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EXPERIMENTAL ARTICLES

Microorganisms in Heat Supply Systems and Internal Corrosion of Steel Pipelines

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Abstract—In laboratory experiments with batch cultures of thermophilic microorganisms isolated from urban heat supply systems, the growth of sulfate-reducing, iron-oxidizing, and iron-reducing bacteria was found to accelerate the corrosion rate of the steel-3 plates used in pipelines. In the absence of bacteria and dissolved oxygen, minimal corrosion was determined. The aforementioned microorganisms, as well as sulfur-oxidizing bacteria, were found to be widespread in water and corrosion deposits in low-alloy steel pipelines (both delivery and return) of the Moscow heat networks, as well as in the corrosion deposits on the steel-3 plates in a testing unit supplied with the network water. The microorganisms were found in samples with a water pH ranging from 8.1 to 9.6 and a temperature lower than 90°C. Magnetite, lepidocrocite, goethite, and X-ray amorphous ferric oxide were the corrosion products identified on the steel-3 plates, as well as siderite, aragonite, and S^0. The accumulation of corrosion deposits and variation in the total and local corrosion of the steel plates in a testing unit were considered in terms of the influence of microbial processes.

Key words: corrosion of pipelines, thermophilic corrosive microorganisms: sulfate-reducing, iron-oxidizing, iron-reducing bacteria; steel corrosion rate; corrosion deposits.

The situation with corrosion in the Moscow heat network is currently favorable. Previously, however, when our study was conducted (1994–1998), the Moscow heat network was affected by significant internal corrosion and differed in its operational characteristics from the heat networks of developed countries of Europe by using additional feeding from water supply systems and, as a rule, lower pH values (from 8.6 to 8.8). According to the European standards, the heat networks lack makeup water and the water pH is maintained at a level of 9.5–10.0. In recent years, efforts have been made to raise the network water pH and thus to reduce the rate of internal corrosion. Theoretically, the content of oxygen in water does not exceed 50 μg/kg.

The results of our previous studies on the heat network microflora have been published as a scientific report [1] and a popular article [2]. The former dealt with the distribution of sulfate-reducing bacteria (SRB) and hydrogen sulfide formation in internal corrosion deposits of the heat-network pipelines filled with artesian sulfate-rich water in a small town in the Moscow oblast. The bacteria of the iron cycle belong to another group of corrosive microorganisms. The origin of ferric oxides on the steel surface in various types of heat systems had been previously interpreted as a consequence of electrochemical corrosion of steel [3]. However, a number of iron minerals and amorphous compounds are known to be generated in cultures of the iron-cycle microorganisms [4]. The distribution of these bacteria in the heat networks and their involvement in corrosion attack have not been studied methodically.

In this study, our aim was to determine the role of SRB and iron-cycle microorganisms in corrosion of the low-alloy steel pipelines of the Moscow heat networks, which are filled with fresh water.

The following problems were set: (1) analysis of distribution of the iron-cycle and sulfate-reducing thermophilic bacteria (a) in Moscow heat-station pipelines filled with differently pretreated water, (b) and in the corrosion deposits that developed at different water pH on the steel-3 plates from bypasses of a heat-network testing unit; (2) estimation of the corrosion rate on the steel plates from bypasses of the testing unit and analysis of the structure and composition of corrosion deposits; and (3) analysis of microbiologically influenced corrosion of steel plates in model laboratory experiments.

MATERIALS AND METHODS

Water samples and internal corrosion deposits from the steel pipelines of the five Moscow heat stations,

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Table 1. Conditions in the pipeline bypasses of a testing unit in different periods of the study

