Fungicidal effects on cement composites with recycled glass from photovoltaic panels

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Abstract. This research was focused on the effects of micromycetes on cement composites with 100% replacement of natural aggregate by the recycled glass from photovoltaic panels. The experiment was performed on samples of small beams measuring 40 x 40 x 8 mm (length x width x height) and cement crumbling with recycled glass from photovoltaic panels in percentages representing 10%, 20% and 40%. The representatives of the selected micromycetes were Aspergillus niger, A. clavatus, Penicillium glabrum, Cladosporium sp. and Zygomycetes sp. Biocorrosion causes changes in the properties of the material, mainly as a result of the action of microorganisms. Due to their large production of acids and enzymes, micromycetes are an important part of microscopic consortia involved in biocorrosion. This experiment focused on evaluating the effect of micromycetes on cement composites – solid structure and crumbling, with 100% replacement of natural aggregate with photovoltaic glass recyclate. The results show a high growth of biomass on solid composites, while on cement crumbling, the growth was minimal due to high pH value. Longer monitoring time was used in case of adaptation to the environment.

1. Introduction

Photovoltaic panels are used throughout the world. As a renewable energy source and versatile energy technology, it can be used for almost anything that needs energy. Research and development in this area have advanced rapidly during the last 20 years [1,2]. Solar photovoltaics is the third-largest technology for producing electricity from renewable sources, after hydro and offshore wind energy [3].

The service life of photovoltaic panels is estimated between 20-30 years. Most solar panels were installed at the end of the 20th century, which means we can expect an increase in the amount of photovoltaic panels to be disposed of in a few years [4]. Directive 2012/19/EU of the European Parliament and of the Council on waste electrical and electronic equipment from 15 August 2018 stipulates that at least 85% of photovoltaic panel materials must be used, and 80% of the materials must be prepared for re-use and recycled [5]. There are research projects on the incorporation of waste materials into the cement matrix [6–9]. One of the new ways to recycle waste photovoltaic glass is its incorporation into cement composites [10].

Since photovoltaic glass, as a secondary raw material, has only limited use in the glass industry, a new way of recycling needs to be found. Photovoltaic glass cannot be re-used in the glass industry because the substances (silicon dioxide, silicon nitride, tungsten oxide, zinc sulphide) used for surface treatment in the form of a thin anti-reflective layer would contaminate the glass charge [11,12].
Cement composites with recycled glass, as well as conventional cement composites, can suffer from biocorrosion. Biocorrosion is understood as a change in the properties of materials caused by the action of living organisms or their metabolites. The organisms involved in biocorrosion are called biodeteriogens, and they are mainly microorganisms that are known for their ability to biotransform and biominerize substances from the environment, in which they mechanically mix organic substances with mineral ones, through their metabolic activity on surface substrates [13] - bacteria, algae, cyanobacteria or microscopic fibrous fungi. However, they can also be plants such as lichens or bryophytes [14]. The biocorrosion of building materials is influenced by many factors that act not only on the cement composite but in interaction with metabolites of microorganisms. They also affect the viability of microbial consortia [15].

Although biocorrosion may not be visible, it can still negatively change the properties of cement composites, which in most cases leads to severe damage to the entire building structure as a whole. Therefore, it is important to identify not only the macroscopic but also the microscopic changes caused by the metabolic activity of microorganisms [14].

2. Preparation of cement composites
Portland cement EN197-1 – CEM I 52.5 R, recycled glass from photovoltaic panels as a 100% substitute for natural aggregates in 4 fractions (0/0.5 mm; 0.5/1 mm, 1/4 mm and 4/10 mm) and mixing water from the water supply system were used for the preparation of the cement composites. According to the determination of the optimal grain size curves, five new recipes (R1-R5) were selected for the preparation of concrete mixtures. The R0 recipe was prepared based on natural aggregates as a comparative one. The photovoltaic glass was a 100% replacement for natural aggregates. The R1-R5 recipes had different ratios of the individual fractions, with two of them (R3, R5) containing all four recycled glass fractions, and the remaining three (R1, R2, R4) were designed without the 1/4 mm fraction. The above-mentioned raw materials were processed into a mixture, which was then worked into moulds in the form of beams measuring 40 x 40 x 160 mm (W x H x L), where they were left until the next day, and then the moulds were removed. The beams were stored in an aqueous environment at a temperature of 20 ºC for 28 days. Subsequently, they were removed and dried to a constant weight.

