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Biocorrosion of Oil and Gas Field Equipment and Chemical Methods for Its Suppression. I

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Abstract—Main groups of corrosive microorganisms are considered. The parameters of the medium that intensify biocorrosion and the conditions for the formation of biofilms are described. The mechanisms of biocorrosion induced by the main groups of unicellular microorganisms are proposed, and the characteristic types of biodamage, specified.

INTRODUCTION

In the production, transport, and processing of oil and gas, a contact of metals with water and ground where microorganisms and algae are almost always present brings about biocorrosion involving such biogenic products as hydrogen sulfide (localized corrosion attacks, such as pitting, and intensified general corrosion) and carbon dioxide (carbonate deposits). Bacterial slime and the increased viscosity of water promotes sludging, which results in an increased pressure in producing and injection oil wells, power overconsumption, rock leaching, a change in the water–salt composition of suboil and stratal waters, and decomposition of process reagents. When adsorbed at rocks, cell biomass intensifies both evolution of H_2S and CO_2 and release of organic acids, thus deteriorating the pool permeability. Finely divided ferrous sulfide and the biomass of dead bacteria fills up the face zone of injection wells, reducing the productivity by 30 to 40% [1–7].

Biocorrosion inflicts considerable damage on an extensive network of oil lines, water pipelines, and equipment of oil and gas wells. Conditions for bacterial growth are especially favorable in water-collecting systems of oil fields [5, 7].

Some experts [4–7] believe that the effect of microorganisms should be taken into account in half the corrosion systems in oil and gas industry. According to others [8], biocorrosion in separate systems accounts for 80% of all corrosion attacks. For instance, annual losses due to biocorrosion in oil and gas industry in the 1990s were estimated at 180 million marks in Norway, $25 millions in Australia, $5 millions in New Zealand, $4 to 6 billions in the US, $700 millions in Germany, and 10 billion rubles in the former USSR [2, 3]. Researches aimed at solving this problem are of topical interest.

It is important to detect contaminated oil-field units, determine their role in the corrosion of oil and gas field equipment, analyze the mechanism of biocorrosion in systems of oil and gas fields, and examine the domestic and foreign experience of developing and using effective and efficient methods of protection.

1. TYPES OF MICROORGANISMS AND THEIR DISTINCTIVE VITAL FUNCTIONS IN OIL AND GAS FIELD MEDIA

There are two main types of unicellular microorganisms causing biocorrosion of oil and gas field equipment [4]: relict prokaryotes (bacteria and blue-green algae (*Cyanobacteria*)) and eukaryotes (higher living forms such as algae, fungi, and protozoa).

Micromycetic corrosion is caused by fungi that penetrate as spores and mycelium to the surfaces of structures (e.g., oil storages). Once the surface is moistened, fungal colonies grown in impurities retain moisture even at a relative humidity below 60% and produce tens of organic acids increasing the corrosivity of the medium [9].

Bacterial corrosion is induced by aerobic and anaerobic bacteria. The latter exist in oxygen-free media at pH 5 to 9 in the presence of sulfur-containing salts and sulfur. The most dangerous anaerobic species are sulfate-reducing bacteria (SRB), which produce hydrogen sulfide by reducing sulfates, sulfites, thiosulfonates, tetrathionates, and other sulfur compounds with absorbed hydrogen as the result of anaerobic respiration. Sulfide ions are involved in the formation of porous corrosion products which in turn facilitate bacterial growth immediately at the metal surface [6, 7].

The bacterial biomass contains carbon (50%), potassium (1%), oxygen (20%), calcium (0.5%), nitrogen (14%), magnesium (0.5%), hydrogen (8%), iron (0.2%), phosphorus (3%), sulfur (1%), and traces of

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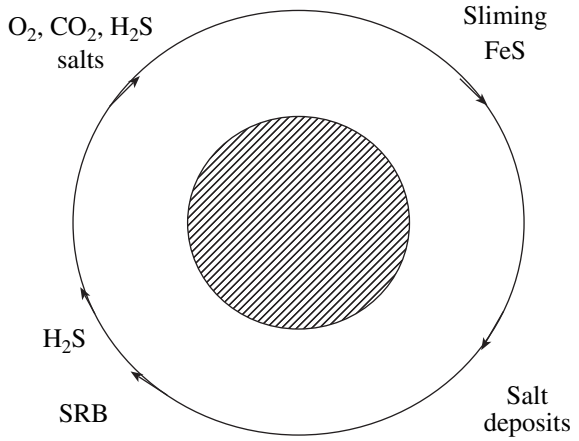

Fig. 1. Closed cycle of biocorrosion in water-collecting systems.

vanadium, manganese, copper, zinc, molybdenum, etc. [4]. The deficiency in vital elements can substantially impede their growth.