Season of exposure, period of the study	Number of days	Water temperature	Water pH in bypasses and the container no.		
			I	II	III
1. Spring (Mar. 23–May 23, 1997)	61	<85°C	9.5	9.2	8.2
2. Summer (June 8–Oct. 7, 1997)	91	60–70°C	9.5	8.6–9.5 (variable)	8.6
3. Winter (Nov. 10, 1997–Feb. 17, 1998)	99	Temperature change depending on the weather conditions: >85°C (43 days) 103–105°C (56 days)	9.5	8.6–9.5 (variable)	8.6

which differed in water pH, were examined, as well as the corrosion deposits on the steel-3 plates from the testing unit containers. The heat stations were supplied with water from the Moscow River and Pirogovskoe Reservoir. Before entry into the heat networks, the influent water was pretreated to reduce the content of calcium and magnesium (sodium cationization), whereas the content of dissolved oxygen was reduced to 50 μg/kg by degassing. In some heat stations, an additional water pretreatment was used (coagulation of the organic compounds, liming). The content of chlorides, nitrates, and sulfates in the water of various heat stations did not exceed several or several tens of mg/l. The water and corrosion deposits were examined microbiologically after sampling from both delivery and return pipelines, where the temperature ranged, respectively, from 70 to 110 and from 40 to 70°C depending on the heating season.

A testing unit set up in a pump station in the center of Moscow represented three bypasses of a delivery pipeline, into which containers with steel-3 plates were placed. The running water pH was varied in different bypasses to range from 8.2 to 9.5 (Table 1). The variable pH of the water in bypasses (8.6–9.5) was achieved by changes in the seven-day cycle of delivery of NaOH-containing water.

In the testing unit, the containers were exposed to different water temperatures in different seasons (Table 1). The heating of water was enhanced with decreasing seasonal temperature. Incubation of media inoculated with samples from the steel plates was performed at 70°C, a temperature favorable for the growth of temperate and extreme thermophiles.

To enumerate the bacteria present in water samples, the method of serial tenfold dilution of the inoculum in the medium was used. To determine the number of microorganisms in the corrosion deposits, 1 g of the latter was ground and suspended in 10 ml of medium under sterile conditions, which was followed by tenfold dilutions. The iron-cycle and sulfate-reducing bacteria were grown in the presence of vitamins and microelements [5]. Medium pH values ranging from 8.6 to 9.6 were obtained by using glycine–NaOH and carbonate buffers [6].

Iron-oxidizing bacteria (FeOB) were enumerated on medium 1 containing (g/l of tap water) $MgSO_4$, 0.02; $FeNH_4PO_4$, 0.05; Difco yeast extract, 0.05; Fe-citrate, oxide, 0.05; Difco agar, 10.0. Microcolonies grown on petri dishes were counted. Growth was visually estimated from ferric oxide accumulation in the colonies.

Various types of iron-reducing bacteria (FeRB) were enumerated on media 2, 3, and 4 containing (g/l of tap water) NH_4Cl, 0.3; KCl, 0.15; $CaCl_2 \cdot 2H_2O$, 0.15; $Na_2HPO_4 \cdot H_2O$, 0.1; as well as Na_2WO_4, 10 μg/l; Na_2SeO_3, 20 μg/l; and 10 ml of freshly precipitated $Fe(OH)_3$ suspension, ~ 500 mg/l. In addition, medium 2 contained sodium acetate and sodium succinate (0.5 g/l of each), medium 3 contained Difco yeast extract, 1.0 g/l, and medium 4 contained either sodium formate, 0.5 g/l, or molecular hydrogen (2/3 of a 30-ml vial). The growth was estimated from magnetite formation (black precipitate with magnetic properties) and by microscopic analysis of the precipitate.

SRB were enumerated in 18-ml Hungate tubes with freshwater liquid Widdel's medium [5] containing reducing agents ($Na_2S \cdot 9H_2O$ and $Na_2S_2O_4$) and either sodium lactate, 3.5 g/l, and Difco yeast extract, 0.5 g/l (medium 5), or sodium acetate, 1.0 g/l (medium 6), or Difco yeast extract, 200 mg/l, and a gaseous phase (8 ml) of H_2/CO_2 at a ratio 80 : 20 vol % (medium 7). The growth was estimated from hydrogen sulfide formation (at least 50 mg/l) in the inoculated medium. Hydrogen sulfide was determined colorimetrically using dimethyl-*N*,*N*-*para*-phenylenediamine [5].

