Abstract. The article describes technological processes of concrete self-restoration with the help of basic bio-additives: calcium concentration, concentration of soluble inorganic carbon, pH value, presence of crystallization center. In transportation construction, there are many building structures in harsh operating conditions that require strengthening or restoration of their physical and mechanical properties for stability, reliability and safety. A number of bacteria, which can be found in soil, sand and natural minerals, have the ability to release calcium carbonate, both in natural and laboratory conditions, are capable of restoring these properties. The laboratory method of self-remediation of concrete used in the construction of transportation structures is considered. Calcium lactate (CaC6H10O6) was used as a starting substance for calcium carbonate formation. In addition, urea required by the bacteria as a source of urease enzyme and yeast extract as a source of carbon and nitrogen were added. This study showed that this simplified representation of the processes occurring during carbonate deposition induced by biomicrobes has a positive effect on the physical and mechanical properties affecting the safety, reliability and sustainability of transportation infrastructure building structures.

Keywords. Concrete structures; bacteria; S. Pasteurii, Bacillus pasteuri, concentration; cracks in concrete.

Introduction.

To improve the technology of biological concrete production, specially selected bacteria of the genus Bacillus with a combination of nutrients were used to create a self-repairing agent in concrete. By using such self-repairing concrete through bacteria, cracks wider than 100 µm can be sealed. In this approach, bacteria in an alkaline environment convert CO2 into carbonate ions, which then interact with Ca ions from the concrete matrix. This leads to the formation of calcium carbonate crystals. In addition, CO2 directly reacts with the calcium hydroxide of the matrix, resulting in the formation of calcite precipitate. The emergence of large-sized calcium carbonate crystals with the participation of bacteria incorporated into self-healing concrete provides superior self-healing ability compared to traditional or engineered environmentally unsafe self-healing cement materials. For this reason, this area of research appears to be a promising alternative to environmentally unsafe cement-based repair methods.

At present, the formation of concrete structure with the required level of fracture resistance is described considering the use of known laws of physicochemistry, mechanics of material formation [1-3]. Improved crack resistance is possible by moving towards the production of concrete with pseudoplastic type of fracture [4, 5].

Currently, biological methods have been proposed to improve the reliability of concrete and reinforced concrete structures [6, 7].
Materials and Methods.

Calcium carbonate precipitation is a chemical process which is mainly governed by four main factors:
1) Calcium ion concentration.
2) Dissolved inorganic carbon (DIC) concentration.
3) The pH value of the medium.
4) The presence of crystallization centers.

Sufficient calcium ions and carbonate ions are required for precipitation so that the ionic activity coefficient of the reaction product (IAP) exceeds the solubility constant (KSO) (formulae (1) and (2)). The state of the degree of saturation (Ω) of the system can be determined by comparing the values of IAP and KSO. If Ω > 1, the system is supersaturated and the formation of precipitate is likely to be maximized:

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3,
\]
\[
\Omega = a (\text{Ca}^{2+}) (\text{CO}_3^{2-})/K_{SO}
\]

The KSO of calcite at 25°C = 4.8 × 10⁻⁹.

The concentration of carbonate ions is related to the concentration of DIC and the pH value in a given aqueous system. In addition, the DIC concentration depends on several environmental parameters, namely temperature and partial pressure of carbon dioxide (for systems open to atmospheric influences).

The equilibrium reactions and constants governing the dissolution process in aqueous media (25 °C and 1 atm) are given in Equations (3)-(6)

\[
\text{CO}_2 (r) \leftrightarrow \text{CO}_2 \text{ (aqueous.) } (pK_H = 1,468),
\]
\[
\text{CO}_2 \text{ (aqueous.) } + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^* (pK = 2,84),
\]
\[
\text{H}_2\text{CO}_3^* \leftrightarrow \text{H}^+ + \text{HCO}_3^- (pK_1 = 6,352),
\]
\[
\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ (pK = 10,329).
\]

At \(\text{H}_2\text{CO}_3^* = \text{CO}_2\text{ (aqueous)} + \text{H}_2\text{CO}_3^*\) microorganisms can influence the precipitation process by altering almost any of the precipitation parameters described above, either alone or in various combinations with each other.

Various reactions appear to occur during calcium carbonate precipitation.

The first scheme involves the Sulphur cycle, in particular sulphate reduction, which is carried out as described in Current Issues in Biomineralization by Sulphate-reducing Bacteria under Anaerobic Conditions.

