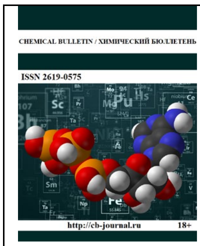

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Overview of developments in the field of biomineralization

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Abstract: *reactions and biological processes in biobetone represent the integration of biological and technological aspects, which opens up new prospects for research in the field of biomineral-ization of building materials. The object of the study is biobetone, in which various biological and molecular interactions of its constituent components occur. A detailed description of the methodology of the literature research was carried out and the current world research on the use of bioadditives in biobetone was systematized. A review was conducted of research in the field of biomineralization, biocementation and its pathways through which precipitation of calcium carbonate can occur. The hydrolysis of urea and the mechanism of self-healing of biobetone are considered. The problems of self-healing of biobetone have been identified and recommenda-tions for further research have been proposed.*

Keywords: *biomineralization, biocementation, urea, hydrolysis of calcium carbonate, bioce-ment, dietary supplements, microcapsulation, calcite precipitation*

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Introduction

Cement-based materials are among the most preferred building materials worldwide due to their accessibility and formability. Despite the many advantages, cement-based materials are prone to cracking due to several factors such as shrinkage, alkali–silica reaction and corrosion of reinforcement steel in the case of reinforced concrete. Cracks in concrete are often unavoidable and can lead to severe structural wear. Concrete structures are sensitive to a wide range of physical, chemical and biological factors, such as temperature fluctuations, aggressive gases, harsh environments and exposure to chemicals. These mentioned factors have a detrimental effect on the durability and structural integrity of concrete, reducing the effective service life of concrete structures, which entail additional repair costs.

Extending the strength and service life of concrete structures minimizes the need for expensive repairs during the service life. The most effective way to increase the service life would be self-healing of concrete. Common crack repair methods require external intervention, which makes it difficult to eliminate cracks in structures with limited accessibility. Thus, there is a need to develop new repair technologies that can "self-heal" without external interference.

The activity of microbes makes a significant contribution to the cementing properties. The natural mechanism behind self-healing is biomineralization.

Biomineralization shows promising results in the field of building materials in the form of a technology called microbiologically induced precipitation of calcium carbonate (MIOC) or biocementation (BC), which is a biomineralization process involving the formation of CO_2 (3 ions) using the basic metabolism of certain microorganisms. These carbonate ions are converted to calcium carbonate $CaCO_3$ in the presence of a calcium source. The technology has been successfully applied in construction and geotechnical fields. Biocementation has found application, including in construction, in the field of crack removal and hardening of cement materials. Biomineralization positions itself as one of the most sustainable construction technologies, since the microbes included in the matrix of the building mix provide long-term protection of building materials due to their self-healing mechanism.

In the period 2019-2024, 99 studies were published on the biocementation of cement-based materials; 18 of which are of a review nature, and 81 research-type articles. The factors influencing the effectiveness of bio-cementation have also been studied in many studies.

Despite numerous successful research works in the laboratory, research conducted in construction conditions remains limited due to the complexity of the hydration process and the high alkalinity of cement-based materials.

The purpose of the study is to study and develop methods for increasing the service life of concrete structures using biomineralization technology, including the use of microbiologically induced calcium carbonate precipitation (MIOC) or biocementation (BC). To achieve the purpose of the study, it is necessary to solve a number of the following tasks:

1. To present a detailed method of literature search and systematization of identified sources for a certain period.

2. Consider the process of biomineralization.

3. Consider the cementation process, including the ways of precipitation of calcium carbonate, hydrolysis of urea and the mechanism of self-healing of bi-obetone.

4. To consider the existing problems of biomineralization related to the effectiveness of species of microorganisms, with sources of calcium, with the use of urea and with the immobilization of bio-cementing agents.

Methods of literature search

This section is aimed at a detailed description of the methodology of the review. At the beginning, the goals and objectives of the study are formulated. The search for scientific literature is carried out using the Scopus database to collect a wide range of relevant works. A combination of relevant keywords "urea AND concrete" and phrases related to the research topic is used. The selected keywords have been selected to ensure the fullest possible coverage of the relevant literature. The time interval corresponded to the period of the last 5 years (from 2019 to 2024, Figure 1a). The keywords are "urease", "calcium carbonate", "concrete", "biomineralization", "self-healing materials", "self-healing concrete", "concrete construction", "urea" and "concretes". Taking into account these keywords and filters, 81 research-type articles and 18 review articles were found over the selected time interval (Fig. 1b).

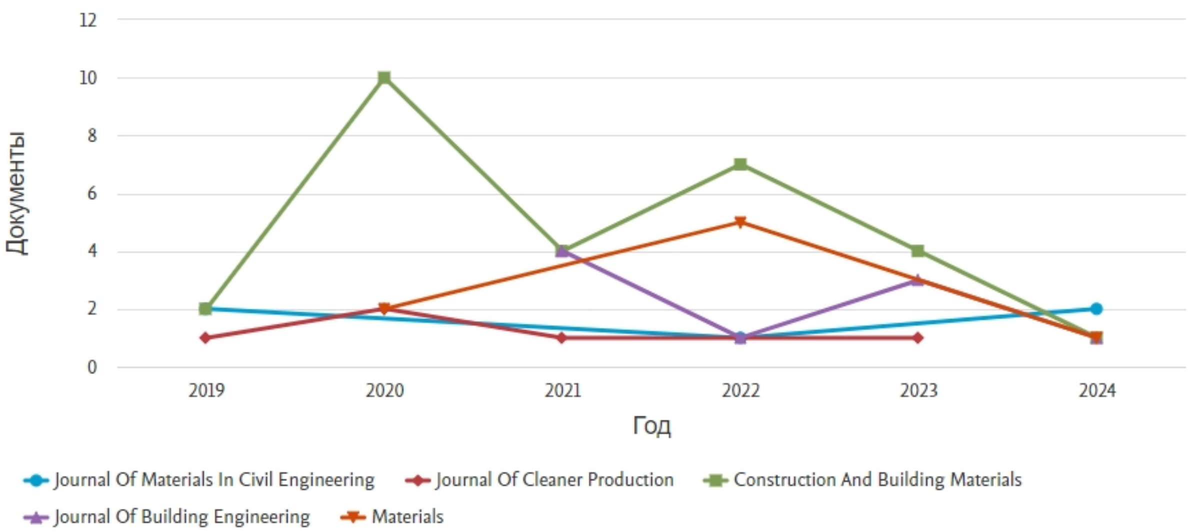

Fig. 1a. Analysis of sources by year.

