Biomodified building materials on the base of mineral binders

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Abstract. In order to increase the service life of structures, there should be taken various measures aimed at damaged elements restoration followed by their due maintenance. Enhancing material’s properties by the ability of self-healing is done with the help of the additive and is seen as the effective method of preservation of the materials’ properties. The analysis of the previous studies has shown that biological and biochemical processes are given preference to facilitate self-healing process. The purpose of the present study was a development of the method allowing for the increase in durability of buildings structures by activating and providing self-healing processes of building materials. The application of the developed bioadditive allows retaining reliability of construction products at the very initial stages of microflaws’ appearance by filling them up with the essential products of bacteria with urease activity. The bacteria are introduced into the body of the material at the manufacturing stage. This method of imparting a self-healing effect to the materials has many points in its favor such as sustainability, cost effective performance, and reduced labor costs for repair and restoration work. The method could be used in the structures of any complexity and for reconditioning of heritage sites. The selected microorganisms act upon the mix as surfactants, that is, they lower the water-cement ratio of sand-cement mortars by augmenting the concentration of bio-surfactants. This feature of cells enhances the efficiency of the developed additive. Application of these microorganisms as a component of a biologically active additive can significantly increase production performance and the efficiency of building structures’ operation due to higher efficiency of microorganisms responsible for initiating self-healing processes in building materials. According to the research results, zeolite could be regarded as the most suitable porous material acting as a carrier of cell immobilization.

1. Introduction

Building materials on the base of mineral binders are exposed to the impact of adverse environmental conditions. This facilitates lowering strength and performance properties of materials. In order to increase the service life of structures, there should be taken various measures aimed at damaged elements restoration followed by their due maintenance. Enhancing material’s properties by the ability of self-healing is done with the help of the additive and is seen as the effective method of preservation of the materials’ properties.

Microcracks in the surface layers of materials could appear when the building structure is exposed to various loads. Atmospheric air and moisture can penetrate microcracks that lead to significant drop in durability of construction products. The self-healing process is based on activation of aerobic
bacteria introduced to the mortar mix at the earlier stages. During the life cycle of these cells, calcium carbonate is being formed facilitating the self-healing process. Calcium carbonate is responsible for filling the formed microcracks, thereby restoring the structure and retaining the properties of the material. Cells’ activity depends on environmental conditions. That is, when the microflaw is clogged, atmospheric air and moisture stop penetrating the material, and as the result, the bacteria become inactive. Correspondingly, when new microcracks resume appearing, the bacteria are reactivated by the inflowing water and air.

The goal of the present research is to enable building materials on the base of mineral binders to self-heal their structure. To achieve the stated goal, the following manipulations have been carried out: the bacteria efficiency has been studied for self-healing mortar mixes and concretes; the impact of environmental factors on maintaining activity of particular microorganisms has been determined; the dependency of the efficiency of self-healing process on a mineral binder has been established; porous materials have been studied as the most suitable ones for cell immobilization.

Currently, there are many scientific researches carried out with the view to improve two factors: ecology and economy. The application of biological surfactants is widely used in manufacturing building materials as they are considered environmentally friendly and cost-saving [1, 2]. Formed by various types of microorganisms [3], biological surfactants have found their practical use in many spheres of human endeavor [4–7]. The analysis of the previous studies has shown that biological and biochemical processes are given preference to facilitate self-healing process.

Thanks to them, structure recovery of building materials becomes cost-effective if compared with the other methods applied [8–14]. It was also required to determine the influence of cells exploitation on the properties of building materials.

Literature references [2, 15] describe how superficially active agents affect the basic and strength properties of sand-cement mixes and concrete grouts. The graphs (fig. 2 and 3) demonstrate the dependency of the strength characteristics of the product on the concentration of the selected cell type.

Concentration of the surfactant has an impact on the quantity of water introduced for mixing. Therefore, a certain admixture content can lower its quantity, by that enhancing the strength characteristics of the material. However, when the additive’s concentration is increased significantly, the access for mixing water to the surface of hydrating grains will be restricted. This is due the increase in the thickness of the substance’s film formed on the surface of hydrated layers that prevents water penetration.

The purpose of the present study was a development of the method allowing for the increase in durability of buildings structures by activating and providing self-healing processes of building materials. The application of the developed bioadditive allows retaining reliability of construction products at the very initial stages of microflaws’ appearance by filling them up with the essential products of bacteria with urease activity. The bacteria are introduced into the body of the material at the manufacturing stage. This method of imparting a self-healing effect to the materials has many points in its favor such as sustainability, cost effective performance, and reduced labor costs for repair and restoration work. The method could be used in the structures of any complexity and for reconditioning of heritage sites.

2. Methodology

For the research purposes, the following components have been chosen: gypsum G-4BI; Portland cement PC-400D0; glass sand with the fineness modulus of 2.1; mixing water; naturally occurring zeolite (produced by the enterprise Orlovsky zeolite) graded up to 0.63mm; granulated foam glass.

