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MICROBIOLOGICAL CORROSION

Inhibition of Microbiological Corrosion of Concrete by Nickel Sulfide

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Abstract—Model experiments were carried out to study the microbiological corrosion of concrete by thionic bacteria *Acidithiobacillus albertensis* DSM 14366^T. Concrete samples were exposed in a liquid medium at initial pH 4.0 for 1 month. The corrosion of concrete was assessed by zinc leaching in the medium and sample weight change. The microbiological corrosion caused by the bacteria *A. albertensis* was shown to decrease if concrete contained 0.10 % nickel sulfide.

Keywords: concrete, microbiological corrosion, thionic bacteria, nickel sulfide

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INTRODUCTION

The problems of investigation and control of microbiological corrosion of materials have a long history. The first scientific report on the microbiological causes of corrosion was published in 1891 [1]. In recent decades, the previous methods of production of new industrial materials and development of new microbiological methods have needed to be improved.

Building materials based on carbonate-type compounds are vulnerable to aerobic acid-forming bacteria. In concrete corrosion, the primary role is conventionally assigned to thionic bacteria, which (1) are not limited in growth because of the absence of organic substrates and obtain carbon from the air and/or carbonates of concrete, (2) obtain energy from oxidation of sulfur compounds in the environment, and (3) produce sulfuric acid and can exist under acidic conditions. Biogenic sulfuric acid corrodes concrete compounds, which leads to either pitting or formation of gypsum salts, followed by distress in concrete due to the changes in volumetric proportions.

The modern notions of the essential role of thionic bacteria in concrete corrosion were developed by microbiologists after Parker's long series of studies of this group of bacteria and concrete corrosion [2–5]. Among other things, Parker isolated a previously unknown acid-forming bacterium from corroded concrete manifold pipes and described it as a novel species with the name of *Thiobacillus concretivorus* for its ability to destroy concrete (*vorus* meaning "devouring," "degrading").

Since approximately the 1980s, it has been commonly supposed that the key factor of biogenic sulfate corrosion is the development of thionic bacteria and the sulfate attack they cause. Subsequent studies confirmed this mechanism of concrete corrosion as the main one and the role of thionic bacteria as an important factor of concrete corrosion [6].

The methods and tools for the abatement of microbiological corrosion of materials include both additional protective coatings that are more resistant than the protected material and the introduction of biocides into the material that inhibit the development of corrosion-active microorganisms. Usually, these toxic substances are added to materials as poorly soluble or insoluble compounds so as to reduce, wherever possible, the loss of biocides from the material and their release into the environment. For example, the Kartocid compound for the protection of building materials (including concrete) is a complex compound on the basis of chlorinated copper and caprolactam [7]. Synthetic polymeric microcapsules have been proposed for water-soluble biocides on the basis of 4,5-diclorine-2-*n*-octyl-3(2H)-isothiazolone [8].

Microbiological studies of leaching and corrosion caused by thionic bacteria have been carried out [9–12]. We have determined nickel concentrations inhibiting the development of leaching thionic bacteria [13]. Here, we report on the results of studying the thionic bacteria-induced corrosion of concrete samples containing insoluble nickel sulfide.

MATERIALS AND METHODS

Materials. Tests were carried out with concrete samples produced according to *GOST* (State Standard) 27677-88 [14] without a large fraction of the filler (*GOST* paragraph 3.1). The materials used for concrete production were the universal dry mix M-150

Table 1. Zinc concentration in the solution surrounding the concrete sample in 1 month of exposure

Description of test variant	Zinc, mg/L		Zinc, % of the maximum
	parallel samples	the average of two samples	
	Without the additive		
Water	0.0	0.0	0.0
	0.0		
Medium DSM 71	1.3	1.2	54.5
	1.1		
Medium DSM 71 + bacterial culture	2.3	2.2	100.0
	2.1		
	With 0.10% insoluble nickel sulfide		
Water	0.0	0.0	0.0
	0.0		
Medium DSM 71	1.3	1.05	47.7
	0.8		
Medium DSM 71 + bacterial culture	1.2	1.3	59.1
	1.4		

(1 kg per 200 mL of water) composed of: M-400 DO cement (*GOST* (State Standard) 10178-85), sand (*GOST* (State Standard) 2138-91), and lime (TU-480/1-22-77). The sizes and hardening conditions of concrete sample also corresponded to *GOST* (State Standard) 27677-88.

