Bio product used in the self-sealing process of microcracks in hydrotechnical concretes

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Abstract. This paper is focused on quantifying the influence of the Bio materials that are used in the self-healing process of concrete. The Bio material that was studied has a high content of calcium carbonate, which, after precipitation, may lead to the sealing of the microcracked surface of concrete. This nucleation process is possible only in humid environments; thus, water has a paramount role in ensuring the mobility of the molecules. The difference between a complete and a partial seal is given by the amount of the Bio product that is available in the cracked area, the size of the calcium carbonate particles and the amount of water. For this study, the SEM Quanta Dual Beam device was used, through which scans were performed by electron microscopy, in order to observe the precipitation of the Bio product on the cracked surface. The chemical process throughout the sealing takes place has been presented through various illustrations and reports. By analysing previous experimental studies, it might be stated that the use of calcium carbonate in various forms is a sustainable and an environmentally friendly repair solution that, also, may improve the durability of cement-based materials. The use of ecological products in new cement-based materials is one of the main topics of worldwide interest for various research teams.

1. Introduction
Due to the extreme phenomena that occurred more and more often after the global warming, the need of population to adapt to severe environmental conditions is accentuated. In order to consolidate the existing constructions techniques and to develop new constructions technologies, various products are created, with the main role of increasing the mechanical and the physical resistance of the construction materials. Nowadays, an important emphasis has been placed on public opinion, namely that these materials must use less raw resources, and thus reducing the emission of harmful emissions. In recent years, researchers have presented in various publications, studies focused on the use of organic raw materials that can either slow down the phenomenon of degradation, or completely remediate the degraded construction elements. This process is referred to as the autogenic self-healing. Among the newly developed and even patented organic materials brought to the public opinion, the most advantageous ones are bacterial and fungal spores that can survive in extreme environments, inside the concrete construction elements. Bacteria survive in the PH 13 environment and, they can stay in latency for long periods of time (over 200 years). Removal from hibernation is possible only at the moment when the degradation phenomenon appears on the construction element and the organic matter comes into contact with oxygen and water. In this frame, the hydrotechnical constructions, due to their constructive nature of being in contact with water (permanent or infrequent), represent one of the main applications of the autogenic self-healing process. However, researchers encountered several issues in choosing the protective layer of organic matter for hydrotechnical concrete elements, due to the fact that the sealing materials activates as soon as they come in contact with water. The incipient phase through which a concrete construction element begins to lose its initial strength is represented by the appearance of microcracks. At the moment of micro-cracking, water and various impurities starts to infiltrate. The longer is postponed the intervention time, the more expensive are the works and the materials used for...
rehabilitation. For these reasons, the premature sealing of microcracks with Bio materials is considered to be a viable alternative to the traditional rehabilitation methods. The two autogenous self-healing processes that use bacteria and fungi as organic raw materials have a common denominator, namely the fact that both precipitate calcium carbonate (CaCO$_3$) in different amounts, on the cracked surface. The higher the amount of organic material is present in the microcracked area, the more complete is the sealing.

2. Stable connections in micro-cracked concrete

2.1. The chemical compounds of the Bio concrete matrix

The processes underlying autogenic self-healing are of a physical, chemical and mechanical nature, as illustrated in figure 1.

![Figure 1. The processes of autogenic self-healing](image)

The physical processes consist in hydrating the cement stone by the absorbed water. The latter induce a swelling inside the crack and, further on, the expansion of constituents cause the closure of about 10% of the cracks (according to statistics) [1].