The second scheme involves the nitrogen cycle, viz:
1) Oxidative deamination of amino acids in aerobiosis.
2) Nitrate reduction under conditions of anaerobiosis or microaerophilia.
3) Decomposition of urea or uric acid under aerobic conditions (by urealytic bacteria).

Another microbial process that leads to an increase in both pH and dissolved inorganic carbon concentration is the utilization of organic acids. This process is widely used in microbial carbonate precipitation experiments. The sedimentation mechanisms described above are commonly found in nature and explain the carbonate precipitation by microbial action (MCP), confirming the validity of the statement by E. Boquete et al. [8] that under suitable conditions, most bacteria are able to induce carbonate precipitation. Due to its simplicity, the most commonly studied MICP system is the hydrolysis of urea by the enzyme urease in calcium-rich medium.
Urease catalysis the hydrolysis of urea to CO2 and ammonia, which leads to an increase in pH and carbonate concentration in the bacterial environment. During microbial urease activity, 1 mol of urea is hydrolyzed intracellularly to 1 mol of ammonia and 1 mol of carbonate, which spontaneously hydrolyses to form an additional 1 mol of ammonia and carbonic acid as follows (with bacteria):

\[
\begin{align*}
2\text{CO (NH}_2\text{)}_2 + \text{H}_2\text{O} & \rightarrow \text{NH}_2\text{COOH} + \text{NH}_3, \\
2\text{NH}_2\text{COOH} + \text{H}_2\text{O} & \rightarrow \text{NH}_3 + \text{H}_2\text{CO}_3.
\end{align*}
\]

In water, these products come to equilibrium, forming bicarbonate, 1 mol ammonium and hydroxide ions, which account for the increase in pH:

\[
\begin{align*}
2\text{H}_2\text{CO}_3 & \rightarrow 2\text{H}^+ + 2\text{CO}_3^{2-}, \\
2\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH}^-, \\
2\text{Ca}^{2+}\text{CO}_3^{2-} & \rightarrow \text{CaCO}_3 \quad (K_{SP} = 3.8 \times 10^{-9}).
\end{align*}
\]

\(K_{SP}\) - is the solubility of the reaction products in equation (11). F. Hammes and W. Verstraete [6] investigated a series of phenomena occurring during urea lytic accumulation of calcium salts, emphasizing the importance of pH value and calcium metabolism in this process (Figure 1).

![Figure 1 - Calcite precipitation by a bacterial cell [6]](image)

The main role of bacteria was attributed to the ability of bacteria to create an alkaline environment as a result of their different physiological activities.

**Results.**

Bacterial surfaces play an important role in calcium deposition. Due to the presence of several negatively charged groups at neutral pH values, positively charged metal ions can attach to the bacterial surface, promoting a heterogeneous nucleation process [9-14]. Generally, carbonate precipitation develops on the outer surface of bacterial cells with subsequent detachment, so bacteria can be embedded in the growing carbonate crystals.

Figure 2 shows a simplified representation of the processes involved in microbe-induced carbonate precipitation.

In solution, calcium ions are attracted to bacterial cell walls due to their negative charge. When urea is added to bacteria, dissolved inorganic carbon (DIC) and ammonium (AMM) are produced in the bacterial microenvironment (A). In the presence of calcium ions, this can lead to
localised supersaturation and hence heterogeneous deposition of calcium carbonate on the bacterial cell wall (B). After some time, the whole cell is encapsulated (C).

Figure 2 - Application of bacteria in construction (developed by the author)

Restriction of nutrient supply leads to cell death. Image (D) shows imprints of bacterial cells involved in the formation of carbonate precipitate. The possible biochemical reactions in urea-CaCl2 medium, where CaCO3 deposition on the cell surface occurs, can be summarized as follows:

\[ 2 \text{Ca}^{2+} + \text{cell} \text{Ca}^{2+}, \]
\[ \text{cell} \text{Ca}^{2+} + \text{CO}_3^{2-} \text{cell} \text{CaCO}_3. \]

Discussion.

As noted above, the products of metabolism of microorganisms carrying out biological corrosion of mineral building materials is a spectrum of organic carboxylic acids, creating on the surface of samples of materials highly reactive environment with low pH values. And the maximum concentration of acids will be observed at higher temperature of the medium. Thus, in fact, not how many microorganisms themselves, but how many products of their metabolism show biocorrosive activity towards mineral building materials. Consequently, it is possible to artificially create conditions that are as close as possible to real conditions and modelling the process of biological corrosion of mineral building materials without the use of microorganisms.