The sulfur-oxidizing bacteria were counted in Beijerinck's liquid medium [7]. The growth was estimated from $S_2O_3^{2-}$ formation [8] and microscopically.

In the laboratory experiments with microbiologically influenced corrosion of steel-3 plates, we used 0.5-l glass flasks closed with rubber stoppers with silicone tubes 0.5 cm in diameter inserted so as to reach the bottom of the flasks to create a weak diffusive air inflow (microaerobic conditions). The upper end of the tube was clamped. Two sterile preweighed and cleaned steel-3 plates were placed in each flask. The plates were hung loosely to prevent their contact with fragments of corrosion deposits introduced into the same flasks. The basic medium used in these experiments was prepared

using heat station water with different pH values. The following salts were introduced into the water (mg/l): KH_2PO_4, 10.0; Na-tripolyphosphate, 10.0; and NH_4Cl, 50. In the experiments with SRB, sodium lactate, 500 mg/l, was introduced into the medium, whereas in the experiments with FeOB and FeRB, sodium acetate, 100 mg/l, and Difco yeast extract, 50 mg/l, were introduced. The flasks were incubated at 60°C. In some experiments, the medium pH was adjusted to 8.4–8.6 and 9.4–9.6 using the glycine-NaOH buffer [6] and CHES buffer [9], respectively. The media were boiled, rapidly cooled to remove dissolved oxygen, and poured into the flasks so that no air bubbles remained. The O_2 analysis was made using Perfil'ev and Gabe's method [10], whose sensitivity was at least 0.005 mg/l. No dissolved oxygen was detected during the entire period of the experiments. In each case, 5 ml of a bacterial culture containing 10^7–10^8 cells/ml was used as the inoculum.

The elemental and mineral compositions of the corrosion deposits were determined using an electron microscope with an X-ray microanalyzer and X-ray diffraction analysis [1], respectively. Aragonite was identified in the white crust of the deposits from its typical luminescence and shape of crystals [11]. Sulfur was extracted from the white deposits with carbon disulfide, and the extract obtained was evaporated on a slide. The slides were examined under a NU-2 (Zeiss) light microscope with a polarization device, and the presence of sulfur was determined from its typical light refraction (cruciform particles).

To determine the corrosion rate of the steel-3 plates, the decrease in their weight and depth of pitting (dotty deepenings) were analyzed. For this purpose, the plates were treated with urotropin hydrochloride for three days to remove the corrosion material [12]. Then the plates were dried until constant weight. The total corrosion rate, Π_{tot}, was calculated from the formula [12] $G_{365}/DST = \Pi_{tot}$, where G is the decrease in the plate weight; D is the steel density equal to 7.8 g/cm^3 or 7.8×10^{-3} g/mm^3; T is the time of exposure, days; 365 is the conversion coefficient for the time of exposure equal to one year; and S is the plate area, mm^2.

The local corrosion rate, Π_{loc}, was determined using a clockwork needle sensor and calculated from the formula [12] $[(d_1 - d_0) \times 365/T] - 2\Pi_{tot} = \Pi_{loc}$, where d_1 and d_0 are the maximal and minimal sensor indications, respectively, which were obtained by putting the needle into the most and the least deep pitting dots, mm; T is the time of exposure, days; 365 is the conversion coefficient for the time of exposure equal to one year; and Π_{tot} is the total corrosion rate, mm/year. The deposit accumulation rate, Π_{dep}, was determined from the difference between the weights of the deposit-containing and deposit-free plates; the plate area and the time of exposure were also taken into account. The tables show the average corrosion rate values determined from the analysis of ten plates. The deposits were estimated from the analysis of two plates. The character of the deposits was examined visually using an LPU-20 binocular magnifier (20×).