By precipitating the calcium carbonate (CaCO$_3$), the calcium ions in the cement matrix react with the carbon dioxide or the carbon ions in water and, they form crystals. [2]. The chemical reactions highlighted by the equations (1, 2, 3), [2], represent the most important mechanism in autogenic healing. Edvardsen [3] stated that the process of crystallization of calcium carbonate involves two distinct phases. In the initial phase, the kinematics of crystallization is generated by the reactions that took place on the surfaces of the cracked concrete element. In the second phase, there are involved several reactions with diffusion ions, through the layer already created in the first stage by the precipitation products. Yang [4] evaluated the efficiency of the above-mentioned chemical mechanism, and concluded that there are two important aspects which influence the outcome. Firstly, the presence of calcium ions is mandatory, in a relatively high concentration, and secondly, the humidity is essential and it can be ensured by alternating the water – air amounts or by repeated immersions. These aspects are highlighted in figure 2.

\[
\begin{align*}
H_2O + CO_2 & \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCNO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (1) \\
Ca^{2+} + CO_3^{2-} & \leftrightarrow CaCO_3 \quad (pH \text{ water} > 8) \quad (2) \\
Ca^{2+} + HCO_3^- & \leftrightarrow CaCO_3 + H^+ \quad (7.5 < pH \text{ water} < 8) \quad (3)
\end{align*}
\]
Figure 2. The activation of the calcium carbonate precipitation due to the interaction of the cement matrix with water and air [2].

The mechanical processes occur by blocking the crack with fine particles (impurities), resulted from the cracking process and residues that exist in the water and infiltrate the crack. The mechanical process can produce effects only in combination with the chemical mechanisms described above [2].

Starting from the two autogenous self-healing processes based on biological compounds, namely the use of bacterial and fungal spores, it can be identified the repetitive use of calcium carbonate (CaCO$_3$) precipitation. Through this specific process, the biological compounds feed on nutrients and they transform these substances into calcium carbonate (CaCO$_3$). A complete sealing of a microcrack is possible if there is a sufficient concentration of curing agent in the respective area.

The experimental outcomes reported so far demonstrate that the autogenous healing of microcracks by precipitation of the calcium carbonate (CaCO$_3$) can be very effective due to an adapted bacterial suspension. Indeed, due to the calcite layer formed on the crack wall, the limiting component is not the carbonate ions, that can be generated by bacterial activity or supplied by air, but the available calcium ions [5].

Whether we are talking about bacteria that activates when they come in contact with oxygen and water, or we refer to the fungal spores which germinate, both processes are based on the same kinetics, namely the precipitation of the calcium carbonate (CaCO$_3$) on the cracked concrete surface.

Kim Van Tittelboom [6] mentions that the calcium carbonate (CaCO$_3$) is highly compatible with concrete and, thus, it represents a sustainable and an environmentally friendly repair solution. In 1938, Bessey et al. [7] identified the formation of calcium-carbo-aluminate in the hydration process of cement, by the time calcium carbonate was incorporated. This phenomenon was named "the chemical effect of calcium carbonate".

Mingli Cao [8] stated that when calcium carbonate is introduced into the matrix its density will increase due to its filling effect and, the hydration process can be accelerated due to its nucleation effect. Thus, the mechanical properties, workability and hydration process of cementitious materials are directly influenced by the size of calcium carbonate particles. The following sizes have been identified by Mingli Cao:
- Macro-Calcium carbonate (> 1 mm) such as coarse limestone sand or limestone aggregates. At this scale the chemical and the nucleation effects are not significant and the effect on the hydration process is negligible; the substance behave like an inert filler in the cementitious compositions [8].
- Micro-Calcium carbonate (1 μm - 1 mm), such as limestone powder and limestone dust, are often used in the manufacture of cement, and due to the fact that they have smaller dimensions than the cement grains they participate in the hydration process and can affect the kinetic factors. The
incorporation of calcium carbonate into the cemented composites may lead to an increase both in the matrix density and their resistance to acid attacks. In general, the nucleation effect is directly proportional to the lime powder content [8].

- Nano-calcium carbonate (<1 μm) in cemented composites can significantly improve their mechanical properties and durability [10]. Nano-calcium carbonate (50 - 120 nm) is very effective in accelerating the hydration of cement, especially for the induction period of tricalcium silicate (C₃S), due to its nucleation effect [8].