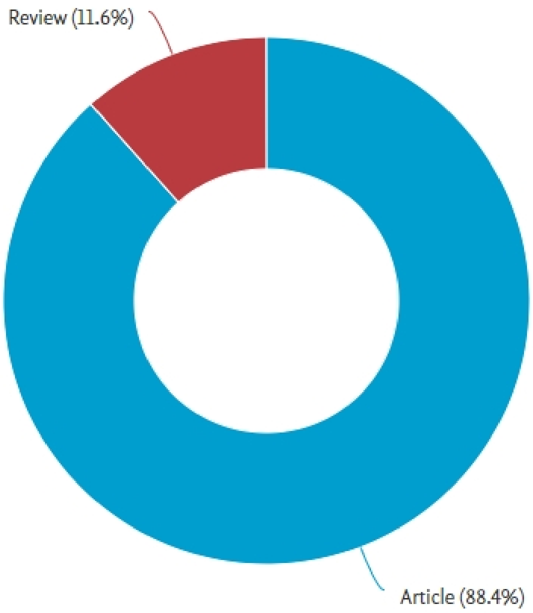

Fig. 1b. Analysis of sources by document type.

Then the results of the search and filtering of literary sources are analyzed using the VOSviewer software, which allows you to create a visual representation of the coincidence of keywords, authors and publications in the dataset (Fig. 2a and 2b).

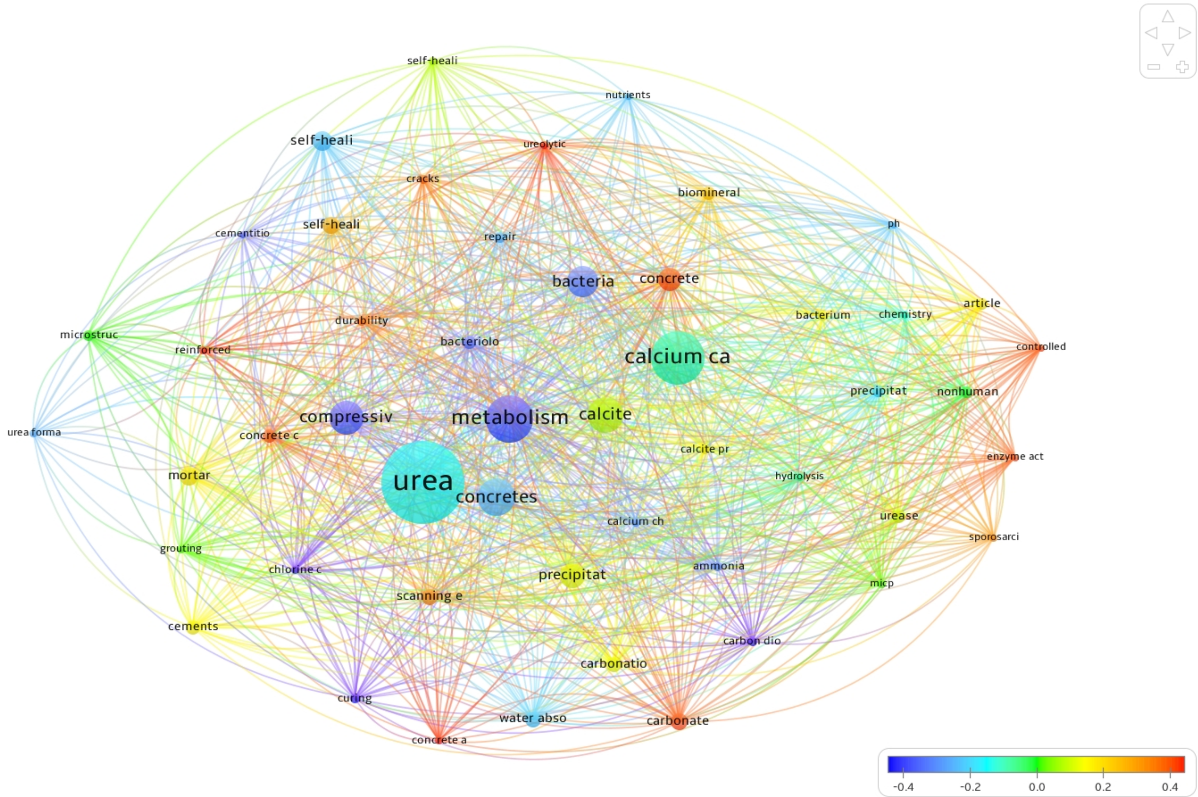

Fig. 2a. Analysis of search results data using VOSviewer software.

Data analysis in the VOSviever software provided information about the most important research topics, patterns and relationships between different concepts.

The results of the analysis were systematized to create a three-dimensional picture of the literary landscape associated with the research topic. The combined results allowed us to identify key research trends, influential authors, and significant groups of related publications. The interpreted results of the data analysis were discussed in the context of the research objectives and the existing literature. The results were critically analyzed to draw meaningful conclusions and identify potential areas for future research.