RESULTS

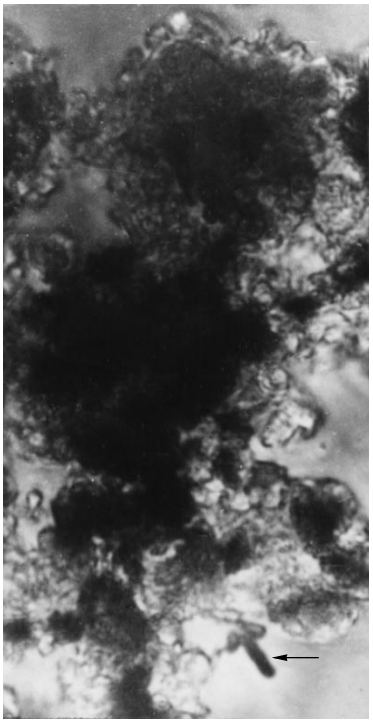
Distribution and Population Density of Bacteria

Heat network. In various heat stations, the water and corrosion deposits sampled from delivery and return pipelines at temperatures of 72–88 and 43–49°C, respectively, contained microorganisms that belonged to various physiological groups. In the heat stations examined, the inflow water differed in the following parameters: (1) pH 8.1–8.8 and no additional treatment (15 samples); (2) pH 8.7 and coagulation of organic compounds (9 samples); (3) pH 9.6–9.8 and both coagulation and liming (5 samples). The microorganisms identified were the following: SRB (lactate- and sodium acetate–containing media), FeOB, FeRB, and sulfur-oxidizing bacteria. They grew at the incubation temperatures of 40–45°C (samples from the return pipelines) and 60–85°C (samples from the delivery pipelines). The population density of these bacteria varied from single cells to thousands of cells per 1 ml of water or 1 g of deposits. Three water samples with a temperature of 100–102°C contained no bacteria.

Testing unit. The results obtained showed that only in spring and summer, when the water temperatures were <85°C and <60–70°C, respectively, the corrosion deposits on plates immersed into water with different pH values (from 8.2 to 9.5) contained SRB, FeOB, and FeRB. Analysis of the results obtained in spring showed that bacteria grew on media with pH 7.2, 8.6, and 9.5–9.6 irrespective of the pH of water in a bypass. In the deposits, the FeOB and FeRB population densities (media 1 and 2–4, respectively) ranged from 10^1 to 10^3 cells/g.

The population density of lactate-degrading SRB (determined on medium 5) was <10–10^4 cells/g; the lowest density (< 10 cells/g) was determined on media with pH 7.2. On H_2/CO_2-containing media (medium 7), only single bacterial cells per g were revealed at different pH values. In the deposits on plates withdrawn from containers I–III in spring and summer, sulfur-oxidizing bacteria were also identified (from single cells to tens of cells/g), which grew on media with pH 7.2, 8.6, and 9.4. Microscopic analysis of superficial deposits on the plates exposed in summer (water temperature 60–70°C, pH 8.6) showed that they mainly contained iron oxidation products generated by FeOB (figure).

In winter, no viable microorganisms were found in the corrosion deposits on the plates in bypasses. During 56 out of 99 days of this season, the network water temperature reached 103–105°C (Table 1). Nevertheless, individual mineralized microbial cells were found within these deposits, which testified to bacterial growth during periodic decreases in the network temperature.



Micrograph of a superficial deposit (on a plate of container III, summer) which contains bacterial microcolonies covered with ferric oxides. Individual, less mineralized cells of microorganisms are indicated with an arrow. Phase-contrast microscopy, 2400×.

Composition of corrosion deposits. Visual analysis showed that the corrosion deposits on plates exposed at different water pH values differed in their character and structure, namely, in coloration, the number of interlayers, degree of friability, and secondary structures. Nevertheless, in the deposits on the plates, magnetite (Fe_3O_4) always predominated, irrespective of the water pH. In addition, hydroxyhydroxides—lepidocrocite (γ-FeOOH) and goethite (γ-FeOOH)—were also present, as well as siderite ($FeCO_3$). An X-ray-amorphous phase of iron hydroxyhydroxides and silicates was also present. Ferrous sulfide was not detected.