For this work, a Bio product with a concentration of over 90% of micro-calcium carbonate (CaCO₃) was used, without adding any other biological compounds. The bonding reactions between the Bio product and the components of the concrete matrix are triggered by the chemical reactions specific to the autogenous self-healing.

2.2. The materials used in the Bio concrete matrix and their chemical compositions

2.2.1. Cement
Cement is a building material provided in the form of a fine powder that is made by grinding the clinker and which, in contact with water, sets and hardens. Cement is the most widely used material in the field of civil, industrial, hydrotechnical, road and bridge engineering. Addition agents are used, primarily, to lower the cost of production and secondly to improve some properties [11]. The chemical composition of normal Portland cement is shown in table 1 [11].

| Chemical composition of Portland cement | Amounts (%) |
|----------------------------------------|-------------|
| Calcium oxide (CaO)                   | 60-67 %     |
| Silicon dioxide (SiO₂)                | 19-24 %     |
| Aluminum oxide (Al₂O₃)                | 4-7 %       |
| Iron oxide (Fe₂O₃)                    | 2-6 %       |
| Magnesium oxide (MgO)                 | 4-5 %       |
| Sulfur trioxide (SO₃)                 | 3 %         |
| Alkaline compounds (K₂O, Na₂O)        | < 1%        |

2.2.2. Sand
Sand is an unconsolidated sedimentary rock, derived from the crushing of minerals, rocks or organisms, which is found in the form of an accumulation of fine grains (0.063 – 2 mm) [12]. The sands used in the preparation of mortars and concretes can be of two types, depending on their origin, namely:

- natural (quarry, river, sea, dunes);
- artificial (obtained by breaking, crushing);

The chemical composition of river sand is presented in table 2 [12].
Table 2. The chemical composition of river sand.

| The chemical composition of river sand. | Amounts (%) |
|---------------------------------------|-------------|
| Silicon dioxide (SiO$_2$)              | 51.00 %     |
| Aluminium oxide (Al$_2$O$_3$)          | 6.83 %      |
| Iron oxide (Fe$_2$O$_3$)               | 0.32 %      |
| Calcium oxide (CaO)                    | 0.48 %      |
| Potassium oxide (K$_2$O)               | 0.40 %      |
| Titanium dioxide (TiO$_2$)             | 0.58 %      |

2.2.3. Bio product

The Bio product is made of micronized powder which is subsequently granulated in dimensions between 2 - 6 mm; this material is strongly reactive. On the outside it is protected with a layer of paraffin (1/2 mass of the Bio product). The chemical composition of the Bio product is presented in table 3 [13].

Table 3. Chemical composition of the Bio product.

| Chemical composition of granular Bio product | Amounts (%) |
|---------------------------------------------|-------------|
| Calcium carbonate (CaCO$_3$)                | 91%         |
| Magnesium carbonate (MgCO$_3$)              | 2 %         |
| Paraffin ½ mass from Bio product            | ~ 47%       |

Paraffin is a white solid, used as a raw material in various industries, with a melting point between 52°C - 54°C. Calcium carbonate is the salt of calcium with carbonic acid. The former is a solid substance, of white colour, with the chemical formula (CaCO$_3$), and the ratio of Ca$^{2+}$ and CO$_3^{2-}$ ions being 1:1 [4, 5].

Calcium carbonate is widely spread in nature, in minerals (calcite, aragonite, vaterite), in bones, teeth, shells, corals and shellfish crust. In rocks it is found in the form of limestone (where it is almost pure), an example being the dolomites, which are a mixture of calcium and magnesium [14].