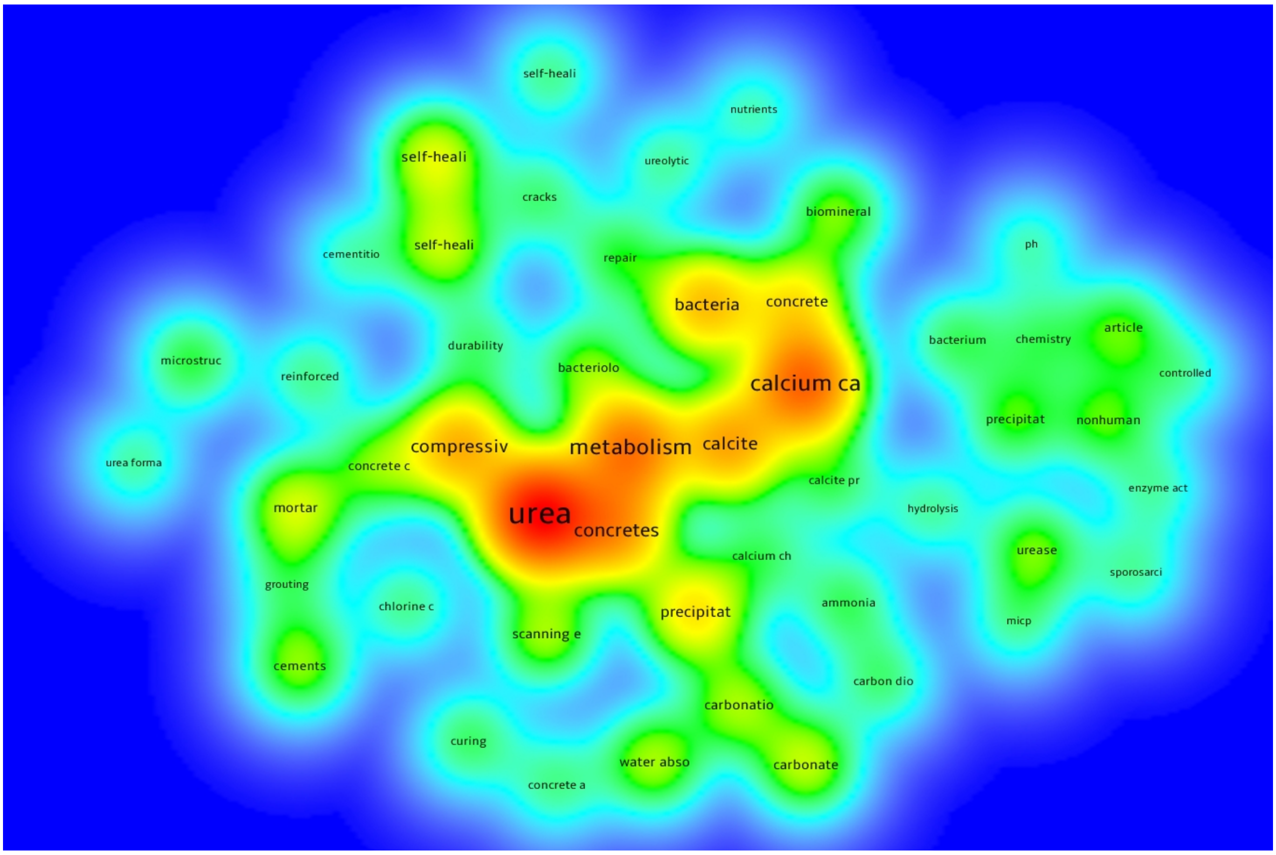

Fig. 2b. Analysis of search results data using VOSviewer software.

This methodological approach allows for a thorough and systematic study of the existing literature and provides a solid foundation for subsequent stages of analysis and discussion.

Literature review

Biomineralization

Biomineralization can be defined as the process of mineral formation by biotic or living beings. The biomineralization process can occur by any of two mechanisms:

a) biologically controlled mineralization (BCM);

b) biologically induced mineralization (BIM) [1].

In a biologically controlled mechanism, organisms activate the process and can control the nucleation and growth of mineral phases. The formation of teeth and bones in higher mammals falls into this category. However, with biologically induced mineralization, organisms do not exercise a high level of control, and the mineral produced is significantly dependent on the environment. Mineralization that occurs during bio-fermentation falls into this category.

Biocementation

Biocementation involves a biomineralization process in which calcium carbonate is induced by the metabolic activity of certain microorganisms. The deposition of $CaCO_3$ is a simple process that is heavily influenced by four determining factors:

- concentration of calcium ions;
- the number of carbonate ions;
- pH;
- the presence of places of origin.

The role of the microorganisms involved is to change any of the mentioned parameters either individually or in combination [2].

Biofermentation pathways

There are various ways in which calcium carbonate precipitation can occur, namely. ammonification (deamination), denitrification, sulfate reduction, photosynthesis, methane oxidation and urea hydrolysis (Table 1) [3].

Table 1

Different pathways of biocementation.

Microorganisms	Description of the bio cementation process	Reactions
Ammonification (nitrogen mineralization)/deamination of amino acids by microbes (usually oxidative). It is widespread in bacteria, including in relation to concrete in Bacillus cereus [4].	Microorganisms secrete ammonia during oxidative deamination of amino acids. The resulting keto acids are broken down under aerobic conditions too CO_2 and H_2O. Carbon dioxide reacts with calcium hydroxide contained in cement. Alkalization with ammonia also promotes crystallization and formation of calcium carbonate.	Аминокислоты+ → NH_3 + Кетокислоты (1), Кетокислоты + O_2 → CO_2 + H_2O (2), $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (3), $CO_2 + OH^- \rightarrow HCO_3^-$ (4). $HCO_3^- \rightarrow H^+ + CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3$ (5)

Continuation of Table 1

Denitrification: reduction of nitrates to molecular nitrogen during anaerobic respiration. Pseudomonas denitrificans, Alcaligenes, etc.	During denitrification, the organic matter is oxidized to CO_2 and H_2O using NO_3^- as the final electron acceptor. At the same time, due to the removal of nitrate ions from the system, the medium is alkalinized, which creates conditions for biomineralization.	$2(CH_3COO)_2Ca + 6NO_3^- \rightarrow$ $\rightarrow 2CaCO_3 + 3N_2 + 6CO_2 + 4H_2O + 4OH^-$ (
Sulfate reduction: reduction of sulfates to sulfides by sulfate-reducing bacteria during anaerobic respiration. Desulfovibrio, Desulfobulbus, Desulfobacter, etc. [5].	Sulfate-reducing bacteria, in a process called sulfate dissimilation reduction, convert sulfate to hydrogen sulfide, while calcium sulfate is replaced by carbonate.	$CH_4(R) + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H^+$ (
Photosynthesis of cyanobacteria and microalgae. The surface of concrete structures is often populated by phototrophic microorganisms, which can participate in the biocementation of surface cracks due to carbonic anhydrase activity.	Photosynthetic microorganisms can cause precipitation of calcium carbonate by metabolism HCO_3^{-3} and CO_2 in the presence of sunlight. HCO_3^- it moves through the membrane and dissociates into CO_2 и OH^- in the cytosol of the cell. This process is facilitated by carbonic anhydrase, which leads to an increase in pH due to the formation of OH^-. The presence of calcium ions in the environment contributes to the precipitation of calcium carbonate.	$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$ (