In plates exposed to network temperatures lower than 85 and 70°C (spring and summer, respectively), the black deposit layers were always covering the metal. In the middle of the deposits, brown, red-brown, and black interlayers alternated. In spring, at the beginning of exposure, the upper layers looked like greenish scales, whereas in summer, they were red-brown tubercles. At variable pH values (Table 1), the middle layers were thin and frequently alternating. The magnetite layers of the deposits were thickest on plates from a container with the water pH 9.5. On the surface of the structural formations (tubercles and scales), white crust was present, which was less frequent at water pH 9.5.

Plate exposure at temperatures >85–105°C (winter) led to changes in the deposits: brownish layers adjoining the metal covered it more (pH 9.5) or less (pH 8.6 or variable values) uniformly. The plates had exscrescenses, which looked like either drops with a black covering and internal cavities or "flowers" on long stems.

The structural formations, such as scales, tubercles, and drops, contained water-filled cavities in fresh deposits. Under these formations, metal pitting (occurrence of dotted depressions was observed. These deepenings were more frequent on plates exposed at pH 8.6 or variable pH values than on plates exposed at pH 9.5. The black deposit layers exhibited magnetic properties and were identified as magnetite. According to the data available in the literature [13], the greenish-blue scales observed in spring represent green rust, which contains Fe^{2+} and Fe^{3+} at various ratios and is a formation that precedes magnetite. The results of X-ray diffraction analysis allowed us to assign the red-brown interlayers to hydroxyhydroxides ($Fe(OH)_3$ also seems to be present), whereas the brown layers were identified as a mixture of magnetite and hydroxyhydroxides, which agrees with the data of other authors [13]. The yellowish tinge of some deposits suggested that they contained siderite. The white coatings of scales and tubercles observed in spring and summer consisted of aragonite, a sort of calcite, which agrees with the results of elemental analysis (Table 2), which showed these structures to be enriched with calcium. The same coatings contained elemental sulfur.

As shown by X-ray analysis, iron predominated in the deposits (Table 2), which also contained Mg, Si, Cl, S, and P. Note that only bound sulfur could be detected by this method [1]. According to data available in the literature, chloride and sulfate ions exhibit high affinity to iron and promote lepidocrocite formation [13]. The presence of chlorine and bound sulfur in the deposits is most likely a result of high concentrations of chloride and sulfate salts in the solutions filling the cavities of corrosion deposits.

Rates of plate corrosion and accumulation of corrosion deposits. Table 3 shows that the total corrosion of the plates, Π_{tot}, was the highest in summer at a water temperature of less than 70°C. In containers with different pH values, the Π_{tot} values were >0.1740–0.20 mm/year. The lowest Π_{tot} values, 0.0899 to 0.1537 mm/year (containers I, II, and III), were determined in winter at a high water temperature (Tables 1 and 3). Irrespective of the season, the Π_{tot} values of plates from containers I and III decreased gradually with increasing pH of the water. In container II with variable pH (8.6–9.5), Π_{tot} ranged widely (from 0.20 to 0.32 mm/year) in summer (the lowest water temperature).

In spring and summer, at water temperatures <85 and <77°C, the pitting corrosion rate, Π_{loc}, was the highest on plates from container II with intermediate or variable pH values, and the lowest on plates from container I. In winter, when the water temperature