Nickel sulfide additive. Nickel salts were chosen as an additive to concrete for its possible protection from corrosion by thionic bacteria. The application of nickel as a protective additive was based on our previous studies of nickel toxicity for corrosion-active thionic bacteria [13]. Nickel compounds are not highly toxic for the environment. Their addition as insoluble nickel sulfide served two purposes: prevention of leaching from concrete and a direct effect on the cells of thionic bacteria oxidizing this sulfide as a substrate.

Nickel sulfide was added into dry concrete mix immediately before making the samples at a final concentration of 0.10% by weight of dry mixture. The samples without nickel sulfide or with a reference additive (up to 0.01%) were used as a control.

Thionic bacterium culture. The culture of *Acidithiobacillus albertensis* DSM 14366^T, the type strain of the species, was used as corrosion-active thionic bacteria. The culture actively grows at 25–30°C, can reduce pH value due to sulfuric acid production from oxidized sulfur compounds, and actively grows at acidic pH values up to 2.0. The cultures were grown in DSM 71 medium with thiosulfate at the initial pH value of 4.0. The same medium was used as a corrosive environment in the experiments on concrete corrosion.

Experiments. The tested concrete samples were placed into a sterile aggressive liquid medium favorable for the tested bacterial strain (DSM 71 medium, pH 4.0) and into the control nonaggressive medium (water, pH 7.2), as well as into the aggressive DSM 71 medium inoculated with the thionic bacterium culture. The bacteria had been previously grown on an agarized DSM 71 medium, transferred into a liquid medium, and resuspended immediately before the experiments. The access of liquid medium to sample surface was provided. The tests were carried out at 28°C for 1 month. The relative brevity of the tests was compensated for by the high initial concentration of the bacteria: no less than 10^3–10^4 cells/mL.

Corrosion analysis. The corrosion of concrete samples was assessed by the changes in dry sample weight. The concentration of leached zinc in the solution as determined by ion chromatography (844 UV/VIS Compact IC, 6.1010.300 Metrosep column) was also a convenient indicator. Zinc leaching from the mineral material, in particular, by thionic bacteria, has been known for a long time [15]; later, it was been shown that zinc is one of the metals that can be used for leaching assessment by their release from the mineral material [16].

RESULTS AND DISCUSSION

Concrete leaching assessed by zinc release into the solution. Table 1 shows the content of zinc in the solution surrounding the samples in 1 month of exposure. It follows from the table that there was no zinc dissolution from concrete into water; i.e., concrete leaching in water does not occur within a month. The maximum leaching occurred in the corrosive environment in the presence of acid-forming thionic bacteria; the leaching value of 2.2 mg Zn/L per month was taken for comparison as 100%. In the same aggressive acidic

Table 2. Changes in the weight of concrete samples (variations of the values for repeated weighing were no more than 0.003 g) in 1 month of exposure

Description of test variant	Concrete sample mass			
	Initial, g	Final, g	Mass change	
			g	% of the initial value
Medium; DSM 71 + bacterial culture + 0.10% nickel sulfide	17.278	17.261	−0.017	−0.1
Medium DSM 71 + bacterial culture + steel	17.647	17.800	+0.153	+0.9
Medium DSM 71 + bacterial culture	16.182	16.409	+0.327	+2.0

medium without the bacteria, zinc leaching was half as great (48–54%). The leaching of zinc from concrete with the nickel sulfide additive was 59%, i.e., little more than the leaching by aggressive medium per se and much less than in the absence of the additive.

The change in concrete sample weight during leaching. Our studies have confirmed the well-known data that the growth of thionic bacteria in a liquid medium is accompanied by the production of sulfuric acid, which reacts with the carbonate components of concrete by substituting sulfates (slightly soluble gypsum) for calcium carbonates. A visually observable gypsum layer (pattern) is gradually formed during the long-term exposure to thionic bacteria (Fig. 1).