Urease activity of bacterial strains has been estimated with the use of Nessler’s reagent on the spectrophotometer Agilent UV-853 at a wavelength of 400 nm. Specimens’ preparation has been carried out as follows: 5 ml of bacterial cells suspension have been placed in glass bottles with 10 ml of the buffer solution and 10 ml of 10% urea solution. After that, the glass bottles have been placed in
the thermostatic regulator and conditioned at 37°C for 24 hours. The selected specimens have been centrifuged at 6000 rpm for 5 min.

The method of determining ammonia nitrogen has been implemented as follows: 1 ml of the tested solution, 3.6 ml of distilled water, 0.2 ml of 50% solution of the Rochelle salt and 0.2 ml of the Nessler’s reagent have been added into the glass bottle. Then, the mixture has been thoroughly stirred for 5 min and the optical density of the solution has been measured. When the solution grew muddy, another 0.2 ml of the Rochelle salt was added. The measuring unit of urease activity is 1 mg NH₄/mg/min. The volume of ammonia nitrogen has been determined using the standard calibration curve.

Types and forms of bacteria which are the most suitable for self-healing process of cement composites have been identified and analyzed. The pH-value and hydration temperature of concrete grouts depend on the chemical nature of mineral binders.

During hydration of cement and gypsum binders there take place exothermic processes affecting the activity of used cells. The impact is negative. Therefore, the authors have conducted a research aimed at finding a specific form of cells that are able to function under specific environmental conditions arising throughout hydration and hardening stage of the mortars on the base of various binders.

The critical factor for selecting a specific type of bacteria was their ability to produce calcium carbonate, essential for prevention of microcracks formation. There have been used the cells of various gram-positive and gram-negative bacteria, such as (Sporosarcina pasteurii, Bacillus pasteurii, B. cohnii, B. sphaericus, B. pseudofirmus, B. cohnii, B. halodurans, B. subtilis, B. megaterium, B. alkalinitrilicus, Pseudomonas putida, Escherichia coli) [1].

The previous studies refer to bacteria Bacillus pasteurii (Cells I). These bacteria have been taken as the reference for comparing the test results with Cells II (microorganisms of Rhodococcus erythropolis type). Urease is an enzyme of hydrolase class that breaks down urea into ammonia and carbon dioxide. Is serves as the indicator of cell efficiency (table 1).

| Biosample | Type of binder | Cell biomass, mg | Initial pH | Final pH | Activity NH₄ mg / g / day |
|-----------|---------------|-----------------|------------|----------|--------------------------|
| Cells I   | Cement        | 0.46            | 8.47       | 10.49    | 32.88                    |
|           | Gypsum        | 0.52            | 8.39       | 8.19     | 39.72                    |
| Cells I I | Cement        | 0.49            | 7.8        | 11.62    | 47.69                    |
|           | Gypsum        | 0.56            | 6.86       | 6.89     | 88.97                    |

3. Result and discussion

As part of the process of binders’ hydration and cells’ functioning, the pH of the medium changes its value. The initials pH-values are higher in the case of Bacillus pasteurii, for both gypsum and cement, if compared to pH-values for cells Rhodococcus erythropolis. This serves as the plausible evidence to more intense formation of NH₄ in the hydration period in the presence of cells II (Rhodococcus erythropolis). This type of cells shows a greater adaptation to changing environmental conditions (pH change), since their enzymatic activity has not dropped with increase of pH-value if compared with Bacillus pasteurii.

The results analysis allow us to draw a conclusion that the use of the cells Rhodococcus erythropolis is more efficient for biocarbonization processes targeted to structure recovery of the mineral matrix of mortar mixes and concretes.

The impact of external factors on the activity of Rhodococcus erythropolis cells. In the setting process of gypsum and Portland cement products, there takes place a substantial liberation of heat energy accompanied by an increase in temperature. In this case, a temperature change can adversely
affect the enzymatic activity of bacteria.

Slow setting of mineral binders is characterized by a low heat release rate and, as a result, no strong negative effect of exothermic effect on cells activity is observed. Nevertheless, for fast-setting binders, this effect is more prominent due to an increase in the hydration rate.

In this paper, the authors have presented the results of investigating the dependency of strength properties of the material on the base of gypsum binder on the concentration of applied cells (table 2).

| Table 2. Change in strength characteristics of specimens as a function of cells II concentration |
|-----------------------------------------------|
| Strength, MPa | Concentration of cells, % by weight of gypsum / series number |
|                | 0/1 | 0.01/2 | 0.015/3 | 0.025/3 | 0.1/4   |
| Bending       | 2.03| 2.01   | 1.99    | 1.84    |         |
| Compression   | 4.17| 3.96   | 3.87    | 3.86    |         |

The influence of changes in the strength of gypsum samples on the concentration of Rhodococcus erythropolis cells. An increase in the cell count is higher than 0.015% by weight of gypsum leads to a drop in the strength properties of the specimen factoring in plasticizing effect of the bio-surfactant in the cells.