Table 2. Elemental composition of deposits on plates in a testing unit

Season of exposure	Container no.	pH	Sample	Peak area (X-ray microanalysis)						
				Mg	Si	P	S	Cl	Ca	Fe
1	I	9.5	The upper scale: green, red, and black layers	14 ± 59	100 ± 68	100 ± 78	200 ± 87	244 ± 94	369 ± 85	31438 ± 373
2		9.5	Total scrape	ND*	89 ± 57	82 ± 65	120 ± 71	20 ± 74	111 ± 65	21487 ± 310
			Wavy brown coating on the metal	80 ± 57	364 ± 89	175 ± 89	499 ± 101	380 ± 108	183 ± 86	41690 ± 429
1	II	9.2	Predominantly red-brown layers	49 ± 72	163 ± 89	105 ± 100	482 ± 116	933 ± 130	347 ± 101	46566 ± 460
2		8.6–9.5	Upper tubercle layer with a white apex	ND	863 ± 89	726 ± 135	836 ± 146	761 ± 149	1037 ± 136	201 ± 131
3		8.6–9.5	Smooth brown coating on the metal	133 ± 63	1265 ± 100	293 ± 93	712 ± 111	217 ± 104	184 ± 79	26142 ± 347
1	III	8.2	Bottom black and red-brown layers	150 ± 63	286 ± 88	94 ± 78	62 ± 107	44 ± 112	35 ± 101	51779 ± 483
			Total scrape with a white apex	198 ± 79	403 ± 105	238 ± 119	1778 ± 154	1377 ± 161	1111 ± 137	70317 ± 565
2		8.6	A tubercle with a white apex	ND	265 ± 75	215 ± 84	358 ± 96	352 ± 91	1499 ± 114	30398 ± 375
3		8.6	Smooth brown coating on the metal and structures (drops, “flowers”)	123 ± 59	1191 ± 93	157 ± 87	420 ± 101	1262 ± 122	–**	30717 ± 376

* No data.
** Absent.

Table 3. Extent of corrosion and accumulation of corrosion deposits on the plates under various operational conditions

Season of exposure	Container no., water pH	Corrosion rate*				Rate of corrosion product accumulation, Π_{dep}	
		Π_{tot}		Π_{loc}		g/cm^2 per year	% of the maximum
		mm/year	% of max	mm/year	% of max		
1. Spring	I—9.5	0.1294	66	0.4969	83	0.1387	67
	II—9.2	0.1707	87	0.5942	100	0.1911	93
	III—8.2	0.1960	100	0.5744	96	0.2055	100
2. Summer	I—9.5	0.1740	82	0.3480	88	0.1865	65
	II—8.6–9.5 (variable)	0.2–0.32	Range	0.3950	100	0.2126	74
	III—8.6	0.2117	100	0.3661	92	0.2867	100
3. Winter	I—9.5	0.0899	58	0.4407	71	0.0261	100
	II—8.6–9.5 (variable)	0.1349	87	0.4857	78	0.0241	92
	III—8.6	0.1537	100	0.6160	100	0.0245	93

* The maximum corrosion and deposit accumulation on plates recorded among the containers during a season was taken as 100%.

exceeded 100°C (Table 1), the highest and the lowest-Π_{loc} values were determined for plates from containers III (water pH 8.6) and I (water pH 9.5), respectively.

Table 3 shows the rates of accumulation of corrosion deposits on the plates. During winter exposure, this parameter was the least (0.024–0.026 g/cm^2 per year), whereas in summer it was an order of magnitude higher. The accumulation rate of corrosion deposits exhibited a certain correlation with the water pH.

Corrosion of steel-3 plates in model laboratory experiments. The results obtained in the laboratory experiments (Table 4) showed that under anaerobic conditions in the absence of microbial activity, plate corrosion was close to zero (experiments 1, 4a, and 4b). The sulfide-forming SRB displayed significant corrosion activity, whereas that of the magnetite-forming FeRB, which grew at the expense of an exogenous electron acceptor (a suspension of $Fe(OH)_3$), was insignificant. In the presence of oxygen (diffusive air inflow), slight plate corrosion was observed even in the absence of microorganisms on the medium with pH 8.6 but not at pH 9.6 (experiments 11 and 12, respectively). Corrosion attack was activated after the introduction of bacteria in the form of cultures of the iron-cycle bacteria or with scrapes from corrosion deposits (experiments 8 and 10). According to data available in the literature, a film of ferrous iron hydroxide, which activates FeOB, is formed under anaerobic conditions on steel-3 plates plunged into water with high pH (8.6–9.6 in our experiments) [3, 13]. In the presence of oxygen, $Fe(OH)_2$ is transformed into amorphous oxidized iron compounds serving as electron acceptors for FeRB [14]. Comparison of the results obtained in experiments 8 and 9 showed that the bacteria identified in the heat station pipelines are adapted to growth at pH values (8.2) similar to those of the source from which they were isolated (8.6) an do not grow at higher pH (9.6).

