Simulation of accelerated concrete destruction by inoculation of an association of bacteria of the genus *Thiobacillus*

E V Fomina$^1$, S V Sverguzova$^1$, E N Goncharova$^1$ and I Flores-Vivián$^2$

$^1$Belgorod State Technological University named after V.G. Shoukhov, 46, Kostukova Str., Belgorod, 308012, Russia
$^2$The Autonomous University of Nuevo León, Pedro de Alba s/n, San Nicolás de Los Garza, Nuevo León, Mexico

E-mail: fomina.katerina@mail.ru

Abstract. The mechanisms of biogenic destruction of concrete under the influence of microbiological corrosion are described. An accelerated method of inoculation of the association of sulfur-oxidizing thionic bacteria *Thiobacillus thioparus* and *Thiobacillus thiooxidans* was used. Beyerink solution was used as a nutrient medium. The impact of two types of microorganisms in model systems imitates microbiocorrosion conditions; this allows reducing the test time and predicting the mechanisms of concrete destruction during operation. The active development of *Thiobacillus thioparus* promotes the leaching of concrete, further bacteria of the genus *Thiobacillus thiooxidans* appear with a decrease in pH, and both species actively synthesize sulfuric acid. The kinetics of the bio corrosion process was monitored for 60 days. The bacterial adaptation period is 16–18 days, after which the pH of the aqueous medium decreases. The rate of formation of a biological acid in an aqueous medium determines the leaching of Mg$^{2+}$, Ca$^{2+}$, and SO$_4^{2-}$ ions from concrete. Concrete when exposed to bio acids for two months loses 30% of its strength. The microstructure analysis of bio corrosion products on the concrete surface was carried out with the help of a scanning electron microscope.

1. Introduction

Building materials are exposed to the environment effect during operation that causes their destruction. Corrosion of building materials, among of which a person spends up to 80% of his life is one of the main problems in the context of globalization of technological development. Among the most aggressive factors causing the degradation of materials the impact of microorganisms, amplifying with simultaneous fluctuations in temperature and humidity is included [1, 2].

Porosity and microzonal colonization of concrete surface by bacteria leads to a change in pH and destruction of the surface layer, calcium carbonate in particular. Destructive microbes are extremely diverse. The most important ones, according to many researchers are nitrifying and sulfur-oxidizing bacteria, as well as microscopic fungi [3], the growth rate of which, the specific composition of metabolites, the concentration of aggressive substances, and the duration of exposure determine the intensity and degree of damage to objects. Aerobic thionic bacteria are considered [4] especially aggressive, exothermically oxidizing the reduced forms of sulfur with the access of free oxygen:

$$\text{(HS, H}_2\text{S)} \xrightarrow{2S^0} \text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{(S}_2\text{O}_3^2-, S^0) \xrightarrow{2\text{H}_2\text{O}} \text{H}_2\text{SO}_4$$  \hspace{1cm} (2)
The action of these bacteria can significantly reduce the service life of concrete structures, for example, from the expected 100 years to 30-50 years [5]. Among the standards for testing materials for microbiological stability, there are no regulatory documents for such tests of building materials [6]. Meanwhile, lightweight concretes and concretes using technogenic raw materials and secondary raw materials are exposed to microbiological corrosion [7–11]. Under natural operating conditions, these processes have a long period, and long-term testing is not suitable for standards. In this regard, rapid methods of microbiological corrosion of concrete are needed.

The purpose of this work is to study the kinetics of the bio corrosion process, since with a wide variety of publications. There is no single view on its mechanism in the literature. The effects of microbiological destruction of concrete were studied by the inoculation method of the association of thionic bacteria *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans*. *Thiobacillus thioparus* bacteria predominate in the environment and on the surface of building materials [12]. *Thiobacillus thiooxidans* predominate in the destroyed facilities and sewage disposal facilities, i.e. bacterial species that prefer lower pH values (Table 1).

### Table 1. Physiological characteristics of the bacteria [5].

| Type of bacteria               | pH for development | Sulfate substrate | Metabolism products                  |
|-------------------------------|--------------------|-------------------|--------------------------------------|
| *Thiobacillus thioparus*      | 6-10               | H₂S, S⁰, S₂O₅⁻³⁻  | Polythionic acids, S⁰                 |
| *Acidithiobacillus thiooxidans* | < 3               | H₂S, S⁰          | S⁰, S₂O₅⁻³⁻                         |

After lowering the pH to 10, *Th. thioparus* sulphate bacteria can colonize and react with concrete surfaces, lowering the pH. Then, as the pH decreases, the bacteria *Ac. Thiooxidans* are included. It should be noted that *Ac. thiooxidans* remains viable at a pH close to 1.0–1.5, which corresponds to a 1.0 N solution of sulfuric acid. The pH limits of the development of various types of bacteria are not fully established and are the subject of research.

2. **Materials and methods**

For the preparation of samples, Portland cement CEMI 42.5N manufactured by PLC Belgorodsky Cement and standard monofractional quartz sand of the Volsky deposit were used. The ratio of quartz sand to cement was taken 3:1 in accordance with Russian Standard GOST 30744-2001.

To study concrete, beam samples 4 × 4 × 16 cm in size were formed. The samples were placed in closed desiccators. Beyerink solution was used as a nutrient medium (Table 2).

### Table 2. The composition of the Beyerink solution, g / l.

|          | Na₂S₂O₃·5H₂O | NH₄Cl | NaHCO₃ | Na₂HPO₄·12H₂O | MgCl₂·6H₂O | FeSO₄·7H₂O | pH  |
|----------|--------------|-------|--------|---------------|------------|------------|-----|
| Amount   | 5            | 0.1   | 1      | 0.2           | 0.1        | traces     | 8   |

In order to intensify microbiological corrosion of the samples, the associations of *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans* cultures were introduced into the desiccator; the number of bacteria per unit volume was 10⁶ cl/ml. As control compositions were samples that did not contain bacteria. In a blank experiment, the behavior of bacteria in the absence of concrete samples was evaluated.