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} & \leftrightarrow \text{Ca(OH)}_2 \\
\text{Ca(OH)}_2 + \text{CO}_2 & \leftrightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\end{align*}
\]

This product has been approved to be used in agriculture, zootechnics, the paint industry, the glass industry, the plastics industry, the mortar and sandstone industry, the steel industry and the rubber industry [13]. Given the fact that this product is also found in the pharmaceutical industry, it might be stated that it can be used in different dosages to treat people who lack calcium [15].

2.3 Autogenous self-healing of microcracks under ideal conditions

In order to establish the intermolecular reactions at the matrix level of Bio concrete, a very important element is mandatory, namely water (H$_2$O). The smaller is the environment in which the microcracking occurs, the shorter is the reaction time of the Bio product. This is due to the fact that there is a smaller area, strongly saturated with (CaCO$_3$), and the nucleation between components is almost instantaneous. Figure 3 illustrates a scenario through which, under the effect of some stresses, a micro-crack of size 0.4 µm appears in a concrete element. The two granules of Bio product cracks, and the water penetrates inside, ensuring the mobility of the molecular species.
Figure 3. Micro-cracking and water penetration into the Bio concrete element.

The more material of Bio product is found in the microcrack, the more complete is the sealing. Figure 4 shows the moment of decomposition of the two granules of the Bio product and the migration of molecules in a humid environment. The molecules detached from the Bio product seek to create stable relationships mainly with the other molecules in micronized form (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$). The chemical process will continue until the molecules in the Bio product are consumed.

Figure 4. Stable bonds in the Bio concrete matrix.

An important parameter in this chemical process is represented by the amount of paraffin that is used to create the protective layer (that conserve the Bio product during concrete mixing). The more the amount of paraffin is absorbed by the Bio product, the less micronized compound (CaCO$_3$) is obtained; thus, the temperature of the paraffin melting process is important. From what has been observed so far, the
paraffin layer being in a relatively small amount, on long-term contacts with water (total immersion) it remains in the form of a spherical shell and the Bio product diffuses into the water. It can also be removed by increasing the temperature of the matrix, phenomena that can be easily reached in common operating environment.

All this kinetics underlies the autogenic self-healing or rather the self-sealing of the concrete micro-cracks up to 0.4 µm. This whole process can be observed with special high precision equipment (SEM). The chemical reactions that occur after nucleation are presented in the relationships below (6, 7, 8)

\[
\begin{align*}
CaCO_3 + Al_2O_3 &= Ca_3Al_2O_6 \\
CaCO_3 + SiO_2 &= Ca_2SiO_5 \\
CaCO_3 + Fe_2O_3 &= Ca_4Al_2Fe_2O_{10}
\end{align*}
\]

Following the chemical nucleation process, stable bonds were obtained (highlighted in figure 5) and sealing took place by deposits on the cracking areas.

The total or partial sealing of the 0.4 µm microcracks presented in the above scenario is influenced by the amount of the Bio product, the amount of existing water and the amount of the protective layer.

3. Scanning electron microscopy (SEM). Case studies

Microbial calcium carbonate has been widely investigated in the self-healing process of concrete cracks. In this chapter are reviewed 2 studies related to the phenomenon of precipitation of the calcium carbonate using bacteria. The outcomes of these studies are in a general good agreement with the ones obtained throughout the investigations presented below, in the 3.2 section.