DISCUSSION

The presence of microorganisms in water and corrosion deposits of the heat network pipelines and on the steel plates from the testing unit, as well as the results obtained in model laboratory experiments, suggest that microorganisms accelerate the electrochemical corrosion of steel. Note that the low population density of microorganisms revealed on nutrient media is, as a rule, an underestimation of the actual content of microorganisms in the deposits [7]. Microbial cells attach to porous substrates and form biofouling due to the secretion of exopolysaccharides and mineral formation [7]. Microzonal growth of microorganisms, both aerobic and anaerobic, occurs in the presence of small amounts of organic compounds and oxygen supplied with continuous water flow. The bacterial colonies attached to particles are often mistaken for individual cells on nutrient media.

The following mechanisms may underlie the effect of microorganisms on electrochemical corrosion. The aerobic FeOB remove Fe^{2+} (by the peroxide mechanism) [7], thus accelerating anode iron dissolution. The microzonal growth of FeOB in the deposits leads to loosening and increased porosity of the latter, oxygen consumption, and irregular gas–metal contact, which stimulates oxygenous depolarization of the cathode and local corrosion. The anaerobic FeRB generate Fe^{2+} from the ferric iron compounds, and it interacts with Fe^{3+} to form magnetite, containing both Fe^{2+} and Fe^{3+}. Magnetite forms a film (precipitate) with various degrees of friability and porosity [4, 14]. Under certain conditions, dense magnetite tightly fixed on the metal surface possesses protective and anticorrosive properties [3, 13]. The anaerobic SRB generate S^{2-} from SO_4^{2-}. The hydrogen sulfide is transformed into iron sulfide, an additional cathode, which stimulates the

Table 4. Effect of various factors on biogenic and abiogenic corrosion of steel (model experiments continued for 120 days)

Conditions	Experiment no.	Corrosive agents	Added to the medium	Medium pH	Main corrosion products[1)]	Loss of metal, g/cm^2 per year[2)]
Anaerobic	1 a, b[9)]	SRB[3)]	–[4)]	8.4; 9.4	–	<0.001
	2	SRB	Na_2SO_4 (0.5 g/l)	8.4	Sulfide	0.180
	3	FeRB	$Fe(OH)_3$, suspension	8.6	Magnetite	0.001
	4 a, b[9)]	Control (without bacteria)	–	8.4; 9.4	–	0.000
Weak diffusive air inflow (dissolved oxygen in the flasks, <0.05 mg/l)	5	FeOB[6)]	–	8.6	HH, XRAP[7)]	0.166
	6	FeOB	–	9.6	HH, XRAP	0.125
	7	FeOB, FeRB	–	8.6	HH, XRAP, magnetite	0.125
	8	Scrapes from the deposits[8)] (water pH 8.2)	HH, XRAP, magnetite	8.6	HH, XRAP, magnetite	0.045
	9	The same	The same	9.6	–	0.000
	10	Scrapes from the deposits[8)] (water pH 9.6)	HH, XRAP, magnetite	9.6	HH, XRAP, magnetite	0.027
	11	Control (without bacteria and scrapes from the deposits)	–	8.6	XRAP	0.023
	12	The same	–	9.6	–	0.000

Note: 1. In the experiments with introduction of bacteria, a small amount of siderite was present in the plate corrosion deposits. 2. The average value for two plates. 3. An enrichment culture of spore-forming SRB isolated from heat station water with pH 8.6. 4. "–", absent; 5. A pure culture of unidentified thermophilic sulfate-reducing bacteria from heat station water with pH 8.6, which was isolated on sodium acetate–containing medium. 6. An enrichment culture of the iron-oxidizing bacterium "*Siderocapsa*" from heat station water with pH 8.6, which was obtained on yeast extract–containing medium. 7. HH, hydroxyhydroxides (goethite, lepidocrocite); XRAP, X-ray-amorphous phase of ferric iron hydroxides. 8. Scrapes from deposits in a corroded pipe of a heat station, which contained SRB and iron-cycle bacteria. 9. (a) pH 8.4; (b) pH 9.4.