By oxidation type and according to the Postgate and Campbell system, SRB are classified into:

Desulfovibrio genus (*D. desulfuricans, D. aestuarii, D. gigas, D. africanus, D. salexigens*, etc.). Their mobile sporeless cells oxidize organic substrates to acetate ions and CO_2 (incomplete oxidation) and use organic compounds such as lactate, pyruvate, malate, ethanol, glucose, etc. as electron donors [9];

Desulfotomaculum genus. Their sporogenous cells are shaped like a swollen spindle. These sulfate-reducing agents actively produce H_2S. The cell size varies from 0.1 to 3 μm. These bacteria grow at pH 5.5 to 8.5 (optimum pH 6 to 7.2), E = 100 to 350 mV, and 20 to 70°C (optimum t = 30 to 35°C). Some thermophilic strains grow at 80 to 90°C and a high pressure. An SRB culture was found to produce H_2S at 104°C and a pressure of 1000 kg(f)/cm^2 [8–10].

The necessary conditions for the growth of SRB are an aqueous medium, hindered access for O_2, and low mineralization (5 to 7 g/l). Halophilic SRB forms can live in media with a high salt content (up to 30%). Larsen composed a series of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Li^+, NH_4^+, Zn^{2+}, and Cd^{2+}) and anions (Cl^-, CH_3COO^-, SO_4^{2-}, NO_3^-, Br^-, ClO_4^-, I^-, CHS^-, and CCl_3^-) that affect bacterial growth. The ion toxicity toward SRB increases from left to right in these series [11–13].

The most favorable conditions for biochemical processes arise in flooded oil pools in the face zone of injection wells. After an induction period, this zone begins to act like a generator of hydrogen sulfide; when passing through it, water pumped into the pool loses a considerable part of its sulfates and becomes enriched with H_2S. Traveling along the productive field, hydrogen sulfide reaches the producing wells and reacts with Fe^{2+} and Fe^{3+} ions present in stratal water to form insoluble ferrous sulfides. Sulfides promote the corrosion attack of the well equipment, discharge and gathering pipelines, and units of the oil treating system and the system maintaining the oil-pool pressure (MOPP). Provided the conditions are favorable, SRB continue to live in ground service lines, oil-field apparatuses, pipes, and tanks under the precipitates of paraffin, corrosion products, and thickened oil [14–20]. Biocorrosion in water-collecting systems can be represented as a closed cycle (Fig. 1).

In [14], the following experiment was reported. A clean carbon-steel plate was immersed in water containing one SR bacterium per five milliliters. After five days, the surface of the plate bore 150 000 SRB/cm^2. According to [4], a water sample from the heater-separator unit contains 22 species of SRB isolated among other anaerobes.

Microbial contamination of oil and gas field media is indicated by a change in the color and viscosity of the medium, the presence of slime, sludge, and other precipitates containing iron salts and oxides; indirect evidence is the failure of film-forming corrosion inhibitors. The qualitative signs of the effect of SRB are darkened water (accumulation of dispersed species of ferrous sulfide), the odor of hydrogen sulfide, and intensified localized corrosion [8].

Quantitative determination of SRB in oil and gas field media is usually oriented to the *Desulfovibrio* genus characterized by a high growth rate and a hydrogen affinity [11]. At present, the contamination level of oil-field media is determined by a lengthy method based on inoculation followed by subsequent microscopic examination. However, a direct fluorimetric method for rapid determination of this SRB species in water–oil systems was also tried out. The method involves detection of specific enzymes (bisulfite reductase and desulfoviridine). Sulfate- and sulfur-reducing bacteria have two types of bisulfite reductases: dissimilatory and assimilatory ones with high and low molecular masses, respectively. All bisulfite reductases belong to the octacarboxylic tetrahydroporphyrin isobacteriochlorine group "cyrogel." When denaturated, desulfoviridine converts into cyroporphyrin showing red fluorescence in alkali, which is behind the detection test. The rapid fluorimetric and microscopic methods were found to agree well when the concentration of *Desulfovibrio* is above 10^4 [12].

The ability to reduce sulfates is also inherent in other bacteria identified in the systems of oil and water preparation, e.g., those of the *Clostridium* genus (*C1. flabilliferum*, *C1. caproicum*, and *C1. cateretsensis*) [14, 15]. These sporogenous anaerobes are heterotrophs withstanding elevated temperature and pressure. *Clostridium*, *Pseudomonas*, *Proteus*, *Flavobacterian*, and *Aerobacterer* bacteria extract sulfur necessary

for generation of H_2S from proteins and amino acids; some *Clostridium* species can reduce inorganic sulfates. Bacteria of the *Proteus* and *Pseudomonas* genera reduce thiosulfates and sulfides. This result should not be regarded as a real norm because in accurate studies, only a few cells sorbed at the metal under the initial conditions. However, this result cannot be ignored since an unknown catastrophic factor can be behind it.

The reduction of sulfates can be indirectly accelerated by bacteria that oxidize (under microaerophilic conditions) oil into simple organic compounds digested by SRB.

The high oxygen content of water favors the growth of aerobic bacteria (sulfur- and iron-oxidizing ones). The former produce sulfur and sulfuric acid, while the latter produce iron salts [16].

