Fungicidal properties of cement composites based on waste sludge water from concrete plant

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Abstract. The present article deals with the fungicidal properties of cement composites based on Waste Sludge Water (WSW) from a concrete plant (CP). The article compares the ability of standard cement composites and cement composites based on WSW to withstand microscopic fungi Aspergillus niger, Trichoderma nereus and Penicillium glabrum. The results of the tests show that the use of WSW as a substitute for pure mixing water in the preparation of cement composites does not have a significant positive or negative effect on the fungicidal properties of the prepared composites.

1. Introduction
Cement composites are frequently used in construction practice due to their very good price-performance ratio. For example, concrete pipes are used for waste water drainage or as process water supply systems to industrial plants due to their favourable properties. However, the presence of microorganisms together with nutrients leads to algae growth on the concrete surface. They are capable of affecting the flow rate [1]. The growth of filamentous fungi poses another problem in the use of cement composites. There are research projects and studies on concrete biocorrosion [2-4] with various surface treatments in controlled conditions as protection against fungal growth [5] or with the addition of various additives as protection against biocorrosion [1,3,6,7]. Recently, there has been increasing pressure to use various waste materials from metallurgical, energy and other industries as secondary raw materials in the production of cement composites. Several studies and research papers address this issue as well [8-12]. The use of secondary raw materials in cement composites has also been studied in terms of added value in the form of improvement of the fungicidal properties of the resulting composites [13,14]. One of the possibilities of the utilization of waste generated in the construction industry is, for example, the utilization of waste sludge water from concrete plants as a partial or complete replacement of mixing water in the production of cement composites. Waste sludge water in a concrete plant is produced during the cleaning of agitation trucks from the remaining transported concrete or other cement-based materials.

This research is currently very popular in terms of environmental protection, thanks to the reduction of waste sludge water and its economic benefits. The aim of these research is compares the ability of standard cement composites and cement composites based on WSW to withstand to most frequently occurrence microscopic fungi in civil engineering industry which are Aspergillus niger, Trichoderma nereus and Penicillium glabrum.

2. Materials and Methods
The cement composites were prepared and tested according to CSN EN 196-1 [15]. A precisely determined amount of pure mixing water and waste sludge water from the concrete plant (see table 1)
was used in the preparation of the cement composites. The parameters of the water are given by the CSN EN 1008 standard [16]. The test specimens with the dimensions of 40×40×160 mm were produced according to formulas R1 and R3 for the purpose of the tests. They were subsequently cut into partial sections with the dimensions of 40×40×10 mm and used for the testing of fungicidal properties.

2.1. Composition of cement composite formulas

Two experimental formulas with the designations of R1 and R3 were designed to verify the possibility of replacing the mixing water in the production of cement composites with waste sludge water from the concrete plant. The composition of the individual formulas is described in Table 1 and is based on the standard requirements for the production of cement composites. The mixing water was replaced with waste sludge water from the concrete plant in the amounts of 25%, 50%, 75% and 100% in both formulas. Portland cement CEM I 52.5 R EN 197-1 [17] manufactured by Cement Hranice a.s. as the binder for mixture R1 was used and Portland mixed cement CEM II / B-LL 32.5 R EN 197-2 [18] manufactured by Cement Hranice a.s. for R2 mixture was used. Standard sand according to EN 196-1 as the filler was used [15].

| Table 1. Composition of designed formulas. |
|-----------------------------------------------|
| **Formula** | **Mixing water repl. [%]** | **K** | **25** | **50** | **75** | **100** | **R1** | **K** | **25** | **50** | **75** | **100** |
|---------------|-----------------|------|------|------|------|------|------|------|------|------|------|------|
| CEM I 52.5 R [g] | 450.0 | 450.0 | 450.0 | 450.0 | 450.0 | 450.0 | - | - | - | - | - |
| CEM II/LL 32.5 R [g] | - | - | - | - | - | - | 450.0 | 450.0 | 450.0 | 450.0 | 450.0 |
| Pure mixing water [g] | 225.0 | 168.8 | 112.5 | 56.3 | - | 225.0 | 168.8 | 112.5 | 56.3 | - | - |
| Waste sludge water [g] | - | - | - | - | - | - | - | - | - | - | - |
| Sand [g] | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 | 1,350 |

2.2. X-ray diffraction of used cements

A Bruker Advance D8 (Bruker, USA) powder diffractometer equipped with a LynxEye linear semiconductor detector and a SOL-XE energy dispersion detector was used for the X-ray diffraction analysis. This system was suitable for quantitative analyses of mineralogical-phase composition of the examined samples. During the sample preparation, we ensured the samples had not come into contact with other components to prevent their contamination with other materials. The samples were ground to an approximate size of 10-50 μm in order to determine the parameters. Subsequently, the cement samples were placed in sample tubes in which they were stable and free from any interactions.