Continuation of Table 1

Аэробное окисление метана. Окисление ме-тана аэробными мета-нотрофными бактерия-ми, в том числе, Methylocystis parvus, Methylobacter sp.	The process begins with the conversion of methane into methanol due to the activity of methanmonooxygenase. In the periplasm of the cell, methanol, which is a carbon source, is converted into a format using several enzymatic processes. The activity of formate dehydrogenase allows methanmonooxygenase to oxidize formic acid to CO_2. The resulting CO_2 then it turns into CO_3^{2-}, leading to precipitation of calcium carbonate around cells in the presence of calcium ions.	$2CH_4 + O_2 \leftrightarrow 2CH_3OH$ (9), $2CH_3OH \rightarrow 2CHOH + 2H_2$ (10), $CHOH + H_2 \rightarrow HCOO^- + 3H^+$ (11), $HCOO^- + H_2O \leftrightarrow HCOOH + OH^-$ (12), $HCOOH \rightarrow CO_2 + H_2$ (13), $Ca^{2+} + CO_2 + 2OH^- \leftrightarrow CaCO_3 + H_2O$ (14
Anaerobic oxidation of methane. Anaerobic methane-oxidizing bacteria	In the presence of calcium ions, aerobic methanotrophic bacteria produce bicarbonates by anaerobic oxidation of methane, where sulfate acts as the main electron acceptor.	$CH_4 + SO_4^{2-} \leftrightarrow HCO_3^- + HS^- + H_2O$ (15 $HCO_3^- \rightarrow H^+ + CO_3^{2-}$ (16), $CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3$ (17).
Hydrolysis of urea by realistic bacteria	Precipitation of calcium carbonate by hydrolysis of urine involves a process that involves the cleavage of urea into ammonia and carbon dioxide in the presence of the enzyme urase, which then react with calcium ions (coming from outside) to form calcium carbonate.	$CO(NH_2)_2 + Ca^{2+} + 2H_2O \rightarrow$ $\rightarrow CaCO_3 + 2NH_4^+ + 2OH^-$ (18).

Ureolysis or hydrolysis of urea is the most studied pathway of biocementation due to the high degree of controllability it provides. The main advantage of the ureolytic method over other biocementation methods is the relatively high precipitation of calcium carbonate with a shorter reaction time.

Many different biogenic minerals, including carbonates, halides, phosphates, oxalates, sulfates and oxides of various metals can be induced by microorganisms. However, biologically induced calcium carbonate is suitable for biocementation in cement-based materials for the following reasons:

1. Calcium is one of the most abundant elements in the earth's crust and is available in most environments. This makes the production of calcium carbonate simpler and more cost-effective compared to other alternatives such as iron or manganese.

2. Calcium carbonate is a highly stable compound, having limited solubility and less exposure to atmospheric influences, thus being more durable and durable compared to other biologically induced minerals.

3. Calcium carbonate can be obtained in various forms, including crystals, shells and aggregates, and can be used in a wide range of applications, from soil stabilization to hardening of concrete and other building materials [6].

4. Calcium carbonate is biocompatible and therefore non-toxic. It does not harm living organisms, including humans. Thus, it is a safer option compared to other biologically induced minerals, such as minerals containing arsenic, lead and mercury.

Calcium carbonate can be obtained using various microorganisms, including bacteria, fungi and algae, which makes this process more flexible and adaptable compared to other biologically induced minerals, which require certain types of microorganisms [7].

Hydrolysis of urea

The types of bacteria that are suitable for ureolysis, that is, capable of secreting the enzyme urease, are known as urease-positive or ureolytic bacteria [8].

Given that cement-based materials are usually associated with a highly alkaline environment, ureolytic bacterial species must be able to withstand harsh and alkaline conditions in a porous solution of cement-based material for effective biocementation. It has been found that urease-positive bacteria are able to grow and perform myocardium even in harsh environmental conditions, and some have the ability to survive in highly alkaline conditions inside the matrices of cement materials for a long time [9].

An important factor to consider when choosing ureolytic bacterial species for myocardium is the pathogenicity of bacterial species.

Biosementing bacteria should be non-pathogenic and should not produce any by-products showing any traces of pathogenicity [10].

For example, the highest urease secretion has been recorded in the bacterial species ureaplasma urealyticum, however, this type of bacteria is known to cause urinary tract infection in humans. Thus, the use of ureaplasma urealyticum and other similar pathogenic bacteria is limited. The recommended bacterial species for biocementation are ureolytic bacteria of the genera bacillus, sporosarcina, spoloactobacilus, clostridium and desulfotomaculum.

Biocementation by hydrolysis of urea involves growing bacteria in a suitable nutrient medium containing all the necessary substances, and then providing them with an environment rich in urea and calcium ions. Fully grown bacteria secrete the enzyme urease as part of their natural metabolism. The urease enzyme hydrolyzes urea to form CO_3^{2-}, which then combines with calcium ions coming from the outside to form calcium carbonate [11].

Fig. 1 shows a detailed sequence of chemical reactions occurring in biocementation by hydrolysis of urea [10].