This work also incorporates the research aimed at determining the efficiency of porous materials of various origins for microcontainers that protect cells and provide them with a nutritive medium. Studies dedicated to finding the most suitable material for microcontainers have been implemented on two types of porous materials, namely: zeolites and granulated foam glass. The results of findings presented in the table 3 enable to draw a conclusion that zeolites are preferable for microcontainers if compared with granulated foam glass.

| Table 3. Change in urease activity of Cells II for various porous microcontainers |
|-----------------------------------------------|
| Specimen         | Specimen’s weight, g | Initial pH | Final pH | NH₄ activity mg / g / day |
| Zeolite          | 2.3               | 7.3        | 9.8      | 2518.95               |
| Foam glass       | 2.0               | 7.54       | 9.33     | 332.38                |

The influence of the microorganisms’ content on the properties of molding mixtures on the base of gypsum and cement binders. Increasing the concentration of Rhodococcus erythropolis cells leads to dramatic change in rheological properties of sand-cement mortars (figure 1). Introducing the cells into one percent of the cement mass allows reducing the value of water-cement ration from 0.45 to 0.41. This is attributed to the presence of bio-surfactants forming the cells. The reduced value of water-cement ratio ensures the conditions required for performance.

The selected microorganisms act upon the mix as surfactants, that is, they lower the water-cement ratio of sand-cement mortars by augmenting the concentration of bio-surfactants. This feature of cells enhances the efficiency of the developed additive.
Figure 1. The dependence of the water-cement ratio W/ C on the concentration of introduced cells in a sand-cement mortar.

The strength properties of the obtained specimens have been estimated under the standard method (figure 2, 3).

An increase in the cells concentration in sand-cement mortars up to 0.5% by weight of the binder improves mixture consistency non affecting water-cement ratio. However, when the concentration of cells exceeds 0.5% by weight of cement, there is observed strength reduction. In this regard, the bacteria count in sand-cement mortars should not exceed the value of 0.05% by weight of the binder. In this case, there has been observed the gain in compression and bending strength of the specimens by 17 and 10% respectively, if compared with test specimens (figure 4).
Figure 3. The dependence of cell concentration on the compressive strength of specimens of sand-cement mortar: 2 - specimens without bioadditive, 2-1 - specimens with a cell concentration of 0.01% by cement weight; 2-2 – specimens with a cell concentration of 0.05% by cement weight; 2-3 - specimens with a cell concentration of 0.5% by cement weight.

Figure 4. The effect of the cells II concentration on the initial and final stage of Portland cement setting.

This is linked to the fact that the formed microflaws of the sand-cement matrix are filled up with calcium carbonate (figure 5, 6).

During their lifecycle, the bacteria selected as the nutritive medium produce calcium carbonate through various biochemical processes. This facilitates filling up the microflaws in buildings structures. Aerobic bacteria are activated by the air penetrating the products through microdefects. Bacterial activity stops when the ingress of air and moisture from the environment is restricted due to microcracks colmatation. Thus, when new cracks start appearing, moisture and air resume the penetration of the material, thereby activating bacteria. As the part of the research, the influence of urease activity on the efficiency of self-healing processes has been determined for the structures of mortar and concrete mineral matrixes.

Also there has been chosen the type of bacteria that is the most suitable for the research purposes. It has been proven that external environmental conditions affect the viability of microorganisms being a
part of the mortar composition. The study results have revealed that cells offer plasticizing properties and can reduce the amount of mixing water, thereby increasing the durability of building materials.

Figure 5. The photo of the surface of the control sand-cement specimen without bioadditive at the hardening age of 28 days.

Figure 6. The photo of the surface of the sand-cement specimen with a cell concentration of 0.05% by weight of cement binder at the hardening age of 28 days.

Bacteria facilitate manipulating setting time and hardening rate of mortar mixtures that could be seen as another advantage of their use [14]. Application of these microorganisms as a component of a biologically active additive can significantly increase production performance and the efficiency of building structures’ operation due to higher efficiency of microorganisms responsible for initiating self-healing processes in building materials.

According to the research results, zeolite could be regarded as the most suitable porous material acting as a carrier of cell immobilization.

Figure 7. Raman spectrography of the point taken from surface of the sand-cement specimen.

4. Conclusion
Using the method of Raman spectroscopy, it was stated that in the points of defect formation in the cement and sand specimens modified by a bioadditive, biocarbonization process facilitates the
formation of calcium carbonate that fills up the microflaws (see Fig. 6). This is clearly observed on spectroscopy results (Fig. 7). In the points highlighted in red in the fig. 6, the peak wave number accounted for $1085.7 \text{ cm}^{-1}$, that corresponds to the response of calcium carbonate minerals. In this regard, it can be claimed that due to colmatation of defects by calcium carbonate, the process of microstructure recovery for the mineral matrix of sand-cement mortars is facilitated.

The present study enables to draw a conclusion about the possible enhancement of operational characteristics of building structures on the base of mineral binders.

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