Among iron bacteria, the *Gallionella*, *Leptothrix*, and *Crenothix* genera are most common in aqueous systems. They actively precipitate ferric hydroxide by assimilation or extraction of iron ions from solution. Precipitated ferric hydroxide forms knobs and scales with anaerobic areas on pipe walls. This results in localized corrosion and gives rise to differential aeration cells and conditions favorable for the metabolism of anaerobic SRB (under coatings) [7].

Freshwater *Gallionella* iron bacteria are filiform cells up to 1.5 to 2 μm in size. They are classified as ochre formers because of rust-colored precipitate. To gain one gram of cell mass, iron bacteria must oxidize ≈500 g of Fe^{2+} to Fe^{3+}, which precipitate as hydroxide; as a result, even a rather weak microbial activity can cause considerable deposition [8, 15].

Most iron bacteria are autotrophs. The carbon source for them is carbon dioxide dissolved in water. If water contains organic compounds, *Crenothix* and *Leptothrix* heterotrophs can grow therein to form slimy deposits [8].

Normal growth of iron bacteria occurs under the following conditions: 5 to 40°C (optimum t = 6 to 25°C), pH 4–7, and the presence of Fe^{2+} salts and oxygen. In media containing a lot of O_2 and few Fe^{2+}, they do not grow.

Thionic bacteria of the *Thiobacillus* genus (*T. thiooxidans*, *T. ferrooxidans*, and *T. thioparus*) oxidize sulfur, thiosulfate, sulfides, sulfites, and polythionates to obtain the energy for cytoplasm construction. The final oxidation products are sulfates and sulfuric acid [6, 16]. Sulfur bacteria, which deposit sulfur in cells and obtain energy by oxidizing hydrogen sulfide, belong to the same type. The final reaction product is H_2SO_4 excreted by cells as sulfates [8].

T. thioparus bacteria are autotrophs, but they can grow in the presence of organic food substances. These bacteria can oxidize CaS and H_2S into sulfur and thiosulfate and tetrathionate into sulfate. Sulfur can also be oxidized by them into sulfate, but the process is slow. The formation rate of H_2SO_4 depends on aeration. Excessive aeration suppresses their growth. The optimum pH value for their growth is 8.5 to 9.8; they stop growing at pH 5, oxidize sulfur at pH not below 3.5, and perish in more acidic media [14].

T. thiooxidans bacteria also contaminate oil-field media; the carbon source for them is CO_2. These bacteria do not grow in neutral media, yet growing in acidic media with pH not below 0.6. They obtain their energy from sulfur.

Anaerobic autotrophs *Thiobacillus ferrooxidans* obtain carbon from H_2CO_3. They are simultaneously sulfur and iron bacteria capable of oxidizing sulfur or hyposulfite into H_2SO_4 and Fe^{2+} into Fe^{3+} (optimum iron content 9 g/l). The optimum pH value for their growth is 1.7 to 2.5, but they exist even at pH 0.6. These bacteria need nitrogen and phosphorus compounds and mineral salts; the concentration of O_2 does not affect their growth. Unlike other thionic bacteria, they do not form distinct deposits [8, 15].

There is a certain sequence among thionic bacteria involved in biochemical processes. *T. thioparus* are suppliers of elementary sulfur, *T. thiooxidans* oxidize it into H_2SO_4, while *T. ferrooxidans* oxidize $FeSO_4$ into $Fe_2(SO_4)_3$ in acidic media. The energy released is used by the bacteria to construct their cytoplasm [7].

Oil-field media also contain hydrogen-consuming anaerobes (nitrate-reducing, hydrogen, and methane bacteria). Hydrogen-oxidizing bacteria of the *Hydrogenomoas* genus were detected in neutral or weakly alkaline media. They reduce carbon dioxide with the energy obtained by the oxidation of hydrogen [7].

Dense masses of Fe^{2+} deposits are produced by bacteria of the *Pseudomonas*, *Flavobacterium*, *Escherichia*, *Aerobar*, and *Bacillus* genera, which grow on tank walls and the inner walls of water pipelines. The deposit layer is a perfect protection for SRB growing under it. These bacteria can exist in both fresh water and brine and use oxygen in their metabolism [3, 17].

At the Mamontovneft' and Yuganskneft' oil fields, eight strains of the bacillary form of the *Bacillus sp.* bacteria and one strain of the *Penicillium sp.* fungus were isolated from samples of suboil water. These microorganisms stimulate corrosion of 09Г2С steel, attacking up to 100% of the bare metal area with pits 3.7 mm deep. Deposits on the inner surface of tanks contain eight strains of fungi (*Ulocladium chartarum*, *Ul. Sp.*, *Penicillium expansum*-1, *P. exp.*-2, *Verticillum punicillium*, *Periconia sp.*, *P. chrysogenum*, and *P. stoloniferm*) and ten bacterial strains (*Bacillum sp.*). The number of microbial cells in a milliliter of water varies from 6.3×10^6 to 6.5×10^7; their number in one milligram of the deposit reaches 10^6. The highest weight losses and the highest corrosion rate were observed in the simultaneous presence of bacteria and a mixture of fungi or the *Periconia sp.* fungus [21].