2.1. Cement composites
The dried cement composites were then cut into test specimens measuring 40 x 40 x 8 mm (W x L x H). All parts were washed with ethanol to prevent the samples from drying out in the agar with inoculated micromycetes.

2.2. Crumbling
Once the beams were dried to a constant weight, they were crushed in a jaw crusher and ground in a ball mill into crumbling with a grain size of <1.5 mm. The prepared crumbling was sterilized in a Stericell SCK-B2V sterilizer for one hour at 180 ºC before use.

2.3. Agar
The used cultivation medium was the same for the experiment on the test specimens and crumbling. It was Sabouraud Dextrose Agar (HiMedia Laboratories, Mumbai, India) with these main components: dextrose, mycological peptone, agar and distilled water, pH 5.6 ± 0.2, prepared in Erlenmeyer flasks in a Sterimat Plus autoclave at 121 ºC.

3. Micromycetes
The following representatives of micromycetes were selected to research fungicidal effects in the biocorrosion process - Aspergillus clavatus, Aspergillus niger, Cladosporium sp., Penicillium glabrum and Mucor sp. Microscopic fungirepresent a stable microbial component involved in biocorrosion together with other symbiotic microorganisms.
Aspergillus clavatus belongs to the class of imperfect fungi, and in biocorrosion, it is responsible for dissolving building stone due to the production of large amounts of organic acids [16]; it causes dark coatings on surfaces [17].

Aspergillus niger also belongs to the class of Euromycetes. It forms characteristic dark to black coatings on the surface [18], and during biocorrosion, it causes redeposition of elements (Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, ...), which impairs the internal stability of the building material [19].

The genus of Cladosporium chelates copper, zinc and iron in the biocorrosion process, it is characterized by rapid growth of rich biomass and grows in colder places [20].

Penicillium glabrum belongs to the most widespread genus of micromycetes and is commonly found on damp walls and building materials. With the help of mycelium, they penetrate building stone, thus contributing to the disruption of stability, weathering and scaling of building stone [21].

The genus of Mucor, like other representatives of Zygomycetes, binds water and produces carbon dioxide, which interacts with surfaces and causes their weathering [14].

4. Experiment

4.1. Cement composite samples

The prepared and washed cement composites (see 2.1) of recipes R0 – R5 were prepared in Petri dishes with a diameter of 90 mm and bathed in sterile agar to the height of the composite. Once the medium had cooled, the selected microscopic fungi were inoculated, and the Petri dish was sealed with parafilm to prevent contamination and drying of the medium. The samples prepared and secured in this way were moved to a place with sufficient sunlight and a constant temperature (24°C), and the growth of biomass was checked and recorded at 7-day intervals. They were evaluated according to ČSN 72 4310 standard [22], determining the degree of fungal growth (Table 1).

4.2. Crumbling

The sterilized crumblings (see 2.2) of recipes R1-R5 were weighed into a Petri dish in the initial ratio of 1:9 to the cultivation medium, which made up 10% of cement crumblings, then in the ratio of 2:8 (20% cement crumblings) and also in the ratio of 4:6 (40% cement crumblings). The weighed crumblings were supplemented with a medium in Petri dishes, and after solidification, the selected micromycetes were inoculated. The dishes prepared in this way were treated in the same way as the cement composite dishes – sealing with parafilm, transfer to the same place, and frequency evaluation of biomass growth (see 4.1).