The process of interaction of organic acids with samples of mineral building materials is quite complex and multistage. The first stage of biocorrosion starts with carboxylic acids forming a thin film around the material sample, with a medium temperature of 25°C and pH = 3. In the second stage of biocorrosion there is an interaction of carboxylic acids (more precisely their hydroxyl groups) with magnesium ions Mg2+ calcium Ca2+ located on the surface of the sample. Then the reaction of complex formation starts and the products of interaction are washed out into the environment surrounding the sample. All this leads to the appearance of initial microcracks on the surface of samples. At the third stage of biocorrosion, the diffusion process prevails, associated with the transfer of carboxylic acids inside the sample through microcracks. The main role in the diffusion process is first played by sterically uncomplicated carboxylic acids, e.g. mono-basic
formic and acetic acids. After that, sterically more voluminous biphasic (oxalic, succinic, fumaric) and further tricarboxylic (citric) acids are connected to the chemical interaction with magnesium and calcium ions. Further, the process of bio-damage can be considered as initiated and has no tendency to fade out. It is known that when the temperature of the model medium increases to 30, 35, 40 °C, the rate of the biocorrosion process according to the Want-Goff rule [15] increases by times and the process of biocorrosion increases dramatically.

The presented approach to modelling of the process of biodamage of mineral materials is impossible without a special hardware design. The described conditions in a general form can be realized, for example, in the form of a special device representing a test vessel made of material resistant to working media or mixtures of acids, at a certain level of which test samples of materials immersed in a model aggressive medium are installed, provided that the upper edge of the medium should be higher than the upper edge of the samples. The apparatus for kinetic studies of the processes of bio-damage of construction materials in model media in laboratory conditions should include three main containers: test, make-up and drain, as well as blocks for regulating the temperature and pH of the medium. Automatic registration of pH of the modelling medium and its temperature, with its maintenance at a constant level and recording on a memory card should be provided. It is assumed that the device for testing samples of construction materials for biostability in model media for a long period of time multiple of 28 days will operate round the clock. The temperature of the modelling medium can be automatically set in the range from 25 to 45 °C with an accuracy of at least 0.01 °C.

The investigated mineral building materials are cement-sand mortar (CSM) modelling fine-grained concrete [16]. The investigated samples of building materials are made in the form of beams of size 160×40×40 mm [17] based on grey cement PC-400-DO [18], quartz sand [19] of 0.5-0.25 mm fraction, water - bidistillate, with water-cement ratio - 0.53. The model media represent both aqueous solutions of single-, bi- and tri-basic organic carboxylic acids (acetic, oxalic, malic, succinic, fumaric, citric, etc.) with different concentrations and possible combinations of them. To study the mechanism of interaction of solutions of one-, two- and three-basic carboxylic acids and their mixtures with CPR samples, pH-metric studies of the media for 24 hours were carried out. It was found that the kinetic dependence of pH ~ τ has a jump-like character for oxalic acid and its mixture with citric acid, and in all other cases - the dependence has a monotonic character (Figure 3) [20].

![Figure 3 – Nature of the kinetic dependence for oxalic acid](image)

To interpret the nature of the obtained kinetic dependences of pH ~ τ, IR spectral studies of solutions of carboxylic acids and their mixtures were carried out.

As a result of these studies it was found that all carboxylic acids. Both in the crystal and in aqueous solutions are in the form of dimers linked by intermolecular hydrogen bonding (2117-2133 cm⁻¹). Based on the literature data [21-23] and the results of the IR spectral study, it can be assumed that mono-basic acetic acid in aqueous solution in the form of cyclic dimers has only two rather weakly dissociated hydroxyl groups and therefore can interact with only one magnesium or
calcium ion: It should also be noted that in acetic acid there is a possible shielding effect of two sterically bulky methyl groups preventing the interaction of the hydroxyl groups of the dimer with magnesium or calcium ions. This apparently explains the monotonic nature of the kinetic $pH \sim \tau$ dependence of the interaction of acetic acid with CPR.

The tricitric acid in aqueous solution appears to be in the form of a chain-like dimer structure (ribbon-like). Of its six hydroxyl groups, only two are dissociated (as in acetic acid). The interaction of citric acid with magnesium or calcium ions leached from the CPR seems to encounter, apparently, a number of difficulties, among which should be noted steric difficulties arising from the interaction of magnesium or calcium ions with the bulk ribbon dimer structure, each fragment of which can react with only one magnesium or calcium ion (similar to acetic acid).