All the detected microbes can live on petroleum hydrocarbons, using them as the main source of carbon.

The enzyme-catalyzed reactions yield acids, which lower the pH of the medium and aggravate electrochemical corrosion of metals.

The biocontamination of the media at many oil fields of West Siberia, Perm, Komi, and Udmurtia is unambiguously indicated by our data presented in Table 1. Data on the species of microorganisms causing corrosion of oil and gas field equipment are summarized in Fig. 2. Note, however, that the classification of microorganisms living in oil-field media has not been completed to date.

2. BIOCORROSION MECHANISMS IN OIL AND GAS FIELD MEDIA

Microorganisms affect oil and gas field equipment both directly and indirectly. The indirect effect is produced by their metabolites. Because of their ability to bind water, cells intensify the destruction of materials as a result of repeated freezing and thawing of water contained in pores. Sulfuric acid is especially dangerous since it can retain a considerable amount of crystal water. The presence of such large molecules in pores of a material makes its structure degrade [17]. According to conventional concepts, microbiological corrosion can follow different pathways:

(1) direct effect of the metabolites (CO_2, H_2S, and NH_3) of microorganisms and that of organic and mineral acids on the metal [5, 7, 22];

(2) formation of products that can act as depolarizers or catalysts of electrochemical reactions [5, 7, 22];

(3) corrosion reactions can also be an immediate part of the metabolic cycle of bacteria [23, 24].

2.1. Aerobic corrosion mechanisms. An electrochemical mechanism was proposed by Baumgartner (Fig. 3) [9]:

at the anode

$$Fe^0 \longrightarrow Fe^{2+} + 2e; \quad (1)$$

$$Fe^{2+} + OH^- \longrightarrow Fe(OH)_2; \quad (2)$$

$$2Fe(OH)_2 + 1/2O_2 + H_2O \longrightarrow 2Fe(OH)_3 \longrightarrow \text{rust}, \quad (3)$$

at the cathode:

$$H^+ + e^- \longrightarrow H^0; \quad (4)$$

$$H^0 + H^0 \longrightarrow H_2; \quad (5)$$

$$H^0 + H^0 + 1/2O_2 \longrightarrow H_2O; \quad (6)$$

$$1/2O_2 + H_2O + 2e \longrightarrow 2OH^-. \quad (7)$$

In the presence of thionic bacteria, corrosion can follow both the chemical and electrochemical mechanisms. In acidic media, the chemical oxidation of sulfur-containing compounds occurs as follows [7]:

$$H_2S + 1/2O_2 \longrightarrow S + H_2O + Q, \quad (8)$$

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 + Q. \quad (9)$$

For instance, *T. thiooxidans* bacteria produce up to 12% H_2SO_4:

$$Na_2S_2O_3 + H_2O + 2O_2 \longrightarrow Na_2SO_4 + H_2SO_4 + Q. \quad (10)$$

Obviously, thionic bacteria can noticeably acidify a medium containing moderate amounts of oxygen and sulfur compounds. In acidified medium, the corrosive effects of H_2S and a precipitate of ferrous sulfide become intenser. *Thiobacillus Pseudomonades* or *Thiobacillus* sulfur bacteria can convert sulfur compounds into sulfates according to the following scheme [25, 26]:

$$FeS_2 + H_2O + 3.5O_2 \longrightarrow FeSO_4 + H_2SO_4, \quad (11)$$

$$2FeSO_4 + H_2SO_4 + 0.5O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O, \quad (12)$$

$$Fe_2(SO_4)_3 + FeS_2 \longrightarrow 4FeSO_4 + 2S^0, \quad (13)$$

$$S^0 + H_2O + 1.5O_2 \longrightarrow H_2SO_4. \quad (14)$$

The effect of this type of bacteria is especially dangerous in grounds where sulfur-containing compounds are present, because resulting sulfuric acid can cause intense corrosion of steel structures. The rate of aerobic corrosion induced by sulfur-oxidizing bacteria can reach 30 to 40 mg/dm^2 day [8].

Apart from H_2SO_4, organic acids, amino acids, sulfolipids, etc. can promote the anodic process [26].

According to Iverson's hypothesis, thionic bacteria can immediately participate in corrosion, capturing electrons via a "trap" mechanism and accelerating their transfer to the corresponding acceptors [27].

Thus, *Thiobacillus* bacteria significantly acidify the medium, thus activating iron corrosion with hydrogen depolarization. If such a medium contains hydrogen sulfide and ferrous sulfide, the corrosion rate increases strongly.

Iron bacteria use the energy released in the oxidation of Fe^{2+} [7–10, 28]:

$$4FeCO_3 + 6H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 4CO_2 + Q \text{ cal}. \quad (15)$$

Ferric hydroxide formed as a colloid solution (hydrosol) coagulates as soon as it passes from a cell to the solution to give a bright yellow hydrogel, which further undergoes substantial transformations [9].