anodic process [15]. However, iron sulfide is not always formed. A chemical reaction between H_2S and ferriferous deposits yields S^0 [1]. Microaerobic sulfur-oxidizing bacteria oxidize hydrogen sulfide to sulfur and then to sulfuric acid [7], which enhances electrochemical corrosion [3]. The presence of sulfur in the white deposit coating may be a result of the activity of these microorganisms. Autotrophic sulfur-oxidizing bacteria are known to be responsible for the formation of calcite [16], aragonite, in particular, which was detected in the deposits on the plates.

The microorganisms that degrade organic substances to CO_2 (SRB, FeRB, and others) promote siderite formation. Some of the aforementioned anaerobic bacteria oxidize hydrogen [14, 15], the removal of which stimulates cathode depolarization and enhances uniform corrosion attack (Π_{tot}) [3].

The following evidence suggests that bacterial processes influenced plate corrosion in the testing unit. The minerals and amorphous iron oxides found on the plates may be formed both in abiogenic physicochemical processes [3, 13] and in processes involving microorganisms [4]. The hypothesis that, in the heat network pipelines, microbiological processes are involved in steel corrosion is supported by the following: (1) the results of model experiments; (2) the presence of bacterial microcolonies in fresh deposits (figure); (3) the variable corrosion rate (Π_{tot}) of the steel plates, which was the highest in summer at a water temperature of <70°C and the lowest in winter, when no bacteria were found at extremely high water temperatures (>100°C) in the pipelines.

According to data available in the literature, uniform metal loss (Π_{tot}) occurs mostly because of cathode depolarization, which is accompanied by the reduction of the water protons in an anaerobic environment in the absence of a thick protective film of ferriferous deposits [3]. Magnetite with a porosity of <30% is the major component of such a film [3]. Theoretically speaking, oxygen is not involved in the processes of cathode depolarization if the content of dissolved oxygen is <50 μg/kg, as it is in the heat network pipelines [3]. Under these conditions, hydrogenous depolarization in electrochemical processes should increase with increasing temperature [3].

In winter, at ultrahigh water temperatures in the network, the plate deposits did not contain continuous black layers of magnetite covering the metal; however, a minimal Π_{tot} was determined. Thus, in our experiments, the latter parameter did not increase with

increasing temperature, which may be a result of suppression of microorganism activity at high temperature. The Π_{tot} value decreased with decreasing pH, which can be explained in terms of the optimal conditions for magnetite formation [3] in both chemical and microbiological processes. Magnetite is resistant to the bacterial effect, and, as mentioned above, it may serve as a protective agent under certain conditions.

The oxygen concentration increased periodically in the heat networks. Note that dissolved oxygen may occur not only in water with a temperature of <100°C, but also at a low concentration in water with a temperature of 100–105°C, because the pressure in the network pipelines is about 1.57 MPa [7]. Thus, the involvement of oxygen in the processes of cathode depolarization cannot be excluded [3, 13]. These processes depend on O_2 consumption by microorganisms, which stimulates local corrosion in porous deposits. The variation of the plate Π_{loc} value may be caused by different rates of pore healing and renewed pore formation in mineral deposits, which are processes dependent upon bacterial and physicochemical factors, particularly temperature [3, 13].

Different rates of deposit accumulation may be accounted for by peculiarities in corrosion deposit formation and growth, which depend on friability [18].

Thus, the results obtained in this study suggest that microbiological factors also account for the variation in the steel corrosion rate observed in Moscow heat network pipelines under different operation conditions. Elimination of additional water feeding, which supplies microorganisms with organic substances and dissolved oxygen, would be helpful in reducing corrosion attack in the urban heat network pipelines of Russia.

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