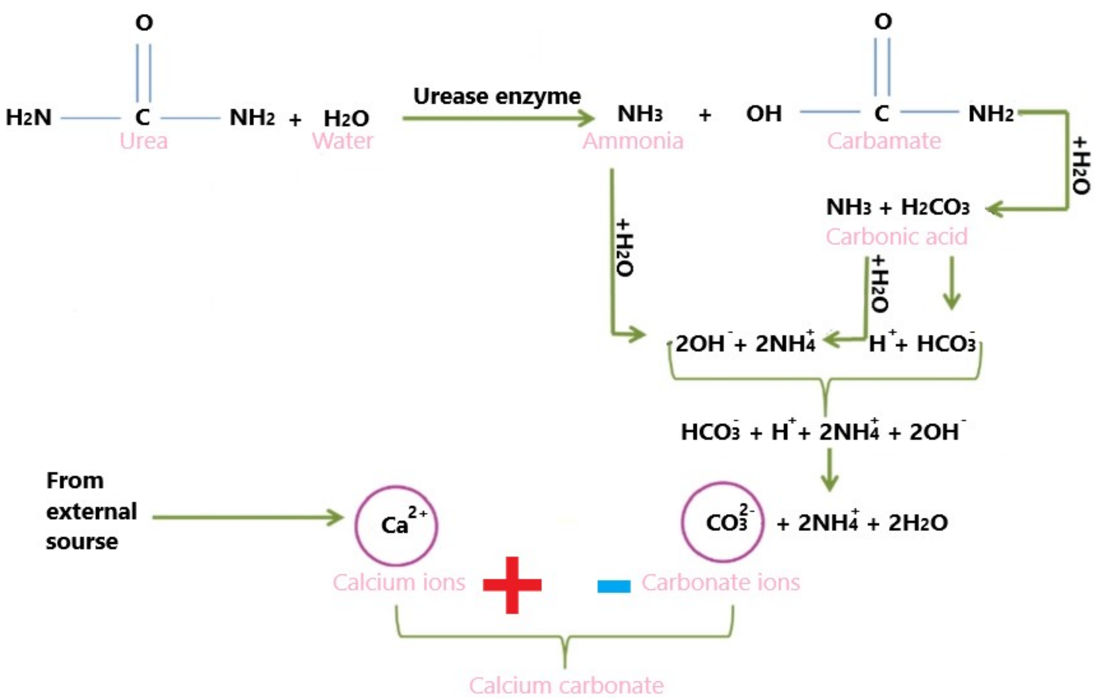

Fig. 3. Urea hydrolysis pathway of biocementation.

Initially, in the presence of urease, urea undergoes hydrolysis to form carbamate and ammonia. As a result of carbamate hydrolysis, one mole of ammonia and carbon dioxide is also formed. These products then react to form one mole of bicarbonate and two moles of ammonium and hydroxide ions, respectively. Due to the increase in pH as a result of these reactions, the bicarbonate equilibrium shifts, which leads to the formation of carbonate ions. Bacteria usually have a negatively charged cell wall that allows them to attract Ca^{2+} from the environment. These cations are deposited on the surface of the bacterial cell, which acts as a place of origin, and then react with CO_3^{2-} ions to form a $CaCO_3$ precipitate.

Self-healing mechanism

When exposed to moisture, lime in solution undergoes a carbonization process, which reacts with carbon dioxide from the atmosphere to form calcium carbonate. This process can take place over a long period when calcium carbonate fills small cracks and voids in the solution, thus effectively sealing and strengthening the microstructure. This process is also known as autogenic healing, as it occurs without the need for external intervention [12].

Ureolytic bacteria of the genus bacillus, which are used for biocementation, are usually spore-forming. Spore-forming bacteria are a type of bacteria that can form highly resistant spores under adverse environmental conditions such as exposure to heat, radiation, or chemicals. These spores are highly resistant to destruction and can remain viable for long periods of time. These spores can be added to concrete along with a source of calcium and urea. When the concrete cracks, water penetrates into the cracks and binds to the core of the spore, the water content in the spore increases, which leads to the formation of a hydrolyzed core. The hydrated core initiates the activation process by triggering the hydrolysis of the peptidoglycan bark of the spore, which is a thick layer surrounding the spore core [13] (Fig. 2).

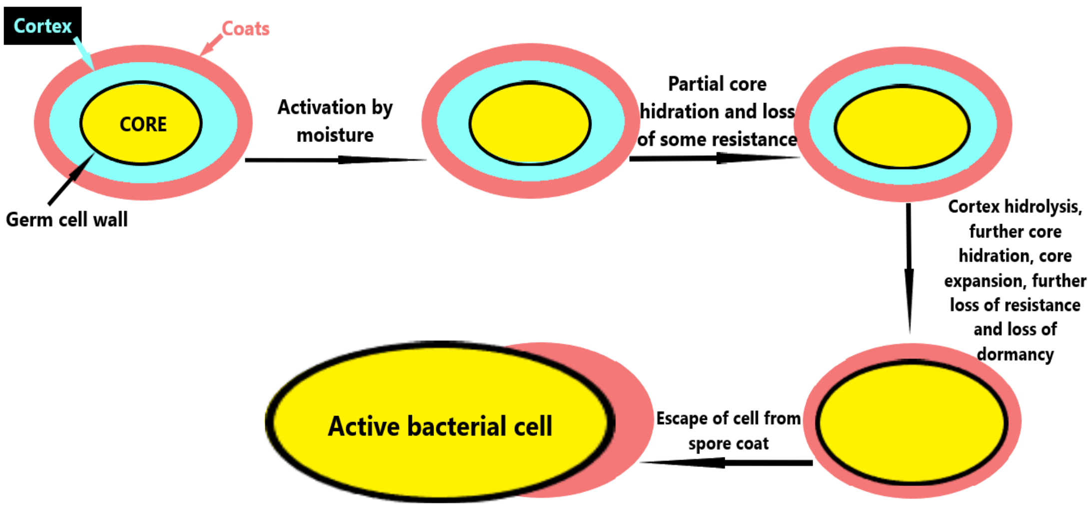

Fig. 4. Mechanism of activation of dormant bacterial spore with moisture ingression.

This activation of the spores leads to their germination and growth into active bacteria. These bacteria can then hydrolyze urea and induce calcium carbonate, which can fill cracks and restore the structural integrity of cement-based materials.

Effective self-healing of structures using these bacterial spores requires long-term sealing, which can be maintained throughout the life of the structure. The survival of bacteria is crucial to achieve this goal. However, adding bioagents directly to concrete can create problems for bacterial survival [14]. Exposure to a highly alkaline environment over a long period can significantly reduce bacterial activity [15]. The longer survivability of bacteria added directly to concrete is still controversial [16]. Bacteria can be encapsulated or embedded in the matrices of cement-based materials to protect them for a longer period and promote self-healing by precipitation of calcium carbonate. Encapsulation is a common method of immobilizing self-healing bacteria in concrete. In this method, the bacteria are surrounded by a thick protective layer that prevents them from leaching out or decomposing. Self-healing bacterial spores are embedded in porous materials. The porous materials are then injected into a cement-based material matrix, where bacteria grow and multiply, and their metabolic activity helps to seal cracks in cement-based materials. Many studies have been conducted to test the ability of various bacterial species. Table 2 shows the biocementation studies conducted using various immobilization methods for the period from 2019 to March 2024.