Corrosion caused by *T. ferrooxidans* bacteria is associated with the reaction [2, 8–10]

$$4Fe^{2+} + 4H^+ + 6SO_4^{2-} + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O, \quad (16)$$

this results in a partial alkalization of the medium and hydrolysis of the salt into ferric hydroxide and sulfuric acid. As a consequence, the optimum pH value (1.7 to 2.5) for bacterial growth is maintained:

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 6H^+ + 3SO_4^{2-}, \quad (17)$$

Physicochemical characteristics of oil-field media and the contamination level of oil-field units

Oil field/unit	pH	General mineralization, g/l	Cl^-, g/l	CO_2, mg/l	H_2S, mg/l	SO_4^{2-}, mg/l	SRB, cells/ml	Thionic bacteria, cells/ml	Hydrocarbon-oxidizing bacteria, cells/ml	Heterotrophs, cells/ml
West Siberia										
Agan BPP-2, 1; CPP-2	7.2–7.3	15–16	9	0–21	0.3–0.6	–	10^6–10^7	10^4–10^5	10^1–10^2	10^6–10^7
Yuzhnyi Agan, BPP-1	6.7–7.3	19–33	12–20	21–66	0–2.4	–	10^5	10^4	10^2	10^6
k. 3, well 142, MOPP CPP-2, k. 11, well 643, MOPP	6.6–7.1	20–30	11–19	22–65	0.1–2.1	–	10^2–10^3	10^3–10^5	10–10^2	10^2–10^4
Vatino CPP-6, CPP-8, CPP-7 (thermophiles)	6.6–6.7	19–24	12–14	24–41	0–1.1	–	10^6–10^7	10^4–10^5	10–10^2	10^6–10^7
k. 133, well 639, MOPP k. 32, well 1062, MOPP	6.7–7.8	20–31	15–16	25–44	0.2–0.9	–	10^5	10^4	10^2	10^6
Megion, CPP-3	7.2	24	15	16	0.84	–	10^2–10^3	10^3–10^5	10–10^2	10^2–10^4
Pokamasovo, CPP-1	7.3	29	17	absent	0.83	–	10^6–10^7	10^4–10^5	10–10^2	10^6–10^7
Perm										
Water-intake unit "Bui"	7.0–8.1	1.1–1.3	22	–	traces	57	10^2–10^4	10^2–10^3	10–10^2	10^2 –10^3
Kueda, COTP, RVP-11	6.6–7.1	44–47	22	–	28–30	480	10^6	10^2	10^2	10^7
Well 870; well 1288	6.0–6.5	225–228	140	–	58–60	442–995	10^2	10	10^2	10^3
Gondyrevo PWDU	7.0–8.1	1.1–1.3	22	–	traces	69	10^7	10^6	10^5	10^6
Komi										
Usa and Vozei, BPP, LCPP	6.7–7.8	29–84	35–84	–	3.7–94	–	10^2–10^5	10–10^2	10–10^3	10^2
Udmurtia										
Gremikhino, BPP	86–108	86–108	86–108	109–200	49–108	400–640	10^3–10^4	10–10^2	10^2–10^3	10–10^2
Mishkino, BPP	82–114	82–114	82–114	88–227	9–23	580–770	10^2–10^3	–	–	–

Note: BPP is the booster pumping plant, CPP is the cluster pumping plant, and MOPP is the system maintaining the oil-pool pressure.

T. ferrooxidans bacteria grow by consuming relatively small amounts of iron [8]:

$$2MeS + 2Fe_2(SO_4)_3 + 3O_2 + 2H_2O \longrightarrow 4FeSO_4 + 2H_2SO_4 + 2MeSO_4. \quad (18)$$

The Fe^{2+} ions formed in reaction (18) can be oxidized by microorganisms to give Fe^{3+} and H_2SO_4, which reenter into the reaction. The compound to be oxidized is sulfide, with the intermediacy of iron.

2.2. Anaerobic corrosion mechanisms. Wolzogen Kühr and van der Vlugt assumed that the sharp intensification of iron or steel corrosion by SRB is due to hydrogen absorption from the cathodic areas of the metal. The corrosion process at a metal in the presence of SRB was represented by the reactions [7, 8]:

anodic

$$4Fe \longrightarrow 4Fe^{2+} + 8e; \quad (19)$$

cathodic $$SO_4^{2-} + 4H_2O + 8e \longrightarrow S^{2-} + 8OH^-, \quad (19')$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS, \quad (20)$$

$$3Fe^{2+} + 6OH^- \longrightarrow 3Fe(OH)_2. \quad (21)$$

The overall reaction is

$$4Fe + SO_4^{2-} + 4H_2O \longrightarrow 3Fe(OH)_2 + FeS + 2(OH)^-. \quad (22)$$

These assumptions are based on Kühr and van der Vlugt's observations showing that living SRB absorb hydrogen from the medium with the subsequent formation of ferrous sulfide and a comparatively small amount of $Fe(OH)_2$ in the bulk of the medium. Having noticed that ferrous sulfide initially inhibits iron corrosion and then stimulates it, they nevertheless assumed that removal of hydrogen (that should evolve at the metal) by bacteria is the main reason for the depolarizing effect of SRB during corrosion.