3.1. Study 1

Hassan A. [16] presents in a study, a comprehensive investigation carried out on bacterial growth and factors influencing the evolution of urea hydrolysis, aiming to accurately describe the precipitation of the calcium carbonate inside concrete. The results obtained by Hassan A. [16] indicate that the bacteria managed to survive in a latent state without any reproduction at a pH level of 12-13. A decrease of almost 75% of the hydrolysis efficiency inside the concrete pores was observed, mainly due to the high pH value (pH = 13) [16]. Moreover, the complete curing of the 0.4 µm microcrack was achieved after 70 days, while the cure ratio was 15% lower inside the concrete. This fact was highlighted by the SEM analysis (figure 6). Hassan A., [16] concluded that these bacteria can self-heal cracks, and can lead to a significant increase in the life cycle of concrete elements.
3.2. Study 2
Shekhar [17] stated that the presence of pores and cracks in the structure allows the penetration of harmful chemicals, gases and moisture, endangering the life of the structure. The basic remedy for these issues is to fill these gaps and cracks with synthetic polymers. The quoted research focuses on the development of a cement bio-mortar using bacteria, with the role of sealing cracks through the process of inducing calcium carbonate precipitation. The results obtained by Shekhar [17] indicated a 28.3% increase in mortar strength and a 12% reduction in water absorption. This biotechnological approach, if adopted, could provide sustainable concrete protection by filling cracks and pores. SEM and XRD analyses were also performed, in order to have a better perspective on the overall process and on the precipitation of the calcium carbonate from the pores, in particular (figure 7).

The results obtained by Shekhar [17] were as follows:
- The biotechnological approach using the bacterial solution helps to improve the properties of the cement mortar;
- An improvement in the compressive strength of mortar by 28.3% is achieved when isolated urea is produced;
- The use of the bacterial solution in the preparation of the mortar reduces the water absorption of the mortar by 12%, at 28 days compared to the control mortar;
- SEM images of mortar prepared with bacterial solution show the precipitation of (CaCO₃) which fills the gaps and makes it dense and compact, which ultimately increases durability;

3.3 Study 3
In order to highlight the existing nucleation process inside a microcrack between the Bio product and the rest of the materials existing in the mortar matrix, the SEM Quanta 200 3D Dual Beam device was used, through which scans were performed by electron microscopy. For this case study, a sample consisting in a slice of mortar, cut from a prism measuring 40x40x160mm, which has a content of about 10% Bio product, was investigated. Figures 8 - 9 shows the fixing of the sample in the clamping system of the device and the adjustments that were performed according to the sample dimensions.

![Figure 8. Fixing the sample in the clamping system of the device.](image1)

![Figure 9. Adjusting the device according to the sample size.](image2)

In figures 10 - 13 the precipitation (CaCO₃) at different distances from the observation point is highlighted. A sealing of the microcrack can be observed in these images, due to the fact that the Bio product is decomposed, and the molecules have entered into nucleation with the others, existing on the surface of the crack.

![Figure 10. Visualization of CaCO₃ precipitation in the microcrack at a distance of 100 µm.](image3)

![Figure 11. Visualization of CaCO₃ precipitation in the microcrack at a distance of 50 µm.](image4)
Conclusions

This work presents the chemical reaction process of Bio product and cement, in a scenario in which the concrete/mortar microcracks are limited to 0.4 µm. The optimal environmental conditions for the Bio product to work at the molecular level with the other molecules present in the concrete matrix were identified. Based on the presented laboratory studies, the following conclusions can be formulated:

- The chemical reactions presented in these studies can be identified only by scanning microscopy;
- Water has an important role in achieving stable bonds, due to the fact that it ensures the mobility of components from the BIO product to the cracked area;
- The reaction time is determined by the dimensions of calcium carbonate (macro, micro and nano);
- The higher the amount of calcium carbonate and the moisture in the cracked area, the more complete sealing can be achieved;
- The working temperature is a key parameter in the activation of the Bio product (the material is protected with a paraffin layer);
- The amount of the protective layer, namely paraffin, must be as small as possible, thus avoiding a partial closure without making stable connections.

The main conclusion regarding the chemistry of the self-healing process of microcracks is that both in the case of using bacteria and the Bio product, the raw material reacts through durable and stable bonds only in the presence of water. As described by other researchers, the presence of calcium carbonate on the cracked surface has a significant role in the self-sealing process. Thus, it can be stated that the use of products based on biological raw materials and Bio product in hydrotechnical construction elements can lead to immediate results in self-healing of microcracks. This fact, also, implies an increase in the lifespan of the concrete element and a reduction in its maintenance costs.

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