Self-healing of biobetone can be divided into several types:

1. In the microbiological form of self-healing, special types of bacteria are used that can fill cracks and restore the surface of concrete.

2. In the chemical form of self-healing, chemical reaction processes take place inside the biobetone, which contribute to filling the crack of concrete and restoring its structure.

3. In autogenous self-healing in conditions of moderate humidity, cement in biobetone reacts and fills microscopic cracks.

4. In physical self-healing, some components of biobetone undergo physical change under the influence of external loads, which contributes to the restoration of cracks.

These methods allow biobetone to maintain its strength and structure even in the event of damage, which makes it a stable and durable material for construction. Table 2 provides a list of biocementation studies using various bacteria and self-healing methods.

Table 2

Biocementation studies to test the self-healing potential of different bacteria.

The healing method	Link
The use of microcapsules of the Preyssler brand with calcium nitrate	[17]
Experiments on different concentrations of bacterial solution and urea in a concrete mixture to identify the best results of microbiological precipitation of calcium	[18]
The use of photosynthetic cyanobacteria Synechocystis pevalekii.	[19]
Comparison of two biomineralization methods: 1 method (use of bacterial spores and nutrient sources in solution and their further use for self-healing of cracks), 2 method (absence of bi-omineral additives in solution, a mixed solution of urea and calcium acetate was used for self-healing)	[20]
The use of calcite-inducing bacteria identified in the alkaline soda lakes of Chita and Abijatta, Ethiopia.	[21]
The application of a deposition process controlled by regulating the rate of release of urease activity and the study of its effect on the mechanical properties of precipitated $CaCO_3$.	[22]
The use of the bacteria Sporosarcina pasteurii and Staphylococcus sp. H6	[23]
The use of Bacillus subtilis bacteria	[24] [25] [26] [27] [28]

Continuation of Table 2

The use of cold-resistant bacteria Brevibacterium frigoritolerans A 779 and A 793 and S. pasteurii fwzy14	[29]
The use of Sporosarcina pasteurii bacteria	[30] [31] [32] [33] [34] [35] [36] [37] [38]
The use of sodium alginate	[39]
The use of Bacillus pumilus bacteria	[40]
The use of bacteria Sporosarcina pasteurii, calcium-urea nitrate and calcium-urea chloride	[41]
The use of bacteria that produce urease, which promotes the formation of hydrated magnesium hydroxycarbonates and improves the strength of concrete of reactive cement MgO	[42]
The use of bacteria Arthrobacter sulphureus, yeast extract, urea, $NaHCO_3$, $CaCl_2$.	[43]
The use of bacteria Priestia megaterium, Neobacillus drentensis, Sporosarcina pasteurii, Bacillus subtilis and Priestia aryabhattai	[44]
The use of mineral-based inoculate (silica smoke, cement dust and rice husk ash), nutrient broth, urea and $CaCl_2$	[45]
The use of soy urease, urea and calcium chloride	[46]
The use of a solution obtained from ureolytic bacteria cultivated in a medium of corn steep liquor	[47]
The use of microcapsules with calcium nitrate	[48]
The use of bacteria E. coli BL21, P. putida KT2440, P. aeruginosa PAO1, S. oneidensis MR-1, S. pasteurii DSM 33 and B. megaterium DSM 319	[49]
Application of microbiological technology for the formation of a protective layer of $CaCO_3$crystals	[50]
The use of bacteria Busarium cerealis, Phoma herbarum and Mucor hiemalis	[51]
The use of bacteria Sporosarcina pasteurii, calcium nitrate ($Ca(NO_3)_2$), urea and calcium chloride $CaCl_2$	[52]
The use of urea and calcium ions	[53]
The use of Bacillus megaterium bacteria	[54]

Continuation of Table 2

The use of Bacillus psychrodurans LC40 bacteria	[55]
The use of bacteria Bacillus megaterium MTCC 3353 and methacaolin	[56]
The use of microorganisms to create a protective layer of crystals on the surface of concrete	[57]
The use of Bacillus sphaericus bacteria	[58]
The use of microorganisms to create a protective layer in biobetone	[59] [60] [61] [62] [63] [64] [65]
The use of Alkalibacterium iburiense EE1 bacteria	[66] [67]
The use of bacteria Bacillus pasteurii, Bacillus alcalophilus	[68]
The use of bacteria Sporosarcina pasteurii ATCC 11859	[69]
The use of organic carbon and nitrate salt	[70]
Using watermelon, pumpkin and soy bean seed powder	[71]
The use of bacteria and nutrients	[72]
The use of bacteria Rhodococcus erythreus S26	[73]
The use of chemically active magnesia cement paste containing Sporosarcina pasteurii bacteria	[74]
The use of a mineral additive and a porous lightweight filler (pumice stone)	[75]
The use of bacteria Bacillus subtilis KCTC-3135T, Bacillus cohnii NCCP-666 and Bacillus sphaericus NCCP-313	[76]
The use of the bacteria Sporosarcina pasteurii ATCC 11859 and the native strain Lysinibacillus sphaericus hass 1	[77]
The use of Lysinibacillus boronitolerans YS11 bacteria	[78]
The use of Bacillus sp. AK13 bacteria	[79]
The use of Lysinibacillus macroides and Bacillus licheniformis bacteria	[80]
The use of calcium lactate, calcium nitrate, calcium formate, urea and yeast extract	[81]
The use of glucose	[82]
The use of Ralstonia eutropha H16 bacteria	[83]
The use of Bacillus cereus bacteria	[84]
The use of bacteria, soil, lentil seeds, etc.	[85]
The use of biological products containing bacteria and organic biocomponents	[86]

Continuation of Table 2

The use of Lysinibacillus sphaericus bacteria	[87]
The use of bacteria and aluminum oxide	[88]
The use of S. pasteurii and B. subtilis bacteria	[89]
The use of Bacillus subtilis natto bacteria	[90]
The use of silicate solutions; sodium silicate, potassium silicate and lithium silicate as the main agents, as well as urea, sodium polyacrylate, catalysts and fluorocarbon surfactants as auxiliary substances to identify their effect on the durability of concrete	[91]

The above-mentioned studies prove the effectiveness of alternative nutrient media. The effect of the origin of bacterial species on the effectiveness of nutrient media is still unclear. Bacterial species isolated from plants grow better in an environment with soil extract. Using their native nutrients leads to better biocementation efficiency, although they can still grow on other media. If bacterial species need to be cultured on a large scale for biocementation, then using their native nutrient sources can help achieve effective biocementation at significantly lower cost. If industrial waste is used as an alternative nutrient medium, it should be sterilized to prevent contamination. The pH of the medium should be maintained in a certain range suitable for bacterial growth [92]. Nutrient concentrations in the medium should also be optimized for bacterial growth. Too few or too many nutrients can negatively affect bacterial growth.