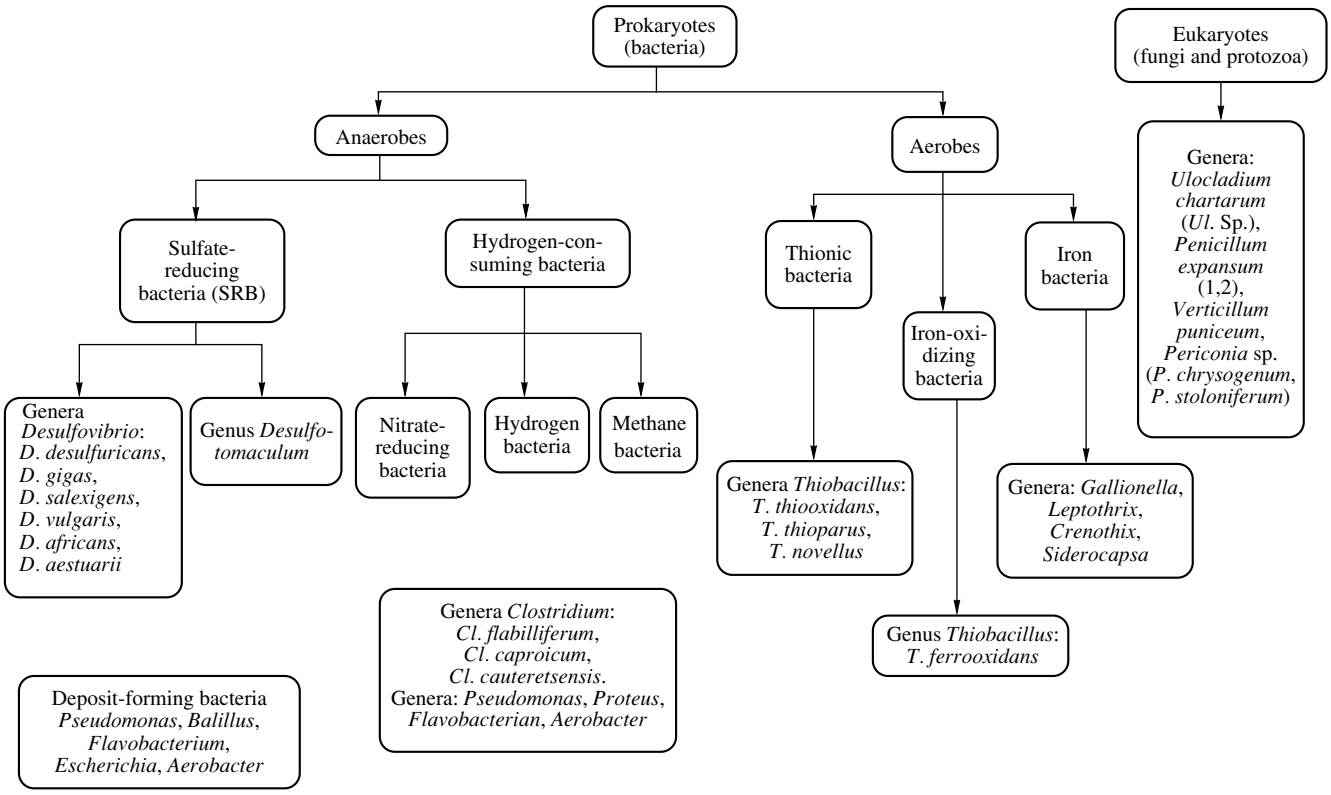

Fig. 2. Classification of microorganisms causing biocorrosion in oil and gas industry.

However, Booth [22] and Iverson [27] arrived at the conclusion that the mechanism of cathodic depolarization due to the consumption of hydrogen by SRB is in conflict with the practically observed high rates of iron corrosion. They reported data on corrosion stimulation by anaerobic SRB, mainly via reproduction in hydrogen sulfide. Particular attention was given to the reaction product FeS.

Skyring and Trudinger proposed the mechanism for biogenic sulfate reduction that involves the initial activation of sulfate ions by adenosine triphosphoric acid (ATP) as a sulfurylase [29]:

$$SO_4^{2-} + ATP \longrightarrow APS + \text{pyrophosphate (PP)}. \quad (23)$$

Adenosine phosphosulfate (APS) is reduced by APS reductase to sulfite and adenosine monophosphate (AMP):

$$APS + 2e \longrightarrow SO_3^{2-} + AMP. \quad (24)$$

The resulting sulfite is reduced by sulfite reductase to sulfide:

$$SO_3^{2-} + 6e + 8H^+ \longrightarrow H_2S + 3H_2O. \quad (25)$$

According to Tomashov [7, 8], the sulfate reduction by SRB involves the reaction

$$SO_4^{2-} \longrightarrow S^{2-} + 2O_2. \quad (26)$$

Thus, wherever SRB are present, a limited amount of oxygen is formed. The oxygen does not accumulate in the system. Its lesser part is involved in the metabolism of SRB:

$$2H + 1/2O_2 \longrightarrow H_2O, \quad (27)$$

while the rest is consumed by electrochemical reduction:

$$1/2O_2 + H_2O + 2e \longrightarrow 2OH^-. \quad (28)$$

The presence of free oxygen brings about corrosion with oxygen depolarization and the oxidation of Fe^{2+} [8].