| DEGREE OF GROWTH | EVALUATION IN WORDS                      |
|------------------|----------------------------------------|
| 0                | fungi do not grow                      |
| 1                | growth is negligible                   |
| 2                | growth is gradual (up to 25% of the surface) |
| 3                | growth is intensive (up to 50% of the surface) |
| 4                | growth is very intensive (up to 75% of the surface) |
| 5                | growth is complete (100% of the surface) |

5. Evaluation

As already mentioned in subchapter 4.1, the growth was evaluated according to ČSN 72 4310 standard (see 4.1). Table 2 shows the growth of microscopic fungi on cement composites, which was very active. Complete growth – 5, 100% of the surface from the first 7-day period was observed in the representatives of Aspergillus (A. niger), Penicillium (P. glabrum) and Zygomycetes (Mucor sp.) genera in all types of recipes (R0 – R5). A slower start of growth was observed in A. clavatus, while in the recipe R5 it did not exceed the value of 3 – intensive growth up to 50% of the surface. In Cladosporium genus stable growth was observed from day 14 up to the value of 4 – very intensive, up
to 75% of the surface. Overall, it can be said that the grain size fractions of the types of recipes did not significantly affect the growth of micromycetes.

Table 2. Fungi growth on cement composites for the duration of 7, 14, 21 and 28 days.

| Fungi species | Aspergillus clavatus | Aspergillus niger | Cladosporium sp. | Penicillium glabrum | Mucor sp. |
|---------------|----------------------|------------------|------------------|---------------------|----------|
| Days          | 7 14 21 28           | 7 14 21 28       | 7 14 21 28       | 7 14 21 28          | 7 4 2 2 8|
| Recipe        |                      |                  |                  |                     |          |
| R0            | 1 4 5 5              | 5 5 5 5          | 2 4 4 4          | 5 5 5 5             | 5 5 5 5  |
| R1            | 1 4 4 4              | 5 5 5 5          | 2 4 4 4          | 5 5 5 5             | 5 5 5 5  |
| R2            | 2 4 5 5              | 5 5 5 5          | 3 4 4 4          | 5 5 5 5             | 5 5 5 5  |
| R3            | 2 4 4 4              | 5 5 5 5          | 3 4 4 4          | 5 5 5 5             | 5 5 5 5  |
| R4            | 1 4 4 4              | 5 5 5 5          | 3 4 4 4          | 5 5 5 5             | 5 5 5 5  |
| R5            | 3 3 3 3              | 5 5 5 5          | 2 4 4 4          | 5 5 5 5             | 5 5 5 5  |

Tables 3 and 4 show the growth values on cement crumbling in the ratio of 1:9 (Table 3) and 2:8 (Table 4). In the case of the 4:6 ratio (40% of cement crumbling supplemented to 100% with medium), the growth of all types of recipes (R1-R5) was zero, which was caused by a lack of nutrients to support the growth from the cultivation medium and a high level of crumbling content in the sample, which also affected the pH value exceeding 11.

In the case of 10% content of cement crumbling (Table 1), immediate growth after 7 days is visible only in *P. glabrum*, although at the beginning, it is negligible and gradual – 1, 2. From the second period, after 14 days, the growth is complete – 5, 100% surface. The highest activity of biomass growth was not recorded in any other representatives; it only reached the value of 4 – growth up to 75% of the surface, was very intensive, and was not in all types of recipes. In the case of *A. niger* and *Cladosporium* sp., a sudden increase in biomass growth was recorded after 21 days of checking – from the value of 0 to the growth value of 4 (very intensive), which can be explained by the longer interval of adaptation to the conditions in an isolated environment; this phenomenon was recorded for all recipe types (R1-R5).