Problems of biomineralization

Problems related to the effectiveness of microbial species

Many researchers have tried to figure out the relationship or interactions between different microbes and their effect on the effectiveness of biocementation. In the study [44], the effectiveness of biocementation of combinations of priestia megaterium, neobacillus drentensis, sporosarcina pasteurii, bacillus subtilis and priestia aryabhattai was studied for their ability to induce the process of microbially induced precipitation of calcium carbonate, especially in alkaline and high-temperature environments. The results showed that strains TBRC 1396 and TBRC 8147, as well as strains TBRC 5949 (Bacillus subtilis) and TBRC 8986 (priestia aryabhattai) are able to generate calcium carbonate at a pH of 9-12 and a temperature of 30-40° C, which is suitable for construction and compaction purposes. Strain TBRC 8147 also demonstrated deposition of $CaCO_3$ at 45°C. Strains TBRC 8986 and TBRC 8147 are non-ureolytic bacteria capable of microbially induced precipitation of calcium carbonate in the absence of urea, which can be used to prevent the formation of undesirable ammonia associated with the ureolytic process of microbially induced precipitation of calcium carbonate. However, the question of choosing the optimal conditions for biocementation and ensuring the stability and preservation of the properties of bacteria remains open. The research does not address the issue of the long-term behavior of biobetone under operating conditions and the need to take into account long-term effects. The problem of insufficient calcite production also requires further research, taking into account the economic benefits and accessibility.

In research [23, 30, 41, 44, 31, 52, 32, 69, 33, 74, 34, 77, 36, 37] the influence of bacteria was considered sporosarcina pasteurii on the biomineralization of concrete. Despite the ability of this strain to restore concrete by calcite deposition and despite the improvement of the mechanical properties of biobetone, the issue of low growth of sporosarcina pasteurii bacteria remains relevant, which slows down the process of biocementation; the issue of creating optimal conditions for the growth of this strain and their ability to survive in operating conditions has not been sufficiently studied.

On the other hand, microencapsulation technology can be used to protect bacteria from harmful environmental influences. [17, 93, 92, 94, 48, 62, 95], this, among other things, also makes it possible to control the release of bacteria into the environment. Microcapsules help to increase the active preservation time of bacteria, thereby reducing their losses. But for this, microcapsules need to create optimal conditions that will not destroy them, but on the contrary will contribute to their safety. There is also a problem of uniform distribution of bacteria in the concrete mixture, which leads to insufficient mineralization of the material. Among other things, when using microcapsules, it is necessary to study the issue of their interaction with other additives and concrete components in order to avoid negative consequences.

More focused research is needed to understand the complexities of the interaction of different bacterial species and their impact on biocementation.

It is necessary to replenish research in the field of optimization of microcapsulation technology and their uniform distribution and interaction with other additives and components of concrete, to investigate the issue of optimizing conditions for the growth and survival of bacteria. Also, to study the long-term behavior of biobetone under operating conditions and pay attention to the economic benefits and availability of components for biomineralization.

Problems related to the source of calcium

No biocementation process can take place without the presence of a calcium source. Calcium ions from the calcium source combine with carbonate ions formed during the hydrolysis of urea to form $CaCO_3$, which precipitates in the matrix of building materials [96].

Calcium chloride $CaCl_2$ is the most widely used source of calcium in research related to biocementation. This is due to the fact that $CaCl_2$ is highly soluble in water and, thus, is able to release a large amount of calcium ions, which leads to an increase in the efficiency of the biocementation process. However, the presence of chlorides in salt can cause corrosion of embedded reinforcement in reinforced concrete structures. Therefore, many researchers have conducted work on alternative sources of calcium, both organic and inorganic in nature, to study their effectiveness in biocementation. Many research groups have also tried to make the biocementation process more sustainable and economical by extracting calcium from various waste sources as well. Table 3 lists some of the most significant studies of alternative sources of calcium.

Table 3

Research on finding alternative sources of calcium $CaCl_2$.

A source of calcium			
Types of bacteria	Results	Notes	Link
Хлорид кальция, ацетат кальция, нитрат кальция			
Sporosarcina pasteurii	The compressive and tensile strength of the samples treated with calcium acetate was approximately twice as high as that of the samples treated with two other calcium sources.	Calcium acetate can replace calcium chloride, which causes corrosion of reinforcement in reinforced concrete.	[97]
Calcium Chloride, Calcium Acetate, Calcium Nitrate			
Sporosarcina pasteurii	Deposition $CaCO_3$ it was highest when using calcium acetate and lowest when using calcium nitrate	Calcium acetate has proven to be the best source of calcium, compared to the other two sources, because CH_3COO^- reacts with NH_3 with education CH_3COONH_4, what reduces emissions NH_3. CH_3COO^- increases the rate of mineralization due to its relatively high molar mass.	[98]
Eggshell			
Bacillus sp.	The compressive strength of the eggshell-treated samples was higher than that of the calcium chloride-treated samples.	The use of eggshells as a source of soluble calcium ions significantly reduces the costs associated with the use of laboratory-grade calcium salts.	[99]
Limestone and lignocellulose biomass			
Sporosarcina pasteurii	The technical properties of sand treated with calcium obtained from limestone were comparable to calcium chloride of laboratory origin.	Limestone powder, formed as airborne pollutants from aggregate quarries, reduces the environmental impact of limestone powder and makes the calcium deposition process more stable.	[100]