Different mechanisms were proposed for SRB-induced anaerobic corrosion of the metal [28–33]. First, the cathodic reaction is stimulated by solid ferrous sulfides through removal of hydrogen by bacteria; second, the anodic dissolution of metal is intensified by sulfide produced by bacteria.

Under anaerobic conditions, SRB were found to produce corrosive H_2S [27] extracellularly, thus promoting iron corrosion (the corrosion also involves phosphorus). In the initial period, biogenic hydrogen sulfide acts as an inhibitor, forming Fe_xS_y films at the steel surface. In terms of such an interpretation, the corrosion rate primarily depends on whether the metal surface becomes covered with a protective film more rapidly than attacked by corrosive bacterial metabolites.

The formation of such a film, which is assumed by the authors to be resistant to additional factors, noticeably inhibits corrosion; otherwise, the corrosion rate is high. Although according to the authors, this assumption was confirmed by their investigations, surface sulfide films are usually ineffective for the protection of ferrous metals in commercial oil-field media.

The reduction of sulfates is associated with the formation of mobile hydrogen forms upon the oxidation of an organic material. The sources of hydrogen (in the absence of a cathodic depolarizer) are organic acids, hydrocarbons, ethanol, and molecular hydrogen.

Corrosion by methane, as well as nitrate- and hydrogen-reducing, bacteria is associated with their reductive effects on oxidized substrates, which releases the energy E for their own metabolisms [32]:

$$4H_2 + 2CO_2 \longrightarrow CH_3COO^- + H_2O + H_3O^+ + E, \quad (29)$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O + E, \quad (30)$$

$$5H_2 + NO_3 \longrightarrow NH_4 + 3H_2O + E, \quad (31)$$

$$2H_2 + O_2 \longrightarrow 2H_2O + E, \quad (32)$$

$$4H_2 + SO_4^{2-} \longrightarrow S^{2-} + 4H_2O + E. \quad (33)$$

In the presence of nitrate-reducing bacteria, the following cathodic reaction occurs [32]:

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O. \quad (34)$$

Methane bacteria can stimulate the corrosion of pipelines through cathodic depolarization in peat soils [32]:

$$CO_2 + 8H \longrightarrow CH_4 + 2H_2O, \quad (35)$$

while hydrogen bacteria stimulate corrosion in clay soils by consuming hydrogen evolved at the cathode [33].

On the whole, the biocorrosion of metals includes several steps:

(1) transfer of microorganisms to the surfaces of metal structures;

(2) adsorption of microorganisms and contaminants at the structures;

(3) formation of microcolonies and their growth to visible sizes, which is accompanied by the formation of corrosive metabolites and local accumulation of electrolytes with an excess content of H_3O^+ ions;

(4) surface accumulation of the metabolites (organic acids, H_2S, etc.) of microorganisms in the metal structures;

(5) stimulation of metal corrosion; and

(6) synergism of biodamage: mutual stimulation of destruction processes (corrosion, aging, and biodamage) and the development of biocenosis due to a number of factors.

2.3. Biofilm formation. Adsorbed microbial cells grow, multiply, and unite into colonies to form a biofilm at the metal surface, which changes the character of

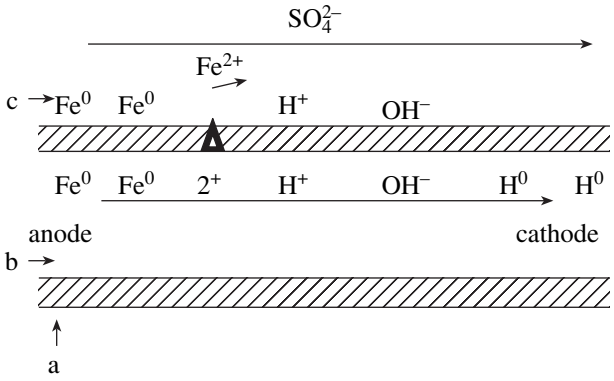

Fig. 3. Baumgartner's general scheme of aerobic corrosion: a is the steel pipe wall, b is the flow of water with oxygen, and c is the anaerobic medium outside the pipe.

electrochemical processes. Both aerobes and anaerobes can exist in such communities. The same microorganisms can affect different electrochemical processes, even after they have perished [5, 12, 15, 20].