Gypsum was not observed during 1-month incubation, but mass measurements showed an increase in sample weight by up to 2% in an aggressive medium in the presence of thionic bacteria, while no mass increase due to gypsum formation was observed in the presence of thionic bacteria with the addition of 0.10% nickel (Table 2). When steel wire was added to a sample of concrete during its production, the increase in its mass in the aggressive medium in the presence of thionic bacteria became smaller but was not eliminated (Table 2).

It may be thought that, in the aggressive medium, there was polarization of steel wire with the formation of a cathodic electrode, which partially slowed down the activity of thionic bacteria. In this case, wire oxidation/rusting occurred, but the corrosion of concrete decreased, which is consistent with the principles of cathodic protection.

Our laboratory experiments have shown that the active culture of thionic bacteria in a favorable

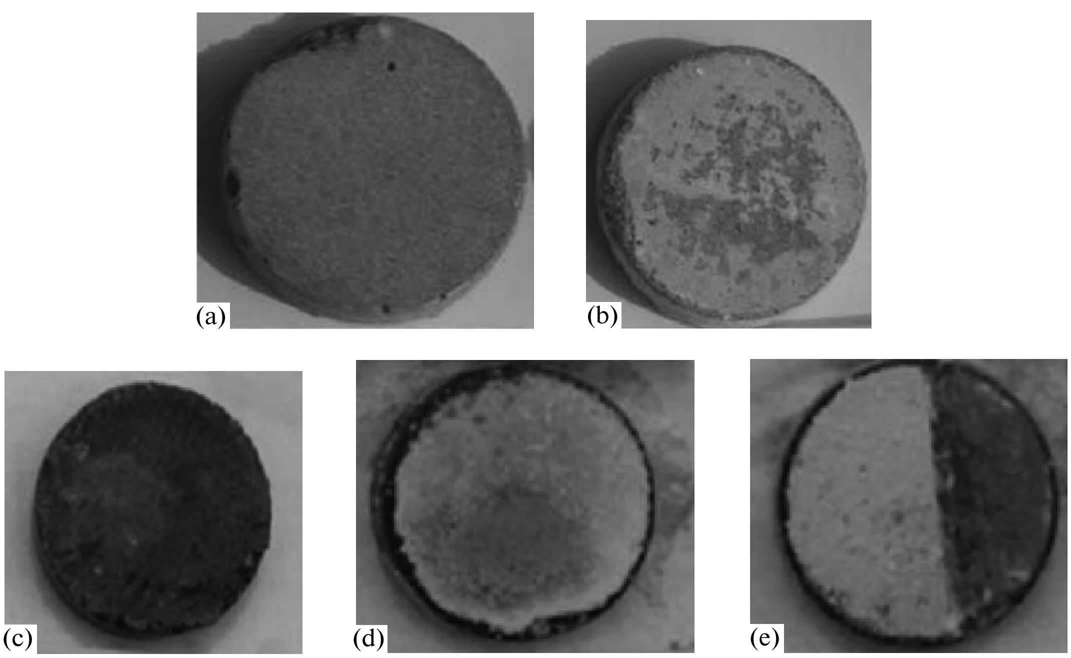

Fig. 1. Changes in concrete sample mass during exposure to thionic bacteria: (a) the control, 3 months; (b) with the bacteria, 3 months; (c) the control, 6 months; (d), with the bacteria, 6 months (a gypsum layer on the surface); and (e) with the bacteria, 6 months (the gypsum layer is partially removed mechanically to show the underlying concrete).

medium makes it possible to detect changes in model concrete samples as early as after 1 month. It has been confirmed that thionic bacteria forming sulfuric acid (the type strain of the species *A. albertensis*) are able to leach concrete (the release of zinc into the solution) and to form gypsum (formation of a gypsum film and increase in the sample mess). The novelty of our results is the revealed decrease in zinc leaching and increase in the specimen weight due to gypsum formation if the sample infected with the bacteria contained nickel sulfide.

Thus, it may be supposed that nickel additives, including nickel sulfide, can reduce the corrosion of concrete induced by thionic bacteria.

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