic chemical, biochemical and electrochemical reactions taking place in a biofilm at the biofilm — metal phases interface and on the metal surface.

Unfortunately, there currently exist a rather limited number of mechanistic models [79] that take into account functioning of biofilms, as a participant in interphase physical and chemical reactions. Moreover, only SRB microorganisms being the mostly studied species are, as a rule, considered in simplified corrosion schemes, as the initiator of corrosion.

Conclusion. When studying the MIC mechanisms in regard to metals, it is necessary to take into account factors, such as the presence of living organisms and species composition in the external environment, their ability to be sorbed on the metal surfaces of various nature and alloys, possibility of creating a new habitat and ensuring the microorganisms functioning (water, oxygen, organic and inorganic substances). Main approach to cells' adaptation and survival on metal surfaces lies in generation of mono- and multi-species biofilms consisting of a community of living cells surrounded by the multicomponent extracellular polymer substance (EPS). Both cells, matrix components, and biofilm could influence the corrosion processes in metals that are developing in accordance with various mechanisms. Cathodic reactions could occur both outside the cells near a metal surface and intracellularly including participation of the electron transmembrane transition from the reducing metal agent to the cytoplasm of a living cell for participation in the metabolic cycle.

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