Microbial incrustation is also a multistep process. As soon as a metal comes into contact with water pumped into oil wells, the nature of the metal–solution interface starts to change by biological and chemical factors. The initial step of biological change is the formation of a thin surface film of insoluble products formed by inorganic ions and organic molecules with high molecular masses. The film facilitates attachment of bacteria to electrostatically charged and wettable surface. The next step is colonization of the surface by microorganisms to form a bacterial film and extracellular polymer compounds [19, 33]. This gives rise to surface zones of differential aeration. Under aerobic conditions, the surface areas under the biofilm become anodes, while the surrounding areas act as cathodes.

The biofilm formation is accompanied by the metal dissolution and deposition of corrosion products and bacterial metabolites at the surface. Corrosion deposits consist of ferrous sulfides and carbonates, as well as ferric hydroxides, and include numerous SRB colonies [34]. Intense pitting attacks metal under the deposits. Oil-well equipment is most liable to localized corrosion and was found to be perforated over several months, during which the corrosion rate increased 15 to 16 times [30].

In [35], it was noticed that the corrosion behavior of metals or alloys in aqueous oil-field media depends inversely on the ordering of the passive layer and the formation of a biofilm at the interface. The biofilm prevents O_2 from diffusing toward cathodic sites, whereas corrosive anions (Cl^-), from diffusing toward anodic sites; removal of corrosion products and bacterial metabolites into the bulk of the liquid is also impeded. If microorganisms consume oxygen more rapidly than it diffuses through the biofilm, then anaerobic conditions arise and the mechanism of the cathodic reaction

changes. Processes in the biofilm accelerate electrochemical corrosion reactions.

In [36], the associated water of the Talin field was found to contain a high concentration of Cl^- ions (3 to 3.5 g/l) and active SRB (1000 cells/ml), which resulted in intense pitting. The presence of sulfur in corrosion products found at the bottom of pit nuclei, as well as the character itself of colony accumulation in combination with the high content of SRB in the associated water, is evidence for the biological nature of the initial pit formation.

The initial step of pitting was associated with biofilm formed at the steel surface and composed of CO_2-producing anaerobes; under these conditions, the cathodic reaction is reduction of H_2CO_3. The low velocity of the liquid flow in a gas pipeline favored accumulation of carbon dioxide as well as sludging at separate surface areas and facilitated the growth of a biofilm and deposits. Migration of Cl^- ions to pitting centers led to autocatalytic corrosion. According to [33, 36], its high rate is due to a substantial dominance of cathodic areas over anodic ones.

Under different conditions, in the water from the separator of a gas-producing platform [37], uniform small hemispherical pits and deeper pits characteristic of undersludge corrosion in the presence of biogenic acids were detected visually and by SEM.

Thus, typical variety of corrosion occurring in oil and gas field media in the presence of bacteria are general, as well as localized (pitting of various types, and grooves), corrosion both without deposits and under sludge.

CONCLUSIONS

The bacterial life in oil and gas field units is concentrated in liquid and dropping liquid media with a salt content from 0.1 to 10% at 20 to 45°C (some sporogenous thermophiles can exist at 50 to 60°C and above). Each species of microorganisms enjoy its own optimal pH and temperature ranges. Many microorganisms are sensitive to the concentrations of O_2 and Fe^{2+} ions in water.

Microorganisms affect metal corrosion both directly and indirectly. Their direct effect is associated with electrochemical (acceleration of electrode reactions at the metal), chemical, and combined destruction of the metal. The energy from some chemical reactions is used by microorganisms for their reproduction.

A variety of microbial species are encountered in various oil-field units. Suboil water and deposits contain different strains of *Bacillus sp.* bacteria and *Penicillium sp.* fungi. Some of them can completely change the character of the anodic reaction.

There is an obvious succession and correlation between biochemical processes for species groups. Microorganisms of one species can create, by their life, favorable conditions for the life of others. Different strains of microorganisms belonging to the same genus (e.g., *Bacillus* sp.) differ in activity. Because of this, the character of biocontamination of the oil-field media at a particular unit can change with time, which requires monitoring for a timely use of necessary protective measures.

Investigations showed that virtually all the oil-field units of West Siberia, Perm, Komi, and Udmurtia are contaminated by such microorganisms as SRB, thionic, and hydrocarbon-oxidizing bacteria. It was noted that SRB are present in considerable amounts (10^6 to 10^7 cells/ml) even in the units (booster and cluster pumping plants, MOPP system, and wells) containing no hydrogen sulfide according to the data from physicochemical analysis. The ability of SRB to produce hydrogen sulfide differs from field to field.

Hence, the problem of biocorrosion of the equipment of oil-field units (oil collectors, pumping plants, water pipelines, wells, and discharge lines) cannot be ignored or remain unsolved; otherwise, considerable losses will result from repairs, fines, and degradation of marketable oil. The problem can be effectively solved by monitoring the biocontamination of oil-field units, mapping regional biocontamination, revealing dominant groups of microorganisms, taking measures aimed at suppression of their growth (e.g., by shifting pH and changing the temperature and chemical composition of the aqueous medium), using appropriate biocides, and introducing new highly effective preparations combining bactericidal and anticorrosive effects.

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