Table 3. Fungi growth on 10% share of crumbling for the duration of 7, 14, 21 and 28 days.

| Fungi species | Aspergillus clavatus | Aspergillus niger | Cladosporium sp. | Penicillium glabrum | Mucor sp. |
|---------------|----------------------|------------------|------------------|---------------------|----------|
| Days          | 7 14 21 28           | 7 14 21 28       | 7 14 21 28       | 7 14 21 28          | 7 1 2 2 8|
| Recipe        |                      |                  |                  |                     |          |
| R1            | 0 0 4 4              | 0 0 4 4          | 0 0 4 4          | 1 5 5 5             | 0 0 3 3  |
| R2            | 1 1 4 4              | 0 0 4 4          | 0 0 4 4          | 2 5 5 5             | 0 0 4 4  |
| R3            | 0 0 3 3              | 0 0 4 4          | 0 0 4 4          | 1 5 5 5             | 0 0 3 3  |
| R4            | 0 0 4 4              | 0 0 4 4          | 0 0 4 4          | 2 5 5 5             | 0 3 4 4  |
| R5            | 0 0 4 4              | 0 0 4 4          | 0 0 4 4          | 2 5 5 5             | 0 1 4 4  |

Table 4 shows the largest growth – 5, 100% of the surface, in biomass of *Cladosporium* genus in all recipes except for recipe R3, where the growth was very intensive. In *P. glabrum*, only negligible growth was observed in recipes R1, R2, R4 and R5, while in recipe R3 the growth was gradual, at the value of 2 to 25% of the surface. In the other representatives – *A. clavatus*, *A. niger* and *Mucor* sp. the growth was zero, which may be due to the lack of nutrients or light.
### Table 4. Fungi growth on 20% share of crumbling for the duration of 7, 14, 21 and 28 days.

| Fungi species          | Aspergillus clavatus | Aspergillus niger | Cladosporium sp. | Penicillium glabrum | Mucor sp. |
|------------------------|----------------------|------------------|------------------|---------------------|-----------|
| Days                   | 7 14 21 28           | 7 14 21 28       | 7 14 21 28       | 7 14 21 28         | 7 1        |
| Recipe                 | R1                   | R2               | R3               | R4                  | R5        |
|                        | 0 0 0 0              | 0 0 0 0          | 0 0 0 0          | 0 0 0 0             | 0 0 0 0   |
|                        | 1 1 1 1              | 0 0 0 0          | 4 4 4 4          | 5 5 5 5             | 1 1 1 1   |
|                        | 1 1 1 1              | 0 0 0 0          | 0 0 0 0          | 0 0 0 0             | 0 0 0 0   |
|                        | 0 0 0 0              | 0 0 0 0          | 0 0 0 0          | 0 0 0 0             | 0 0 0 0   |

Figure 1 shows Petri dishes with crumblings (recipes R1-R5) in a ratio of 1:9 and the growth of the fungus *P. glabrum* after a 7-day evaluation and Figure 2 is a detailed view of the mycelium and conidia of the fungus *Penicillium glabrum* under 76x magnification, in the background, there is a clear pattern of the beam of the recipe R4.

#### 6. Conclusion

This research evaluated the fungicidal effects on cement beams and crumbling with 100% replacement of natural aggregates with glass photovoltaic recyclate; photovoltaic glass was mixed in different ratios from four fractions of different grain size classes. Solid samples (cement composites) and cement crumbling were exposed to the effects of micromycetes—*Aspergillus clavatus*, *Aspergillus niger*, *Cladosporium* sp. *Penicillium glabrum* and *Mucor* sp for the duration of 28 days, while the biomass growth was evaluated every 7 days. The conclusions drawn from this research are as follows:

- micromycete growth was more successful on solid samples –cement composites;
- the intensity of biomass growth on cement composites was at the same level from day 14 (5 – complete growth, 100% of the surface);
- in the case of cement crumbling in the ratio of 1:9, the representative of the genus *Penicillium*-*P. glabrum* was the most successful, value 5 – complete growth;
- at the ratio of 2:8 of cement crumbling and medium, the full growth values of 5 were achieved in case of genus *Cladosporium*;
- in the case of 40% share of cement crumbling, there was zero growth in all selected representatives due to the very low input of nutrients from the medium and high pH value>11;
• longer adaptation time to the environment was visible during the growth of biomass on cement crumbling; the presence of growth was clearly visible only after 14 days from the beginning of the experiment.

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