2.3. Mixing water

Drinking water from the water supply system together with waste sludge water from the concrete plant were used for the preparation of the cement composites. The properties of pure mixing water and waste sludge water from the concrete plant are presented in Table 2. The properties were determined according to CSN EN 1008 standard [16].

2.4. Testing the resistance against fungi

For the testing of the fungicidal properties of cement composites were selected microscopic fungi Aspergillus niger, Trichoderma nereus and Penicillium glabrum because they are most frequently occurring microscopic fungi in civil engineering industry. These microscopic fungi were obtained as new isolates from metal-contaminated environments of sludge beds after ore extraction [19–22]. The strains were inoculated in a standard manner on Malt Extract Agar (M137, HiMedia Laboratories, Mumbai, India) in the following composition: malt extract 30.0 g, mycological peptone 5.0 g, agar 15.0 g, final pH (at 25 °C) 5.4 ± 0.2. The samples of composites in the form of beams with the dimension of 40×40×10 mm were sterilized in closed beakers in Stericell sterilizer (BMT Medical technology, Czech Republic) at 180 °C for 60 min. The sterilized composite specimens were then placed in sterile Petri dishes and bathed in sterile growth medium for the cultivation of microscopic filamentous fungi, see figure 1. Sabouraud Dextrose Agar (M063, HiMedia Laboratories, Mumbai, India) was selected as the
culture medium containing: dextrose (glucose) 40.0 g, mycological peptone 10.0 g, agar 15.0 g, final pH (at 25 °C) 5.6 ± 0.2. To verify the activity of the composites, the beams were overlaid with a thin layer of the medium. Spores of cultured microscopic fungi (15-day cultivation) were evenly applied on the prepared dishes using moistened transport swabs (Transsystem, Dispolab, Czech Republic). Each fungus was placed on a separate Petri dish with growth medium. The duration of the experiments was 30 days.

**Table 2.** Properties of mixing water for the preparation of cement composites.

| Tested Properties | Pure Mixing Water From A Concrete Plant | Waste Water From A Concrete Plant | Limit Concentrations According To ČSN EN 1008 |
|-------------------|----------------------------------------|---------------------------------|-----------------------------------------------|
| pH                | 6.84                                   | 12.31                           | > 4                                           |
| Temperature [°C]  | 17.0                                   | 17.0                            | -                                             |
| Conductivity [µS/cm] | 335.20                              | 15.30                           | -                                             |
| Humus substances  | acceptable                             | acceptable                      | paler than yellow-brown                       |
| Chlorides [µS/cm]| 12.30                                  | 156.5                           | < 600 < 2,000 < 4,500                         |
| Sulphates [mg/l]  | 40.268                                 | 875.3                           | < 2,000                                       |
| Nitrates [mg/l]   | 9.4                                    | -                               | < 500                                         |
| CODCr [mg/l]      | 5.236                                  | -                               | -                                             |
| Na [mg/l]         | 31.326                                 | 135                             | < 1,000                                       |
| Pb [mg/l]         | 0                                      | 0.1821                          | < 100                                         |
| Zn [mg/l]         | 0.0655                                 | 0.0232                          | < 100                                         |
| Ca [mg/l]         | 33.47                                  | 1.108.5                         | -                                             |
| Mg [mg/l]         | 5.27                                   | 935                             | -                                             |
| K [mg/l]          | 3.96                                   | 691                             | -                                             |
| SS [mg/l]         | 2.0                                    | 134,900                         | -                                             |