Incubation was carried out in a thermostat at a temperature of 30 °C. The content of calcium, magnesium, sulfates in solution and samples was determined according to Russian Standard GOST 5382-91. pH was measured using a pH-150M ionomer. The microstructure of concrete was studied using a high-resolution scanning electron microscope TESCANMIRA 3 LMU.
3. Results and discussion

Evaluation of the leaching rate of mineral constituent and hydrated phases of concrete is important to establish timeframe when the strength loss occurs during exploitation. Number of microorganisms can live on surface of without revealing any vital activity, but capable of rapid growth and destroying building materials under appropriate conditions. Therefore, the understanding of vital activity of the microorganisms is crucial to address durability issues of building materials.

In Figure 1, thionic bacteria in a blank experiment cause acidification of the medium, starting after 8–10 days and reaching pH = 2–3 after 20 days of the experiment. A stable pH value of 8–9 for concrete was observed in the control experiment. In the presence of microorganisms, after a period of their adaptation (16–18 days), the pH of the medium drops sharply and on the 24th day, pH = 3.

![Figure 1. Measurement of pH in an aqueous medium containing: 1 - thionic bacteria without samples (blank experiment); 2 - concrete with bacteria; 3 - sample of concrete without bacteria.](image)

The influence of an alkaline environment formed in the presence of concrete promotes the active development of *Thiobacillus thioparus*, further bacteria of the genus *Acidithiobacillus thiooxidans* appear with acidification of the medium, and both species actively synthesize sulfuric acid. Sulfuric acid of bacterial origin interacts with the components of concrete - unreacted oxide of calcium, magnesium, aluminum with the formation of medium and acid sulfates; calcium carbonate, sulfate, and orthosilicate to form hydrocarbonates, hydrosulfates, and hydroorthosilicates.

These reactions cause alkalization and there are jumps in increasing the pH to 8.4. In the future, the general direction of the process remains, although some emissions on the kinetic curve and the appearance of sulfur flakes in the solution on the 30th day and their subsequent disappearance on the 48th day are associated with the oxidation of thiosulfate ions $S_2O_3^{2-}$ and the subsequent process of the formation of sulfuric acid by the reaction Eq. (3) [13]:

$$S + H_2O + 3/2O_2 \rightarrow H_2SO_4$$

Leaching of calcium and magnesium ions from the samples in the absence of bacteria does not occur (Fig. 2).

![Figure 2. Leaching of ions in an aqueous medium with concrete.](image)
However, in the presence of microorganisms with the completion of their adaptation (18 days), the release of $\text{Mg}^{2+}$ ions into the solution begins, reaching up to 14 meq/l to 60-th day (Fig. 3).

![Figure 3. The content of magnesium ions $\text{Mg}^{2+}$ in an aqueous medium containing thionic bacteria and concrete.](image)

In the future, hydrolysis probably occurs with the formation of magnesium salts in the aquatic environment. These reactions in concrete in the presence of alkalis are undesirable, since they lead to deformation of concrete [14].

Leaching of calcium salts as a result of bacterial activity is significantly less pronounced. The concentration of $\text{Ca}^{2+}$ ions up to 13 meq/l is noted to 60-th day.

![Figure 4. The content of calcium ions in an aqueous medium containing thionic bacteria and concrete.](image)

The increment in the concentration of sulfate ions in the initial solution in the presence of bacteria and concrete from the very beginning of the experiment was caused by the period of bacterial adaptation. With the further formation of calcium, magnesium, and aluminum sulfates and hydrosulfates, the sulfate ions consumed for these reactions from the surrounding solution decrease, which is noted in the figure when the concentration decreases from 3.3 to 2.4 meq/l (Fig. 5).

![Figure 5. The content of sulfate ions in an aqueous medium containing thionic bacteria and concrete.](image)
In a further experiment, starting from 18-th day, there is a dynamics of an increase in sulfate concentration, which is associated with the development of bacteria and the synthesis of sulfuric acid. After 60 days of conducting the experiment, a visual analysis of the surface layers of concrete showed a white coating up to 1 mm thick after exposure to bio corrosion. Ingrown crystals and white salt deposits were visible on the surface (Fig. 6 a).

![Figure 6. Concrete samples: a – white coating - bio corrosion products; b – SEM analysis of concrete surface after bio corrosion.](image)

SEM analysis made it possible to establish the morphology of crystals on the surface of the sample with a predominance of tabular, columnar, prismatic neoplasms characteristic of sulfates (Fig. 6 b). The bacteria’s production of sulfuric acid leads to the dissolution of the cement matrix and the formation of sulfate compounds in the form of gypsum and ettringite. The growth of these crystals causes cracking in concrete and its destruction. In addition, one can observe crystals of calcium carbonate, which have a pronounced lamellar morphology.

Corrosion resistance was evaluated by the coefficient of resistance, which is the ratio of the strength of the test sample to the control one, which was not influenced by bacteria during the experiment. The corrosion resistance after two months of the experiment was decreased as indicated by 30 % strength reduction.

4. Summary
The simultaneous effect of two types of microorganisms in model systems simulating microbiocorrosion conditions allows reducing the test time and evaluating the expected course of destruction and leaching of the main components of concrete. Effect of the bacterial acid *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans* increases the solubility of the concrete surface, making it vulnerable to mass transfer and structural degradation. The data obtained can be used to model the processes of corrosion of concrete caused by the action of sulfuric acid of biological origin.

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