Continuation of Table 3

Calcium Chloride, Calcium Acetate, Calcium Nitrate			
Bacillus cereus	Deposition $CaCO_3$ it was highest when using calcium acetate and lowest when using calcium nitrate.	Calcium acetate, which is a weak acid, leads to minimal loss and, therefore, the maximum deposition $CaCO_3$. The use of calcium acetate replaces $CaCl_2$ as a source of calcium ions and, therefore, compensates for the disadvantage associated with $CaCl_2$.	[101]
Нитрат кальция и лактат кальция			
Sporosarcina pasteurii	Deposition rate $CaCO_3$ using calcium lactate was twice as high as using calcium nitrate.	Organic sources of calcium can replace inorganic ones and lead to the formation of more sediment.	[102]

Due to the limited solubility of calcium hydroxide contained in concrete, it is difficult to use it for biocementation, which requires the need to use an external calcium source to ensure effective precipitation of calcium carbonate. In the case of concrete mixed with mineral additives, calcium hydroxide is also required for the formation of secondary calcium silicate hydrate, therefore, for effective biocementation, it requires a larger amount of calcium source than conventional concrete. The efficiency of biocementation is directly proportional to the solubility of the calcium source, since it ensures the effective dissociation of Ca^{2+} ions in a pore solution and, thus, leads to the effective deposition of $CaCO_3$ in the matrices of cement-based materials. However, if the calcium source is added in excess, it can be washed out, which will lead to porosity of the concrete and affect its durability.

Problems related to the use of urea

The ureolytic pathway is the most common and widely used mechanism of biocementation. However, the use of the ureolytic pathway is associated with some disadvantages. Ureolysis inevitably leads to the release of gaseous ammonia (Figure 1) Ammonia can have harmful effects on human health and the environment [103].

With an excess of ammonia, if an excessive amount of ammonium is present in the concrete mixture, biobetone self-damages, since it can turn into nitric acid, increasing the risk of corrosion of steel in reinforced concrete [104].

The accumulation of ammonia can also interfere with biocementation, leading to low-quality precipitation. Excessive levels of ammonia can disrupt vital cellular functions and interfere with the metabolic processes of bacteria, thereby reducing their ability to produce urease enzymes. In addition, the volatilization of ammonia in ureolytic systems causes a decrease in pH, leading to the dissolution of previously precipitated $CaCO_3$ [105].

All of the above aspects require that ammonia emissions be taken into account when researching and identifying effective methods for precipitation of calcium carbonate.

Problems related to the immobilization of bio-cementing agents to improve the self-healing ability of cement-based materials and related solutions

There are several approaches regarding the inclusion of immobilized biocementitious bacteria, nutrients and precursors (a source of urea and calcium in the case of urea hydrolysis) in cement-based materials [106]. The most common inclusion methods include the use of:

1. Separate capsules for bacterial spores and other components. With this approach, bacterial spores are encapsulated in one set of capsules, while other components or materials are encapsulated separately.

2. Single capsules with separate layers. This method involves the use of a single capsule containing bacterial spores in one layer, and other ingredients or components in a separate layer. These layers are designed to separate the capsules until they break or dissolve, which usually requires certain conditions, such as a change in pH. It is expected that after the capsule is destroyed, spores and other components will react with each other inside the concrete [107].

3. Bacterial spores and other components embedded in individual porous materials. This approach involves the introduction of bacterial spores and other components into various porous materials, which are usually aggregates for concrete. When cracks appear, moisture penetrates these porous materials and simultaneously releases spores and other components, allowing them to interact and participate in crack healing [108].

Although encapsulation of biocementitious agents is one of the most common methods of their long-term preservation, this is associated with a number of problems. The capsules must be strong enough to resist abrasion during concrete mixing, but at the same time they must be sensitive enough to feel the appearance of cracks and automatically collapse with the release of calcium carbonate. Both options are mutually exclusive.

As a rule, bacterial spores, precursors and nutrients are enclosed in separate capsules, which makes it difficult to control their distribution in cement-based materials. Ideally, when cracks form in concrete, the various capsules containing spores and nutrients should be positioned next to each other and burst at the same time to ensure the deposition of $CaCO_3$ and the healing of the crack. The effectiveness of biocementation in the event of cracks has not been studied.

The application of microbiological calcium deposition can be expanded by identifying problems and promoting solutions proposed in various studies.

Some changes in the use of alternative sources of urease and calcium may lead to a significant increase in the efficiency of biocementation. The limitations of the urea hydrolysis pathway during the precipitation of calcium carbonate can be mitigated by ammonification, denitrification, the use of carbonic anhydrase, etc.

The correct choice of methods for the immobilization of bio-cementing agents in cement-based material matrices is crucial for effective bio-cementation.

Conclusions

Research interest in the field of biocementation of materials increased significantly between 2019 and March 2024, which indicates an increasing desire to introduce this method into construction.

The current work presents the following results:

1. A detailed method of literature search is presented and the identified sources for a certain period are systematized.

2. The process of biomineralization is considered.

3. The process of biocementation is considered, including the ways of precipitation of calcium carbonate, hydrolysis of urea and the mechanism of self-healing of biobetone.

4. The existing problems of biomineralization related to the effectiveness of species of microorganisms, with sources of calcium, with the use of urea and with the immobilization of biocementizing agents are considered.

Mixed microbial cultures are the preferred choice in terms of biocementation efficiency compared to isolated species, as they can form beneficial microbial associations that allow them to individually withstand highly alkaline conditions in cement-based materials.

To ensure effective biocementation in cement-based materials, it is extremely important to choose a non-corrosive calcium source that has higher solubility in pore solution and minimal effect on cement hydration.

To reduce the undesirable concentration of ammonia produced by the ureolytic method of biocementation, the deposition of struvite as an alternative to calcium carbonate or the use of alternative methods, biocementation methods that completely eliminate the production of ammonia can be studied.

Porous fillers are the preferred option for the immobilization of bacteria in cement-based materials compared to encapsulation in natural and artificial organic materials, since the former provide better compatibility with the cement-based matrix and the correct distribution of bio-cementing agents.

More focused research is needed to understand the complexities of the interaction of different bacterial species and their impact on biocementation.

It is necessary to replenish research in the field of optimization of microcapsulation technology and their uniform distribution and interaction with other additives and components of concrete, to investigate the issue of optimizing conditions for the growth and survival of bacteria. Also, to study the long-term behavior of biobetone under operating conditions and pay attention to the economic benefits and availability of components for biomineralization.

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The correct choice of methods for the immobilization of bio-cementing agents in cement-based material matrices is crucial for effective bio-cementation.

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