**Figure 1.** Cement composite samples at the beginning of fungi resistance test.
3. Results and Discussion

3.1. X-ray diffraction of the used cements

Table 3 shows the X-ray diffraction results of the individual cements used in the production of the cement composites. The results show that the composition of cements is not mineralogically different, only the percentage of the individual components is different. Cement CEM II / B-LL 32.5 R contains a higher proportion of limestone, a lower proportion of dicalcium silicate (C2S - Belite), tricalcium aluminate (C3A - Celite), tricalcium silicate (C3S - Alite) and calcium sulphate.

| Cement type                     | X-ray analysis                  | [%]  |
|---------------------------------|---------------------------------|------|
| Portland cement                 | C₃S monoclinic (NISHI) Hatrurite| 65.752|
|                                 | Gypsum                          | 1.815|
| CEM 52.5 R EN 197-1             | C₃A cubic                       | 6.198|
|                                 | C₄AF Brownmillerite(Si,Mg)      | 9.850|
|                                 | C₂S beta Larnite                | 10.268|
|                                 | Calcite                         | 4.096|
|                                 | Portlandite                     | 2.019|
| Mixed Portland cement           | C₃S monoclinic (NISHI) Hatrurite| 63.390|
| CEM II/B-LL 32.5 R EN 197-2     | Gypsum                          | 0.718|
|                                 | C₃A cubic                       | 5.554|
|                                 | C₄AF Brownmillerite(Si,Mg)      | 6.843|
|                                 | C₂S beta Larnite                | 3.596|
|                                 | Calcite                         | 17.883|
|                                 | Portlandite                     | 2.016|

3.2. Results of fungi resistance test

After the fungi resistance test, the individual beam samples were evaluated according to CSN 724310 [23] as shown in table 4. The results of the evaluation are summarised in table 5 below.

| Degree of fungi growth | Description                                                                 |
|------------------------|-----------------------------------------------------------------------------|
| 0                      | No growth of fungi                                                           |
| 1                      | The growth of fungi is negligible (the colonies of fungi are dispersed)     |
| 2                      | The growth of fungi is gradual (numerous small fungi colonies which cover 25% of the sample surface) |
| 3                      | The growth of fungi is intensive (fungi colonies cover up to 50% of the sample surface) |
| 4                      | The growth of fungi is very intensive (fungi colonies cover up to 75% of the sample surface) |
| 5                      | The sample surface is fully covered by fungi (fungi colonies cover 100% of the sample surface) |
Table 5. Antifungal efficiency of cement composites with waste sludge water.

| Sample | Penicillium glabrum | Aspergillus niger | Trichoderma nereus |
|--------|---------------------|------------------|---------------------|
| comp.  | 0                   | 0                | 1                   |
| 25%    | 0                   | 0                | 1                   |
| R1 50% | 0                   | 0                | 1                   |
| 75%    | 0                   | 0                | 1                   |
| 100%   | 0                   | 0                | 1                   |
| comp.  | 1                   | 1                | 1                   |
| 25%    | 1                   | 1                | 1                   |
| R3 50% | 1                   | 0                | 1                   |
| 75%    | 1                   | 0                | 1                   |
| 100%   | 1                   | 0                | 1                   |

The results clearly show that the samples of R1 mixture containing waste sludge water corresponded to the results of the comparative mixture containing only pure mixing water and showed high resistance to Penicillium glabrum and Aspergillus niger fungi. The samples of mixture R1 showed a slight growth of scattered colonies at the edges of the beam in case of Trichoderma nereus fungi, see figure 2.

Figure 2. Illustration of slight growth of Trichoderma nereus fungi on the edges of beams in mixtures R1(a) and R3 (b).

4. Conclusion

The aim of this paper was to evaluate the effect of waste sludge water, used as the substitute for pure mixing water in the preparation of cement composites, on the resistance to fungal growth. The fungicidal properties have been studied in three strains of filamentous fungi, namely Penicillium glabrum, Aspergillus niger and Trichoderma nereus. The test specimens were exposed to fungi for 30 days and the results suggest that:

- the use of waste sludge water as a substitute for pure mixing water does not in any way impair the properties of the cement composites compared to the comparative sample prepared using pure mixing water;
- 50% or higher replacement of pure mixing water with waste sludge water showed a slight improvement in fungicidal properties against the growth of Aspergillus niger.

It can therefore be stated that the use of waste sludge water as a substitute for pure mixing water does not impair the fungicidal properties of cement composites.

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