In the case of bidentate oxalic acid, the atoms forming the cyclic dimer lie practically in the same plane, and the hydrogen bonds are almost linear. In this connection, it can be assumed that both flat dimer cycles are located in space one above the other, i.e., a kind of rigid (due to the absence of bulk substituents at carbon atoms) “sandwich” structure is created (Figure 4), in which, apparently, only small displacements of dimer cycles horizontally are possible:

“Sandwich” structure of oxalic acid dimer, apparently, and explains its “anomalous” properties, compared to acetic and citric acids, which are manifested as a jump kinetic dependence of $pH \sim \tau$.

Using selected one-, two- and three-basic carboxylic acids, based on the level of reduction in the strength characteristics of the CPR, the quantitative ratio of acids in the model mixture was experimentally selected. For this purpose, the DPC samples were exposed for 28 days in mixtures of organic acids with different ratios, while maintaining the pH of the medium at $= 3$. The composition of the model medium used in the present study is presented in Table 1 [23].

<table>
<thead>
<tr>
<th>Medium component</th>
<th>Mass fraction of acids</th>
<th>Acid concentration %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>2</td>
<td>0.33</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>3</td>
<td>0.05</td>
</tr>
<tr>
<td>Citric acid</td>
<td>1</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Further, the bio-damage processes occurring during the interaction of the DPC samples with the model medium were studied IR spectrally [21-23]:

Figure 4 – Sandwich structure of oxalic acid dimer
As can be seen from the spectra shown in Fig. 2, after the interaction of the model medium with CPR samples, the intensity of reflections of characteristic bands decreases significantly, which, apparently, indicates the interaction of the CPR sample with the model medium.

Biostability of mineral building materials samples is determined by their chemical resistance coefficients (and), which characterise the change in compressive and flexural strength characteristics of CPR samples before and after exposure in the model medium, Table 2.

Table 2 - Variation of strength characteristics of CPR samples during exposure in the modelling medium

<table>
<thead>
<tr>
<th>Sample Series</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sj}$, MPa, after exposure in the medium</td>
<td>10,85</td>
<td>11,6</td>
<td>12,50</td>
</tr>
<tr>
<td>$R_{sj}$, MPa, after exposure in the medium</td>
<td>15,28</td>
<td>15,40</td>
<td>15,80</td>
</tr>
<tr>
<td>$R_{iz}$, MPa, after exposure in the medium</td>
<td>4,3</td>
<td>3,7</td>
<td>3,9</td>
</tr>
<tr>
<td>$K_{sj}$</td>
<td>0,71</td>
<td>0,75</td>
<td>0,79</td>
</tr>
<tr>
<td>$K_{iz}$</td>
<td>0,82</td>
<td>0,74</td>
<td>0,79</td>
</tr>
</tbody>
</table>

As a result of the conducted studies to assess the influence of the model environment on the strength characteristics of CPR samples (Table 2), it was found that the level of reduction of strength characteristics in three series of samples for 28 days differs relatively insignificantly, so on average, the value of the chemical resistance coefficient for compressive strength was 0.74, and for flexural strength - 0.77.

The presented approach will allow us to obtain an array of data on kinetic parameters of biological damage processes of mineral building materials based on Portland cement of different grades and to obtain a generalized picture of biocorrosion processes of building materials.

On the basis of complex analysis of kinetic dependences of pH ~ $\tau$, $K_{sj}$ ~ $\tau$, $K_{iz}$ ~ $\tau$ it will be possible to make fundamental conclusions, which will allow to develop theoretical bases of the processes of diffusive bio-damage of mineral materials, which will make it possible to create a kinetic model of the process of biological damage of building materials, allowing to describe with the necessary accuracy the process of biocorrosion of mineral building materials in different environments and temperatures.
Conclusion.

The conducted study showed that this is a simplified representation of the processes occurring during microbe-induced carbonate precipitation. However, the actual role of bacterial sludge remains a matter of debate. Some authors consider this sludge to be an undesirable and accidental by-product of metabolism, while others believe that it is a special process providing ecological advantages for the settling organisms.

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[7] Citation: Bilek, V.; Sucharda, O.; Bujdos, D. Frost Resistance of Alkali-Activated Concrete – An Important Pillar of Their Sustainability. Sustainability 2021, 13, 473. https://doi.org/10.3390/su13020473


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